Biodegradation Kinetics of Benzene and Naphthalene in the Vadose and Saturated Zones of a (Semi)-arid Saline Coastal Soil Environment

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Biodegradation is a key process for the remediation of sites contaminated by petroleum hydrocarbons (PHCs), but this process is not well known for the (semi)-arid coastal environments where saline conditions and continuous water level fluctuations are common. This study differs from the limited previous studies on the biodegradation of PHCs in Qatari coastal soils mainly by its findings on the biodegradation kinetics of the selected PHCs of benzene and naphthalene by indigenous bacteria. Soil samples were collected above, across, and below the groundwater table at the eastern coast of Qatar within a depth of 0 to -40 cm. Environmental conditions combining low oxygen and high sulfate concentrations were considered in this study which could favor either or both aerobic and anaerobic bacteria including sulfate-reducing bacteria (SRB). The consideration of SRB was motivated by previously reported high sulfate concentrations in Qatari soil and groundwater. Low- and high-salinity conditions were applied in the experiments, and the results showed the sorption of the two PHCs on the soil samples. Sorption was dominant for naphthalene whereas the biodegradation process contributed the most for the removal of benzene from water. Losses of nitrate observed in the biodegradation experiments were attributed to the activity of nitrate-reducing bacteria (NRB). The results suggested that aerobic, NRB, and most likely SRB biodegraded the two PHCs, where the combined contribution of sorption and biodegradation in biotic microcosms led to considerable concentration losses of the two PHCs in the aqueous phase (31 to 58% after 21 to 35 days). Although benzene was degraded faster than naphthalene, the biodegradation of these two PHCs was in general very slow with rate coefficients in the order of 10^{-3} to 10^{-2} day^{-1} and the applied kinetic models fitted the experimental results very well. It is relevant to mention that these rate coefficients are the contribution from all the microbial groups in the soil and not from just one.

1. Introduction

The process of biodegradation has been given considerable interest globally for the purpose of cleaning up the sites contaminated by petroleum hydrocarbons (PHCs) [1–6]. Attention has also been given to natural source zone depletion (NSZD) especially for contaminated sites at their later phases of remediation [7], in which, naturally occurring processes of dissolution, volatilization, and biodegradation result in mass losses of PHC constituents from the subsurface. In addition, bioremediation is a common and cost-effective technique for the treatment of media contaminated by PHCs [8]. A mechanistic understanding of the coupled geochemical and biological processes controlling PHC degradation and metabolisms of the microorganisms is the key for the success of bioremediation. Furthermore, in subsurface environments contaminated by PHCs, the geochemical conditions near the groundwater table, in particular the
availability of oxygen and other oxidative agents, moisture content, salinity, pH, redox potential, nutrient concentrations, and temperature, are key determinants of the biodegradation of PHCs \([1, 9-14]\) and groundwater quality changes. Some studies have shown that tide-induced seawater circulations can cause frequent groundwater table fluctuations in coastal aquifers which in turn can enhance the biodegradation of PHCs after an oil spill (e.g., \([15-18]\)). This enhancement can occur as a result of the redistribution or diffusion of electron acceptors (e.g., oxygen) and donors (e.g., nonaqueous phase liquids or LNAPLs) across the groundwater table during water table rise and fall, thus helping local bacteria for their metabolisms. The variability of biodegradation with depth in PHC-contaminated coastal sediments was in general linked to the presence and distribution of electron acceptors in the subsurface, with oxygen dominating near the surface while for example nitrate, manganese, iron, and sulfate could become dominant with depth \([19]\). Some studies have also investigated the potential of microbial communities to biodegrade PHCs in coastal environments after their exposure to these contaminants by oil spills. Kostka et al. \([20]\) characterized the microbial community involved in the biodegradation of PHCs (C\(_8\) to C\(_{40}\)) in Gulf of Mexico beach sands which were exposed to heavy oil contamination from the well-known Deepwater Horizon oil spill in 2010. They identified up to 24 bacterial strains capable of degrading these PHCs. The biodegradation of naphthalene in seawater-impacted coastal sediments was studied by Jin et al. \([21]\) with enriched cultures established using seawater and modified minimal media containing naphthalene. Their results showed that naphthalene and other polycyclic aromatic hydrocarbons (PAHs) such as phenanthrene and anthracene could be degraded in the sediments over time.

