Biotic and abiotic bisphenol-A removal from wastewater by activated sludge: effects of temperature, biomass, and bisphenol-A concentrations

Olcayto Keskinakan and Behzat Balci

ABSTRACT

In this study, bisphenol-A (BPA) removal from synthetic wastewaters using a laboratory-scale activated sludge system was achieved. Activated (biotic) sludge was used for BPA elimination, whereas inactivated (abiotic) sludge was used during the adsorption study. In each step, six different BPA concentrations (5, 10, 20, 30, 40, and 50 mg L\(^{-1}\)) were tested, and temperatures were set to 10, 20, and 30 °C in the shakers. Four different activated sludge concentrations (1,000, 2,000, 3,000, and 4,000 mg TSS L\(^{-1}\)) were applied in the biotic study, and only 2,000 mg TSS L\(^{-1}\) was used in the abiotic study. After settlement of the sludge in the shakers, supernatants and control groups were filtered and analyzed for BPA using high performance liquid chromatography. In the biotic study, BPA and chemical oxygen demand (COD) concentrations were reduced at 100% and 99% levels, respectively. However, the BPA concentrations during the abiotic study changed slightly at varying temperatures, whereas there was no change of BPA concentration observed in the control groups. Results indicate that the main factor of BPA removal in an activated sludge system is biological. Kinetic studies were also conducted. BPA removal was best fit to zero- and first-order reaction kinetics, and the reaction rate constants are provided in this paper.

Key words | activated sludge, batch reactor, bisphenol-A, BPA elimination, COD

NOMENCLATURE

BPA  | bisphenol-A
TSS  | total suspended solids (mg L\(^{-1}\))
VSS  | volatile suspended solids (mg L\(^{-1}\))
COD  | chemical oxygen demand (mg L\(^{-1}\))
\(V\)  | specific substrate elimination rate (mg BPA g\(^{-1}\) SS \(^{-1}\) h\(^{-1}\))
\(V_{\text{max}}\)  | maximum substrate elimination rate (mg BPA g\(^{-1}\) SS \(^{-1}\) h\(^{-1}\))
\(K_C\)  | half-saturation constant (mg L\(^{-1}\))
\(K_i\)  | inhibition constant (mg L\(^{-1}\))
\(q_t\)  | amount of BPA adsorbed at time \(t\) (mg g\(^{-1}\))
\(q_e\)  | amount of BPA adsorbed at equilibrium (mg g\(^{-1}\))
\(q_m\)  | maximum adsorption capacity (mg g\(^{-1}\))
\(C_0\)  | initial BPA concentration (mg L\(^{-1}\))
\(C_t\)  | BPA concentration at time \(t\) (mg L\(^{-1}\))
\(C_e\)  | BPA concentration at equilibrium (mg L\(^{-1}\))
\(K_L\)  | Langmuir isotherm constant (L mg\(^{-1}\))
\(K_F\)  | Freundlich isotherm constant (L mg\(^{-1}\))
\(B_D\)  | Dubinin-Radushkevich constant (mol^2 kJ\(^{-2}\))
\(\varepsilon\)  | Dubinin-Radushkevich constant
\(K_J\)  | Jovanovich isotherm constant (L g\(^{-1}\))
\(K_{VS}\)  | Vieth-Sladek isotherm constant
\(b_{VS}\)  | Vieth-Sladek isotherm constant
\(K_{FS1}\)  | Fritz-Schlunder isotherm constant
\(K_{FS2}\)  | Fritz-Schlunder isotherm constant
\(m_1\)  | Fritz-Schlunder isotherm constant
\(m_2\)  | Fritz-Schlunder isotherm constant
\(k_0\)  | zero-reaction rate constant (mg L\(^{-1}\) min\(^{-1}\))
\(k_1\)  | first-order reaction rate constant (min\(^{-1}\))
\(k_2\)  | second-order reaction rate constant (L mg\(^{-1}\) min\(^{-1}\))
INTRODUCTION