Biodegradation studies generally focus on determining the microbial species involved in the mineralization of various compounds and also on the quantification of this process by kinetic or equilibrium parameters. While these two types of studies have been conducted considerably for saline and nonsaline environments in mostly nonarid regions of the world, there is still limited information available on quantitative kinetic parameters of the biodegradation of PHCs in (semi)-arid saline coastal environments such as in Qatar. This study therefore considers the saline coastal environment of Qatar as an example of a (semi)-arid region to generate more information on such quantitative kinetic parameters. Situated in the Arabian Peninsula, Qatar has a (semi)-arid climate with an average annual evaporation rate of 30 times greater than a negligible amount of precipitation \([22, 23]\). Its main source of economy is from the energy sector as the country possesses large oil and natural gas reservoirs and thus, production of PHCs is very large. The North Gas Field and Al-Shaheen Oil Field are the two largest oil and natural gas fields of Qatar and they are located offshore and northeast of the country. The energy sector is also represented in the northeast coastal city of Ras Laffan by PHC facilities such as the Oryx and Pearl gas-to-liquid plants \([24]\). Based on the above characteristics, the northeastern and eastern coasts of Qatar can be classified as areas with high risk to environmental contamination by PHCs.

Moreover, due to the strong dynamics and interaction of seawater and groundwater at the coast, PHC contaminants could migrate from the sea to aquifers and vice versa. Sediment contamination was shown by Soliman et al. \([25]\) who measured concentrations of total PAHs between 2.6 and 1025 ng g\(^{-1}\) in sediments from the eastern coast of Qatar and offshore between oil and gas fields. Offshore and mainly harbor locations generally had higher concentrations of PAHs compared to other coastal locations. The analysis of concentration ratios between pairs of PAHs suggested that PHC was the main source of contamination at most of the locations while it was pyrolysis of fossil fuels (e.g., for residential heating \([26]\)) at some inshore locations.

Despite the limited amount of previous studies on PHC contaminants in Qatari soil and groundwater environments, volatilization, dissolution, sorption, and biodegradation are among the key processes which can control the fate of PHC in subsurface coastal soil environments. Based on a crude oil report of Al-Shaheen Oil Field showing an American Petroleum Institute (API) gravity > 10 (i.e., lighter than water) \([27]\), PHCs in Qatar could behave like LNAPLs. They can then float on the shallow groundwater table and undergo both volatilization to the vadose zone and, due to groundwater table fluctuations, dissolution into groundwater. Ngueneu et al. \([28]\), using batch experiments, showed that the benzene and naphthalene sorbed on a coastal soil from the eastern coast of Qatar at different magnitudes and sorption increased in general when the temperature decreased and the salinity increased. Studies on biodegradation of PHCs in Qatari soils are very limited. The existing few studies include the work of Al Disi et al. \([29]\) who studied the effects of oil weathering due to long exposure to harsh weather conditions on the diversity, adaptation, and activity of hydrocarbon-degrading bacteria using contaminated soils from autoworkshops and industry waste management sites. In their study, with a purpose to help bioaugmentation strategies, the bacteria were isolated by growing them in the laboratory on the collected soils and using culture media with specific composition. Another study by Al-Thani et al. \([30]\) was on a laboratory extraction of PAH-degrading bacteria from Qatari soils collected at an industrial zone. They used an enrichment medium with a specific composition and either naphthalene, phenanthrene, or anthracene as the sole source of carbon and energy. The increase of optical densities of the isolates showed that they were able to grow on the tested PAHs, and their results showed the potential of using soil bacteria for the bioremediation of sites contaminated by PAHs. The above studies are great contributions for the bioremediation of sites contaminated by PHCs in Qatar and other (semi)-arid regions, but information in this field is still limited especially for the coastal area where a particularly saline environment with continuous water table dynamics exists. An important information still missing is the quantitative evaluation of PHC losses and associated rate coefficients due to biodegradation at the Qatari coastal soil and groundwater environments, and this is the main focus of our study.