Wastewaters introduced to treatment facilities can contain personal care products, pharmaceuticals, household and industrial chemicals, and xenobiotic organic compounds. Activated sludge systems are common wastewater treatment methods; however, they are not designed to remove or degrade xenobiotic organic chemicals from water. Moreover, a certain amount of xenobiotic organic chemicals can be removed from the water phase by sorption, chemical, and/or biological elimination, vaporization, and stripping mechanisms (Fauser et al. 2005). Bisphenol-A (BPA) is widely used in producing various organic chemical substances, epoxy resins, and polycarbonate plastics. Many studies have concluded that BPA is an endocrine disrupting chemical, and it is classified as a chemical that should be removed (Lister & Van Der Kraak 2001; Auriol et al. 2006; Esplugas et al. 2007; Chapin et al. 2008; Roy et al. 2009). Studies have shown that BPA is associated with certain diseases such as cancer, diabetes, liver, kidney, and brain function disorders, sperm count reduction, early sexual maturation in females, obesity prevalence, and immunodeficiency (Wetherill et al. 2002; Gong et al. 2010; Chung et al. 2011; Kundakovich et al. 2013). Additionally, some researchers have reported that the effective removal of BPA is vital to maintaining public human health (Joseph et al. 2011).

BPA has been found in water, surface waters, ground waters, wastewaters, sediments, sewage sludges, landfill leachates, influents and effluents of wastewater treatment plants, garbage leakages, and even tap water (Yamamoto et al. 2001; Furhacker et al. 2004; Vethaak et al. 2005; Urbatiska et al. 2007; Focazio et al. 2008; Shao et al. 2008; Seyhi et al. 2011, 2013; Nie et al. 2012; Jardim et al. 2012; Bruchet et al. 2014), revealing the potential risk of public exposure to BPA. For example, the maximum concentra-
tions of BPA were found to be 17.2 mg L\(^{-1}\) in waste landfill leachates (Yamamoto et al. 2001).

Lee & Peart (2000) concluded that BPA removal rates vary greatly in activated sludge systems after conducting experiments on actual wastewater treatment plants. BPA concentrations found in the effluent of wastewater treatment plants are in the range of 0.16–0.36 \(\mu\)g L\(^{-1}\) (Korner et al. 2000). Seyhi et al. (2011) reported that they used initial BPA concentrations ranging from 1.0 to 15 mg L\(^{-1}\) to determine the BPA removal capability of membrane bioreactor containing activated sludge in their study. According to researchers, residual BPA concentrations in the mixed liquor varied between 0.017 to 0.004 mg L\(^{-1}\). Kim et al. (2007) demonstrated that ammonium-oxidizing activity within nitrifier-enriched activated sludge has BPA biodegradation capability. They used initial BPA concentrations ranging from 10 to 100 mg L\(^{-1}\) to determine that BPA removal capability of nitrifier-enriched activated sludge and residual BPA concentrations recorded in the mixed liquor remained between 1.9 to 3.0 mg L\(^{-1}\), respectively. Zhao et al. (2014) used initial BPA concentrations ranging from 2.5 to 20 mg L\(^{-1}\) in wastewater to determine that the BPA removal capability of activated sludge and residual BPA concentrations recorded in the mixed liquor remained at 6.17 ± 0.41 mg L\(^{-1}\). Orozco et al. (2013) studied the effect of sludge age and acclimation strategy on the degradation of BPA and pointed out that the initial BPA concentration was maintained at 40 mg L\(^{-1}\) and the specific BPA degradation rate of acclimated activated sludge ranged between 65 and 90 mgBPA gTSS\(^{-1}\) d\(^{-1}\). Orozco et al. (2013) also stated that the biomass operated at a sludge age of 30 days had a higher stability against BPA and that its acclimation rate was also higher. Stasinakis et al. (2010) performed batch and continuous-flow system experiments to show the biodegradation of BPA by activated sludge and they maintained their experiments at 40 \(\mu\)g L\(^{-1}\) BPA concentration. They found 90% BPA removal efficiency in their study. Zhang et al. (2015) operated a submerged membrane bioreactor at the laboratory scale and they carried out their experiments with synthetic municipal sewage which contained 5 mg/L BPA concentration. According to Zhang et al. (2015), 90.11% of BPA was removed from the synthetic influent.

In addition, the literature suggests various BPA concentrations for waste sludge from municipal unit plants such as 0.033–56.7 \(\mu\)g g\(^{-1}\) in Canada (Lee & Peart 2000), 30–330 \(\mu\)g g\(^{-1}\) in Germany (Meesters & Schroder 2002), and 28.3 \(\mu\)g g\(^{-1}\) in China (Shen et al. 2005), indicating that BPA is not completely eliminated during wastewater treatment. Differences between removal rates may be due to many environmental parameters. Thus, wastewater treatment plants can be important point sources of BPA. According to literature given, it can obviously be seen that BPA concentrations were very different in the influent wastewater introduced to activated sludge systems, waste sludge and the mixed liquor in the aeration basin. In addition, the effluent of various factors such as temperature, BPA and biomass concentration on the BPA removal process in the activated sludge systems still remains to be investigated.

Although there is a considerable amount of literature on the removal of BPA in activated sludge systems, performance of activated sludge under various physico-chemical conditions...
conditions, such as temperature, pollutant and activated sludge concentrations, are rarely subjects of the treatment processes. The primary purpose of this research was to investigate the effect of the amount of biomass, temperature changes, and concentrations of BPA on its removal in activated sludge systems. The study assessed activated sludge's BPA adsorption and BPA elimination capabilities, which may contribute to system design approaches for treating BPA-containing wastewaters. Data from this study could also be incorporated into pilot and full-scale applications by determining the adsorption and BPA elimination characteristics of the activated sludge of interest.

**EXPERIMENTAL**

**BPA adsorption study**

**Preparing the adsorbent**

Activated sludge biomass used in this study was obtained from a local beverage plant in Adana, Turkey. 10 L of activated sludge was collected and transported immediately to the laboratory within 30 min and aeration was started with air pumps. In the first 30 days, the bioreactor content was acclimatized to the modified synthetic wastewater without BPA. Components of the modified synthetic wastewater were as follows: glucose (19 mg L\(^{-1}\)), peptone (192 mg L\(^{-1}\)), meat extract (138 mg L\(^{-1}\)), K\(_2\)HPO\(_4\) (16 mg L\(^{-1}\)), NH\(_4\)Cl (23 mg L\(^{-1}\)), Na\(_2\)HPO\(_4\)\(\cdot\)2H\(_2\)O (32 mg L\(^{-1}\)), NaHCO\(_3\) (294 mg L\(^{-1}\)), NaCl (60 mg L\(^{-1}\)), and FeCl\(_3\)\(\cdot\)6H\(_2\)O (60 mg L\(^{-1}\)) (Merck and analytical grade) in 1 L tap water without the presence of BPA. Before the beginning of the adsorption (abiotic) study the activated sludge was inactivated using 2 g L\(^{-1}\) sodium azide for the batch experiments. To minimize the floc deformation in activated sludge, instead of using physical methods (e.g. autoclaving), sodium azide method was preferred. Inactivation of the biomass was monitored by chemical oxygen demand (COD) removal. Pre-trials showed that 2 g L\(^{-1}\) sodium azide is sufficient to stop the COD removal for 24 hours. After sodium azide application, biomass was examined under a microscope to inspect the morphology of the biomass. Microscopic examination showed that sodium azide did not cause remarkable morphological changes on biomass flocs.

**Adsorbate**

Preparation of a stock solution of BPA was achieved using distilled water. The structure of BPA is shown in Figure 1.

Molecular weight, molecular size, liquid molar volume, and solubility in water of BPA are shown in Table 1.