We hypothesized that high sulfate concentrations in Qatari coastal soil and groundwater \([22, 28]\) indicate the
potential presence of sulfate-reducing bacteria (SRB). Therefore, aerobic and anaerobic bacteria could coexist in the vadose and shallow groundwater zones with low oxygen concentration. The main objectives of this study were (1) to quantify the biodegradation kinetics of two PHCs in a (semi)-arid saline coastal soil, which was influenced by groundwater table fluctuations and seawater intrusion, by indigenous bacteria at a low oxygen concentration; (2) to investigate the potential difference in biodegradation behavior with depth by considering the vadose and saturated zones of shallow coastal soil environment of Qatar, and the effect of salinity on biodegradation due to seawater intrusion, and (3) to propose a model which takes into account the biodegradation kinetics of the PHCs used in this study to predict the fate of PHCs in (semi)-arid saline coastal soil environments.

2. Materials and Methods

2.1. Field Site and Sampling. The coastal soil, seawater, and groundwater samples were collected from the Sumaysimah beach located on the eastern coast of Qatar. In this site, vertical fluctuations of water levels at the shoreline occur in both the sea and the coastal aquifer due to their continuous interaction. An oil spill at the site could then result in the formation of a smear zone of light PHCs (i.e., LNAPLS) in the shallow subsurface. It was then planned to collect soil samples at different shallow depths including the vadose and saturated aquifer zones (see below). Prior to sampling, the Sumaysimah beach site was investigated for relevant site features and a cross-sectional view of the beach site from the south is shown in Figure 1. This view shows the tidal area between a human-made levee and the sea, and it is along two locations denoted as location A (N25°34'20.9", E51°29'20.3") and location B (N25°34'21.8", E51°29'21.7"), which were situated on sloping and flat areas, respectively. The soil at location A was sandy and contained some small seashells, whereas the soil at location B was silty and clayey at the surface but mostly sandy with some small seashells after a depth of a few centimeters. Visible organic matter was negligible. Seawater was visible at about 100 m from location A and was at low tide (Figure 1(b)) because a clear line made of leaves released by the sea and passing through location A was visible along the shoreline, indicating that the normal high tide was at location A (Figure 1(c)). It was also interpreted that the storm high tide was at or near the foot of the levee (Figure 1(d)). Soil and groundwater samples used in this study were collected at location A in order to have samples within the observed vertical fluctuation zone of seawater (Figures 1(b) and 1(d)) whose amplitude was similar to the amplitude of historical seawater levels of about 1 to 2 m [31].

Soil samples were aseptically collected with a clean shovel at location A at different depths, and they were labeled from the ground surface as A1 (0 to -15 cm), A2 (-15 to -30 cm), and A3 (-30 to -40 cm) (Figure 1(e)). Groundwater was encountered at a depth of about -27 cm below the A2 layer. A2 and A3 were collected saturated with groundwater to preserve their microbial communities and stored saturated. The soil samples were collected disturbed in double black plastic bags placed in sturdy boxes which were afterwards tightly closed. Soil sampling and packaging were performed quickly to minimize the potential effect of oxygen on potential anaerobic bacteria including SRB. 0.5 L of groundwater at location A was collected in an amber glass bottle, and 50 L of seawater was collected in a plastic container. The pH and the electrical conductivity (EC) were measured for groundwater on site using a portable pH meter (Horiba LAQUAtwin B-713) and a conductivity meter (Hach sensION 5). The groundwater table rose after sampling and a height difference of 4 cm was measured between a defined time interval \( dt \) of 55 minutes. As the hole made during sampling had a circular cross section (radius of \( \sim 20 \) cm) and a cylindrical shape, it was then possible to estimate upward groundwater flow parameters such as the flow rate (volume of water which filled up the hole during \( dt \) divided by \( dt \)) and the Darcy velocity (flow rate divided by the cross-sectional area of the hole) [32]. This estimation assumes that the dominant flow
component is vertical in case any potential horizontal flow component may have also contributed.

Groundwater and seawater samples were later analyzed for ion compositions by a Metrohm 850 professional ion chromatography (IC) instrument with two columns for anion (Metrosep A Supp 5-150/4.0, flow rate: 0.7 mL min⁻¹, pressure: 10.30 MPa, and temperature: 24.2 °C) and cation (Metrosep C 4-150/4.0, flow rate: 0.9 mL min⁻¹, pressure: 8.33 MPa, and temperature: 24.2 °C) analyses. About 55 to 65 g of fresh soils A1, A2, and A3 was previously put in the oven and dried at 105°C for 48 hours in order to determine their water content gravimetrically. The soil and seawater samples were stored in the lab at a room temperature of 22°C until their use in batch experiments. Measures were taken to minimize the exposure of potential anaerobic bacteria to oxygen by purging the bags containing the soils with argon gas from time to time and the experiments started 14 days after soil sampling.