**Adsorption tests**

The batch adsorption tests were conducted at 10, 20, and 30 °C in 500-mL conical flasks that included 500 mL of activated sludge using an orbital shaker at the aforementioned temperatures. The initial pH values in the adsorption tests were between 6 and 7 during the batch experiments. During the adsorption test no pH adjustment was made. Therefore, all of the sorption experiments were conducted at pH values between 6 and 7. 2,000 mgTSS L\(^{-1}\) inactivated biomass was added to each flask containing synthetic wastewater and placed in the orbital shaker. The initial BPA concentrations for the experiments were 5, 10, 20, 30, 40, and 50 mg L\(^{-1}\), and the incubation times were 5, 15, 30, 60, 90, and 120 min. After contacting, the contents of the flask were filtered to separate the biomass from the solution. The filtrates were then analyzed with a high-pressure liquid chromatography (HPLC) vessel (HPLC 2000 UV/VIS, Perkin Elmer Technologies, Waltham, MA 02451, USA) to determine the BPA concentrations in the samples. The specific adsorption \(q\) for inactivated sludge was calculated from Equation (1):

\[
q = \frac{(C_0 - C_e)V}{W}
\]

where \(C_0\) and \(C_e\) are, respectively, the initial and equilibrium concentrations of the BPA in the aqueous phase, \(V\) is the volume of the aqueous phase and \(W\) is the

**Table 1** Properties of the BPA (Ocampo-Pérez et al. 2012)

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Molecular weight (g mol(^{-1}))</th>
<th>Molecular size (x,y,z)</th>
<th>V(_2) (cm(^3) mol(^{-1}))</th>
<th>Solubility in water (g L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA</td>
<td>228.29</td>
<td>1.27 × 0.86 × 0.68</td>
<td>294</td>
<td>0.09</td>
</tr>
</tbody>
</table>

\(V_2\) Liquid molar volume at the normal boiling point.
amount of adsorbent (g) employed as calculated from the wet weight of the inactivated sludge.

Control experiments were achieved for BPA to analyze any adsorption onto the glassware and filter paper. Neither precipitation nor adsorption onto the walls of the flasks and filter paper was observed. The results of the BPA analysis were used to calculate the specific adsorption (mg BPA adsorbed g\(^{-1}\) of inactivated sludge). All of the experiments were performed twice and the results were presented as the mean values. The variation was <5%. To evaluate the BPA adsorption capacity of non-living activated sludge, data were applied to various isotherm equations such as Langmuir, Freundlich, Dubinin-Radushkevich, Jovanovic, Vieth-Sladek, and Fritz-Schlunder.

**Biotic BPA elimination study**

This set of batch experiments was performed to evaluate the kinetics of the BPA elimination process at different temperatures, BPA and biomass concentrations. In this set of experiments, the elimination of BPA concentrations of 5, 10, 20, 30, 40, and 50 mg BPA L\(^{-1}\) in the synthetic wastewater were evaluated. Four different biomass concentrations (1,000, 2,000, 3,000, and 4,000 mgTSS L\(^{-1}\)) and three different temperatures (10, 20, and 30 °C) were tested for each BPA concentration. The percentage of volatile suspended solids (VSS) to total suspended solids (TSS) was determined to be between 81 and 84%.

The BPA elimination tests were achieved in 500-mL conical flasks that included a 300 mL mixture of acclimated activated sludge and synthetic wastewater containing BPA at the aforementioned various concentrations. The activated sludge was prepared as described in the ‘Preparing the absorbent’ section, as was the composition of the synthetic wastewater. The initial COD of the influent wastewater was 475 ± 25 mg L\(^{-1}\). Erlenmeyer flasks were mixed at 350 rpm in an incubator-shaker for 24 h. At the end of the shaking period, samples were taken from flasks at certain time intervals and centrifuged at 5,000 rpm for 10 min and the supernatant was analyzed. All experiments were conducted in duplicate. At all stages of the experiments, the pH values of the synthetic wastewater were quite similar to those measured in the flasks. A kinetic analysis of the data on BPA elimination was performed on the basis of Haldane’s equation (Equation (2)), expressing BPA elimination of a substrate by activated sludge (Qu et al. 2005). The data obtained from the elimination study via experiments performed with 2,000 mg L\(^{-1}\) biomass at 20 °C were used to calculate the Haldane equation constants.

\[
V = \frac{V_{\text{max}} C}{K_C + C + \frac{C^2}{K_i}} \quad (2)
\]

where \(V\) and \(V_{\text{max}}\) stand for the specific and the maximum specific substrate elimination rates (mgBPA g\(^{-1}\) SS\(^{-1}\) h\(^{-1}\)), respectively, and \(K_C\), \(C\), and \(K_i\) represent the half-saturation constant, substrate concentration, and inhibition constant (mg L\(^{-1}\)), respectively. The calculations of kinetic constants were performed using Origin\(^{\circledR}\) 7.0 scientific software. Since the Haldane equation includes three unknown parameters \(V_{\text{max}}\), \(K_C\), and \(K_i\), the Origin\(^{\circledR}\) 7.0 scientific software solver package was applied to determine the values of \(V_{\text{max}}\), \(K_C\), and \(K_i\), which corresponded to the correlation coefficient, \(r\). In order to calculate the kinetic constants, the data from elimination study were used as inputs, parameters were defined, and Equation (2) was used the software. Finally, the software performed the iteration to fit the data to the equation. The software calculated the output graph and the table containing the kinetic parameters obtained.

**Analyses**

To calculate the concentration of BPAs in the aqueous solution, the detection of BPA was achieved using an HPLC/UV detection device. In the 100% methanol mobile phase, at a wavelength of 278 nm, using a Zorbax Eclipse XDB-C18 column (4.6 × 150 mm) of 5 μm, the injection volume was 10 μL and the flow rate was 1.0 ml min\(^{-1}\) (Chen et al. 2008).

**RESULTS AND DISCUSSION**

**Results of the basic adsorption study**

In the adsorption experiments, the equilibriums were obtained for six different BPA concentrations at three different temperatures. The adsorption process was slow (90 min). Equilibrium plots are provided in Figure 2.

Adsorption of BPA on inactivated biomass increased with the decrease of temperature. These results indicate that the sorption of BPA is dependent on an exothermic reaction. Considering this result, one can say that increasing the temperature may increase the desorption rate of BPA from the surface of activated sludge biomass. To better calculate the maximum adsorption capacity (\(q_m\)) and
To understand the adsorption process, data from the BPA adsorption by inactive biomass experiments were applied to some of the adsorption isotherms. The data obtained from the adsorption study were used to calculate the isotherm equations. Regression values of the linear equations as a result of the isotherm graphs were considered because a regression coefficient closer to 1 signifies increasing compliance to the isotherms (Chiou & Li 2002). List of adsorption isotherms are given in Table 2. Accordingly, Langmuir, Freundlich, Dubinin-Radushkevich, Jovanovic, Vieth-Sladek, and Fritz-Schlunder isotherm equations were evaluated and the results are provided in Table 3.

Beside the Langmuir and Freundlich isotherms, Dubinin-Radushkevich, Jovanovic, Vieth-Sladek, and Fritz-Schlunder isotherm equations were also used and for comparison, the corresponding equilibrium values for the isotherms are considered in the study.

Table 2 | List of adsorption isotherms

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Equation</th>
<th>Plot</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e )</td>
<td>( q_m ) and ( K_L ) was calculated by plotting ( C_e/q_e ) against ( C_e )</td>
<td>Langmuir (1918)</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( \log q_e = \log K_F + \left( \frac{1}{n} \right) \log C_e )</td>
<td>( K_F ) and ( n ) was calculated by plotting ( \log q_e ) vs ( C_e )</td>
<td>Freundlich (1926)</td>
</tr>
<tr>
<td>Dubinin and Radushkevich</td>
<td>( \varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) ) ( \ln q_e = \ln q_m - B \varepsilon^2 )</td>
<td>( q_m ) and ( B \varepsilon ) was calculated by plotting ( \ln q_e ) against ( \varepsilon )</td>
<td>Bennani et al. (2009)</td>
</tr>
<tr>
<td>Jovanovic</td>
<td>( q_e = q_m (1 - e^{(b C_e)}) )</td>
<td>( q_m ) and isotherm constants was calculated by maximizing the correlation coefficient between the experimental ( q_e ) and predicted ( q_e )</td>
<td>Fontan et al. (2013)</td>
</tr>
<tr>
<td>Vieth and Sladek</td>
<td>( q_e = K_{VS} C_e + \frac{q_m b_{VS} C_e}{1 + b_{VS} C_e} )</td>
<td></td>
<td>Vargas et al. (2011)</td>
</tr>
<tr>
<td>Fritz and Schlunder</td>
<td>( q_e = q_m K_{FS1} C_e^{m_1} )</td>
<td></td>
<td>Hamdaoui &amp; Naffrechoux (2007)</td>
</tr>
</tbody>
</table>
Results of the BPA elimination study