2.2. Petroleum Hydrocarbons and Analysis. The PHCs of interest in this study were benzene (C₆H₆) and naphthalene (C₁₀H₈) because they are among the common aromatic products of oil companies in Qatar and can then become source of hydrocarbon contaminants in the soil and groundwater environments [28]. Liquid benzene (99.9+%, Sigma-Aldrich, #270709) and naphthalene in crystal form (99+%, Sigma-Aldrich, #184500) at high purity grade were used in the batch biodegradation experiments. Based on the data shown in Table 1, benzene is lighter (molecular weight), less hydrophobic (K_{oc}) and has a lower affinity to organic carbon (K_{oc}) than naphthalene; however, benzene is more soluble than naphthalene [28].

A solution of the organic solvent dichloromethane (CH₂Cl₂) containing the internal standard metafluoroluene (C₉H₇F) was used for the microextraction of benzene and naphthalene from aqueous samples, and extracted samples were analyzed by gas chromatography (GC). The instrument was an Agilent 7890A GC Series equipped with a GC Sampler 80 and flame ionization detector (minimum detection limit: 0.005 mg L⁻¹, DB5 capillary column: 0.25 mm × 30 m with a film thickness of 0.25 μm, injection port temperature: 275°C, initial column temperature: 35°C, heating rate: 15°C min⁻¹, final temperature: 300°C, and detector temperature: 325°C).

2.3. Batch Biodegradation Experiments. Ngueleu et al. [28] studied the sorption of benzene and naphthalene on a saline coastal soil from the Sumaysimah beach site, where the soil was similar to the soil used in this study whose properties are assumed to also be similar. Their leaching experiment conducted with samples of the coastal soil did not show any sign of contamination by benzene and naphthalene [28]. In the current study, the focus was on the biodegradation of benzene and naphthalene, even if sorption and biodegradation processes had to be run simultaneously and then separated during the analysis. Since the soil samples were collected at different depths and the seawater sample was available, it was possible to consider different environmental conditions for simultaneous sorption and biodegradation experiments, namely, (i) three biodegradation zones which were defined as above the groundwater table when using the soil A1, slightly across the groundwater table when using the soil A2, and below the groundwater table when using the soil A3 and (ii) the salinity levels of the soil which were natural when using Millipore water, denoted hereafter as low salinity, and a salinity level much higher than natural when using seawater, denoted hereafter as high salinity.

The low and high salinities corresponded to EC values measured in saturated soil microcosms averaging 3.1 ± 0.3 and 60.0 ± 0.9 mS cm⁻¹, respectively. Four batch experiments at a constant temperature of 22°C were conducted by combining the above conditions as follows: soil A1 at low salinity, soil A2 at low salinity, soil A3 at low salinity, and soil A3 at high salinity. The latter experiment could help to understand the effect of seawater intrusion on the processes investigated because the EC of groundwater was smaller than that of seawater at the time of sampling (Section 3.1). This study primarily considers that sulfate [28] and oxygen are the main electron acceptors available in the coastal shallow subsurface at the site. It was later found in the results of the investigation that nitrate is also another electron acceptor available in the soil but at low concentrations (see Section 3.2). Therefore, the relevant biodegradation pathways in this study were ultimately three of those described by Acosta-González and Marqués [19] for tidal zones and driven by aerobic bacteria (Equations (1) and (2)), SRB (Equations (3) and (4)), and nitrate-reducing bacteria (NRB) (Equations (5) and (6)):

\[
\text{C}_6\text{H}_6 + 7.5\text{O}_2 + 3\text{H}_2\text{O} \rightarrow 6\text{HCO}_3^- + 6\text{H}^+ \quad (1)
\]

\[
\text{C}_{10}\text{H}_8 + 12\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 10\text{HCO}_3^- + 10\text{H}^+ \quad (2)
\]

\[
\text{C}_6\text{H}_6 + 3.75\text{SO}_4^{2-} + 3\text{H}_2\text{O} \rightarrow 6\text{HCO}_3^- + 3.75\text{HS}^- + 2.25\text{H}^+ \quad (3)
\]