Results suggest that BPA removal efficiency increased with increasing temperature and activated sludge biomass. Figure 3 shows the effect of the amount of biomass on BPA elimination rates at 20°C.

As shown in Figure 3, to obtain high BPA removal at 30 mg L⁻¹ or more of applied BPA concentrations, the amount of biomass should be increased.

Figure 4 shows the effect of the temperature on BPA elimination with 4,000 mg of activated sludge L⁻¹. 1,000 mg of activated sludge L⁻¹ was enough to decrease the 20 mgBPA L⁻¹ concentration below the detection limit at the end of 720 min shaking period at 10, 20 and 30°C. Additionally, the 4,000 mg of activated sludge L⁻¹ was enough to decrease the concentration of 20 mgBPA L⁻¹ below the detection limit after 480 min at 30°C (Figure 4). In all of the amounts of biomass and temperatures applied, the initial concentrations of 5, 10 and 20 mg L⁻¹ of BPA dropped below the detection limit (Figures 3 and 4).

The increased removal rate is probably dependent on increasing temperature. However, activated sludge was not adequate for the full elimination of the 40 and 50 mg BPA L⁻¹ initial concentrations at all of the applied temperatures and biomass concentrations. As well known, various industrial pollutants may have toxic effects on cells. Effects of these toxicants could increase with increase of temperature in influents. As a result of this, removal rate would decrease with increasing temperature due to toxicant effect of pollutants. BPA, for example, would show toxic effect and this effect may rise when temperature is increased. On the other hand, in a biological system, removal rates of various pollutants may vary with increasing temperature. In addition to this, adsorption of BPA on activated sludge is exothermic. This means that BPA adsorption decreases with increasing temperature. At the same time, the first step of biological degradation is adsorption of pollutants onto activated sludge. Under these conditions, increasing temperature will affect the relationship between adsorption and biological degradation.

In order to show the simultaneous COD and BPA elimination efficiency of activated sludge, data obtained from experiments at 20°C have been used and are shown in Figure 5. It can be seen from Figure 5 that COD removal efficiencies were slightly decreased with the addition of BPA. However, removal efficiencies never dropped below 90% even when BPA was used.

In Figure 6, the BPA removal by both inactive and activated sludge and the control experiments at 50°C and 2,000 mg L⁻¹ biomass concentration are provided for

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Table 3 | Summary of regression coefficients and isotherm parameters

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Parameters</th>
<th>Temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Langmuir</td>
<td>q_m (mg g⁻¹)</td>
<td>3.21</td>
</tr>
<tr>
<td></td>
<td>K_L (L mg⁻¹)</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.963</td>
</tr>
<tr>
<td>Freundlich</td>
<td>n</td>
<td>2.232</td>
</tr>
<tr>
<td></td>
<td>K_f (L mg⁻¹)</td>
<td>2.169</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.985</td>
</tr>
<tr>
<td>Dubinin-</td>
<td>q_m</td>
<td>2.012</td>
</tr>
<tr>
<td>Radushevich</td>
<td>B_D (mol² kJ⁻²)</td>
<td>2.544</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.754</td>
</tr>
<tr>
<td>Jovanovic</td>
<td>q_m</td>
<td>2.543</td>
</tr>
<tr>
<td></td>
<td>K_1 (L g⁻¹)</td>
<td>-0.0687</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.946</td>
</tr>
<tr>
<td>Vieth-Sladek</td>
<td>q_m</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>K_VS</td>
<td>0.029</td>
</tr>
<tr>
<td></td>
<td>β_VS</td>
<td>0.310</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.975</td>
</tr>
<tr>
<td>Fritz-Schlunder</td>
<td>q_M</td>
<td>2.33</td>
</tr>
<tr>
<td></td>
<td>K_FSI</td>
<td>0.321</td>
</tr>
<tr>
<td></td>
<td>K_FS2</td>
<td>0.669</td>
</tr>
<tr>
<td></td>
<td>m_1</td>
<td>0.459</td>
</tr>
<tr>
<td></td>
<td>m_2</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.980</td>
</tr>
</tbody>
</table>