\[
\text{C}_{10}\text{H}_8 + 6\text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow 10\text{HCO}_3^- + 6\text{HS}^- + 4\text{H}^+ \quad (4)
\]

\[
\text{C}_6\text{H}_6 + 15\text{NO}_3^- + 3\text{H}_2\text{O} \rightarrow 6\text{HCO}_3^- + 15\text{NO}_2^- + 6\text{H}^+ \quad (5)
\]

\[
\text{C}_{10}\text{H}_8 + 24\text{NO}_3^- + 6\text{H}_2\text{O} \rightarrow 10\text{HCO}_3^- + 24\text{NO}_2^- + 10\text{H}^+ \quad (6)
\]

where the presence of oxygen could however inhibit the activity of anaerobic bacteria [34].

The methodology applied for the batch biodegradation experiments through a simultaneous sorption and biodegradation approach was similar to that of the batch sorption experiments reported in Ngueleu et al. [28] with some

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight (g Mol⁻¹)</th>
<th>K_{oc} (⁻)</th>
<th>K_{oc} (⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>78.11</td>
<td>135</td>
<td>65</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>128.17</td>
<td>1950</td>
<td>940</td>
</tr>
</tbody>
</table>

Table 1: Properties of benzene and naphthalene used in this study. K_{oc} and K_{oc} are the octanol-water partitioning coefficient and organic carbon-water partitioning coefficient from Mabey et al. [33], respectively.
modifications. The soils were not homogenized prior to sample preparation to limit the exposure of potential anaerobic bacteria to oxygen. Aseptic technique was employed throughout the experiments. For each batch biodegradation experiment at the low or high salinity, two separate 2.6 or 3.9 L solutions of benzene and naphthalene were prepared in amber bottles by first purging Millipore water or seawater with argon gas until the dissolved oxygen (O₂) was about 0.058 mmol L⁻¹. This treatment allowed to have a background concentration of oxygen to represent groundwater into which oxygen would have slowly diffused from the vadose zone due to water table fluctuations. Teflon-coated magnetic stir bars and 10 mmol L⁻¹ of sulfate as electron acceptor for SRB from anhydrous sodium sulfate (Na₂SO₄) were then quickly added in each solution. The final concentrations of sulfate were about 10 and 43.9 mmol L⁻¹ with Millipore water and seawater, respectively. Although oxygen could inhibit the activity of SRB, the addition of sulfate was because the soil samples also contained it as a major anion based on the work of Ngueleu et al. [28] and it was also measured in groundwater (in contact with A2 and A3 on site) and seawater samples (see Section 3.1). The only electron donors and energy or carbon source available for the indigenous soil bacteria were benzene and naphthalene. The solutions were then spiked separately with benzene and naphthalene to get concentrations of about 0.2 and 0.1 mmol L⁻¹, respectively. The bottles were immediately tightly closed with caps having Teflon-faced septa. The solutions were afterward put on two stirrers to dissolve benzene and naphthalene for about 1 to 2 weeks. When dissolution was complete, duplicate 19 mL samples of the solutions of benzene and naphthalene were collected and a microextraction of benzene and naphthalene was performed using the previously prepared solution of dichloromethane containing metafluorotoluene. For a more detailed explanation of the applied microextraction method, the reader is referred to Ngueleu et al. [28]. The extracted samples were analyzed for benzene and naphthalene concentrations by GC to confirm the concentrations in initial solutions. In order to inhibit microbial activities in controls, a stock solution of 230.2 mmol L⁻¹ of the biocide mercury(II) chloride (HgCl₂) was also prepared using Millipore water deoxygenated with argon gas using a cannula, and finally filled with the solution of either benzene or naphthalene using a bottle-top dispenser having a PTFE inlet tubing. Small volumes of the initial solution were sampled before and after dispensing into the serum bottles to validate the initial concentrations of benzene, naphthalene, and sulfate. For each sampling time during the batch biodegradation experiments, there were three bottles which received only either benzene or naphthalene, denoted hereafter as biotic microcosms, and two bottles which received 0.280 mL of the stock solution of mercury(II) chloride in addition to either benzene or naphthalene, denoted hereafter as abiotic controls. The final concentration of mercury(II) chloride in the abiotic controls was about 1.1 mmol L⁻¹ and provided the minimum of 500 mg of mercury(II) chloride per kg of soil to inhibit microbial activities [35]. Controls and biotic microcosms were employed to distinguish between mass losses by sorption and by combination of sorption and biodegradation, respectively. The volumes of the aqueous phases were determined gravimetrically, and the final liquid-to-solid ratio (LS) was 1.6 mL g⁻¹ (56 ± 0.4 mL of solution divided by 35.1 ± 0.08 g of soil). The headspace was minimized in all bottles in order to limit the loss by volatilization. The bottles were immediately closed using open-top unlined aluminum caps with Teflon-faced septa, then firmly cramped and placed on their side in a large black plastic bag in an open-top box. The box was placed and sealed in a dark-shaking incubator in a room with temperature maintained at 22°C, then shaken at 160 rounds per minute to keep the soil particles in suspension and allow the dissolution of salts that bacteria could need for their metabolism.