Langmuir and other isotherm constants at different temperatures are listed in Table 3. As shown in Table 3, the adsorption capacity of the abiotic sludge increases with decreasing temperature. Zeng et al. (2006) also found similar results when they researched the BPA adsorption capacity of the Xiangjiang River sediments in China.

The regression coefficients listed in the above table show that Freundlich isotherm could fit the data obtained from adsorption tests better than the other adsorption models with a regression coefficient of 0.985 at 30°C. Vieth-Sladek and Langmuir isotherms described the adsorption process best with regression coefficients of 0.999 and 0.996, respectively, at 10°C. As mentioned in the material and methods section, the primary purpose for using these isotherms was to evaluate the different BPA adsorption capacities of nonliving activated sludge. The q_m values obtained from Langmuir isotherm were very close to experimental q_e values (Figure 2). Therefore, Langmuir isotherm predicted the q_m values better than the other isotherms. The adsorption tests for BPA showed that inactivated sludge would adsorb BPA at all concentrations (Figure 2). The data also show that a contact time of 90 min was sufficient to achieve equilibrium.
comparison. As shown in Figure 6, biotic elimination appears to be more effective than abiotic BPA removal from wastewater. In the control groups, BPA concentrations did not change over time, however BPA has been completely removed, especially in the biotic groups. According to Figure 6, it can be stated that BPA is nonvolatile because the BPA concentration did not change with time in the control groups. Because the adsorption capacity of inactivated sludge was found to be very low (4.99 mg g\(^{-1}\) abiotic sludge) in comparison with the results of the biotic group (Figure 6), it is concluded that the primary BPA reduction mechanism was most likely biodegradation. Zhang et al. (2015) stated that BPA did not accumulate in sludge liquor because of the oxidation by microorganisms and 90.11% of BPA was removed from the synthetic influent. In this study, removal efficiencies in abiotic groups were between 12.5 and 30%, whereas removal efficiencies in the biotic study were between 62 and 100%. Removal efficiencies in the biotic study were 100% at the 5, 10, 20, and 30 mgBPA L\(^{-1}\) concentrations. Removal efficiencies were 85% and 62.5% at the 40 mgBPA L\(^{-1}\) and 50 mgBPA L\(^{-1}\) concentrations, respectively. These results show that biological elimination was the dominant removal mechanism, and influent concentrations higher than 30 mgBPA L\(^{-1}\) should be avoided in the activated sludge systems.

**Kinetics**

To show the reaction rates, data were used in the zero-, first- and second-order reaction equations. Kinetic constants that depend on the zero, first and second order for BPA removal by BPA elimination are provided in Table 4.

The linear equations of zero, first, and second order are given as Equations (3), (4) and (5), respectively.

\[
C_t = C_0 - k_0 t
\]  
\[
\ln C_t = \ln C_0 - k_1 t
\]  
\[
\frac{1}{C_t} = \frac{1}{C_0} + k_2 t
\]

where \(C_t\) is the residual dye concentration (mg/L), \(C_0\) is the initial dye concentration (mg L\(^{-1}\)), and \(k_0\) (mg L\(^{-1}\) min\(^{-1}\)) is the rate constant of zero-order reaction kinetics. \(k_0\) can be obtained from the plot of \(C_t\) vs \(t\).

\(\ln C_t = \ln C_0 - k_1 t\)

where \(k_1\) is the (min\(^{-1}\)) rate constant of first-order reaction kinetics. \(k_1\) can be obtained from the plot of \(\ln C_t\) vs \(t\).

\[
\frac{1}{C_t} = \frac{1}{C_0} + k_2 t
\]

where \(k_2\) is the (L mg\(^{-1}\) min\(^{-1}\)) rate constant of first-order reaction kinetics. \(k_2\) can be obtained from the plot of \(1/C_t\) vs \(t\).
The data do not fit well to second-order reaction kinetics. According to the zero- and first-order reaction constants, generally the reaction rates increased with increasing temperature. Regression values of elimination reactions were fit to the zero order as well as the first-order degree of the reaction kinetics. As shown in Table 4, the elimination rate of BPA increases with the increasing temperature. However, it can be seen that the elimination rate of BPA decreases with the increasing BPA concentrations.

To better understand the removal kinetics, Haldane’s equation (Equation (2)) was also used for describing the removal of BPA by activated sludge. Based on Haldane’s
equation, the removal ability of activated sludge was exhibited. The Haldane equation has been widely used to estimate the elimination of many substrates (Qu et al. 2005). The graph for the elimination of BPA according to Haldane’s equation is given in Figure 7.

The kinetic calculations showed that the specific BPA elimination rate increased with the increasing initial BPA content up to 10 mg L$^{-1}$, peaking at 11 mgBPA g$^{-1}$ SS$^{-1}$ h$^{-1}$, then decreasing for the initial BPA contents between 11 and 50 mg L$^{-1}$ (Figure 7), which indicates an inhibitory effect.
of BPA at concentrations exceeding 53 mg L\(^{-1}\). The kinetic parameters estimated with the least-squares error method were \(V_{\text{max}} = 923.1 \text{ mgBPA g}^{-1} \text{ SS}^{-1} \text{ h}^{-1}\), \(K_C = 7582 \text{ mg L}^{-1}\), and \(K_I = 53242 \text{ mg L}^{-1}\), with a correlation coefficient \((r)\) of 0.9071 \((P < 0.0001)\).

Therefore, the resulting kinetic equation is:

\[
V = \frac{1923.1 C}{7582 + C + C^2 / 53242}
\]  

\(\text{(6)}\)

**CONCLUSIONS**

BPA can be successfully removed in an activated sludge system provided that the influent BPA is lower than 30 mg L\(^{-1}\). The adsorption rate for BPA was slow, and a comparison of the \(q_m\) values obtained from six different isotherms demonstrated that the adsorption capacity of abiotic sludge was very low. According to Langmuir’s isotherm model, \(q_m\) of activated sludge was found to be 4.99 mg g\(^{-1}\) at 10 °C. Because BPA is a nonvolatile compound, and the BPA adsorption capacity of the activated sludge is limited, the removal of BPA from wastewater was naturally and highly attributed to biodegradation compared to the abiotic mechanisms. In other words, activated sludge could remove BPA much more effectively than inactivated sludge. Although BPA is known to be toxic, the removal efficiency of BPA in the biotic study was at a 100% efficiency in 5, 10, 20, and 50 initial BPA concentrations. The removal efficiency was never below 63%, even at 40 and 50 mgBPA L\(^{-1}\) concentrations. The BPA elimination kinetics was best fit to first-order reaction kinetics. According to Haldane’s equation, a 53 mg L\(^{-1}\) concentration of BPA has an inhibitory effect on activated sludge organisms.

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**REFERENCES**


Bisphenol-A removal from wastewater by activated sludge. Water Science & Technology | 73.2 | 2016

Furhacker, M., Scharf, S. & Weber, H.


Joseph, L., Heo, J., Park, Y. G., Flora, J. R. V. & Yoon, Y.


Wetherill, Y. B., Petra, C. E., Monk, K. R., Puga, A. & Knudsen, K. E. 2002 The xenoestrogen BPA induces inappropriate


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