Sampling of the aqueous phase for hydrocarbon (benzene and naphthalene) and ion (sulfate, calcium, and magnesium) analyses occurred successively after 2 hours and 1, 4, 7, 14, 21, and 35 days. Sampling for the experiments with soil A3 at high salinity was stopped after 21 days as the rates of combined sorption and biodegradation reached the same magnitude as observed with the other conditions at 35 days (Section 3.2). At each sampling time, the pH of the aqueous phase was measured and aqueous samples were analyzed for hydrocarbons and ions by GC and IC, respectively.

2.4. Numerical Modeling. The kinetics of simultaneous sorption and biodegradation of benzene and naphthalene data were determined using the two-site sorption kinetic model presented in Ngueleu et al. [28]. (Note: Ngueleu et al. [28] only studied the sorption process, not the biodegradation.) In brief, the model assumes that two sorption sites exist on the soil particles and while sorption is instantaneously in equilibrium on one site, it is rate-limited on the other site and the Langmuir sorption isotherm was used to define the sorption on the equilibrium site. The model can
therefore be written in its more general form by adding a reaction term $R$ (mmol day$^{-1}$) as follows:

$$
V \frac{\partial C}{\partial t} + m \left( \frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} \right) = R,
$$

$$
\frac{\partial S_1}{\partial t} = \frac{\partial}{\partial t} \left[ f_{eq} \left( \frac{S_{\text{max}} C}{K + C} \right) \right],
$$

$$
\frac{\partial S_2}{\partial t} = \lambda \left( f_{eq} \left( \frac{S_{\text{max}} C}{K + C} \right) - S_2 \right),
$$

where $V$ (L) is the volume of the aqueous solution in the serum bottles, $C$ (mmol L$^{-1}$) is the aqueous concentration of benzene or naphthalene, $t$ (s) is the time, $m$ (kg) is the mass of the soil in the serum bottles, $S_1$ (mmol kg$^{-1}$) is the sorbed concentration at the site with instantaneous equilibrium sorption, $S_2$ (mmol kg$^{-1}$) is the sorbed concentration at the site with kinetic sorption, $f_{eq}$ (-) is the fraction of equilibrium sorption with values between 0 and 1, $S_{\text{max}}$ (mmol kg$^{-1}$) is the maximum sorbed concentration, $K$ (mmol L$^{-1}$) is the half-saturation concentration, and $\lambda$ (day$^{-1}$) is the first-order rate coefficient of kinetic sorption. The results of the abiotic controls from batch experiments containing inactive bacteria and those of the biotic microcosms containing active bacteria were then modeled separately. For the controls, the model denoted hereafter as model M1 was the same as described in Ngueleu et al. [28] by setting the reaction term $R$ equals to zero. For the biotic microcosms, the model denoted hereafter as model M2 was defined by assuming that biodegradation can be described by a first-order biodegradation rate, which led to $R$ having the following expression:

$$
R = -k_b CV,
$$

where $k_b$ (day$^{-1}$) is the first-order biodegradation rate coefficient. For each batch experiment, model M1 was first run and the fitting parameters were $f_{eq}$, $\lambda$, $S_{\text{max}}$, and $K$. The MATLAB function fminsearchbnd was used to fit the experimental data, and the boundaries were applied to the above four parameters except $\lambda$. The boundary values of $S_{\text{max}}$ and $K$ were taken from Ngueleu et al. [28] and corresponded to the ranges of the parameters of Langmuir sorption isotherm of their experiments conducted at 25°C and natural salinity. The average mass of soil (~35.1 g) and volume of aqueous phase (~56 mL) were among the input variables. The root mean square error (RMSE) between measured and simulated data was minimized during model fitting and was used as a criterion to evaluate the goodness of the fit. Since the abiotic controls were run in parallel with the biotic microcosms, it was then possible to assume that the process of sorption was the same in both types of experiments. Therefore, the simulated values of $f_{eq}$, $\lambda$, $S_{\text{max}}$, and $K$ from model M1 were used in model M2, which was set up similarly to model M1 except that the only fitting parameter was $k_b$.

### 3. Results and Discussions

#### 3.1. Properties of Groundwater, Seawater, and Soil Samples

The EC, pH, and temperature of the field sampled groundwater were measured as 5.3 mS cm$^{-1}$, 7.4, and 25°C, respectively. In the laboratory at 22°C, before starting the batch experiments, the EC and pH of the groundwater sample were measured again and the values were the same as in the field and the EC and pH of the seawater sample were 63.3 mS cm$^{-1}$ and 8.2, respectively. Note that a seawater pH scale was not used because calibration of the pH meter was not done using a buffer made of a synthetic seawater medium such as Tris buffers [36, 37]. The seawater was more saline than the groundwater based on the above EC values. The groundwater was near-neutral whereas the seawater was slightly alkaline but the difference between their pH was fairly small. In general, it would be possible that the EC and pH of groundwater are within or near the ranges defined by both groundwater and seawater values due to the interaction between the two water sources in the coastal area. This statement is consistent with the study of Shomar [22] who reported the EC and pH in inland and coastal groundwater in Qatar in the ranges of 0.022-30.6 mS cm$^{-1}$ and 7-8.22, respectively.

The concentrations of major cations and anions measured in the groundwater and seawater samples are presented in Table 2. Sodium (Na$^+$) and chloride (Cl$^-$) had the highest concentrations in both waters. The relative abundance of major ions in groundwater followed the same pattern presented in Kuiper et al. [38], where the concentrations of cations were as sodium (Na$^+$) > calcium (Ca$^{2+}$) > magnesium (Mg$^{2+}$) > potassium (K$^+$) and for anions as chloride (Cl$^-$) > sulfate (SO$_4^{2-}$) > bromide (Br$^-$). For seawater, the relative abundance was the same as in groundwater for anions but different for cations (Na$^+$ > Mg$^{2+}$ > K$^+$ > Ca$^{2+}$). The origin of major ions in groundwater was linked to the limestone and gypsum composition of the native rock and soil as well as sea salt aerosols [38]. Shomar [22] also stated that dissolved ions could precipitate as calcite and gypsum in the vadose zone after the evaporation of groundwater. The concentration of Mg$^{2+}$ in seawater is close to that of standard seawater [39]. The concentration of SO$_4^{2-}$ used in the batch biodegradation experiments in this study was similar to the concentration in the groundwater (natural or low-salinity condition).

<table>
<thead>
<tr>
<th>Water type</th>
<th>Na$^+$ (mmol L$^{-1}$)</th>
<th>K$^+$ (mmol L$^{-1}$)</th>
<th>Ca$^{2+}$ (mmol L$^{-1}$)</th>
<th>Mg$^{2+}$ (mmol L$^{-1}$)</th>
<th>Cl$^-$ (mmol L$^{-1}$)</th>
<th>Br$^-$ (mmol L$^{-1}$)</th>
<th>SO$_4^{2-}$ (mmol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>40.61 ± 1.16</td>
<td>1.35 ± 0.05</td>
<td>6.62 ± 0.19</td>
<td>3.66 ± 0.12</td>
<td>43.86 ± 0.92</td>
<td>0.03 ± 0.00</td>
<td>10.83 ± 0.14</td>
</tr>
<tr>
<td>Seawater</td>
<td>532.71 ± 93.98</td>
<td>11.76 ± 1.35</td>
<td>10.59 ± 2.36</td>
<td>55.92 ± 14.26</td>
<td>702.81 ± 129.00</td>
<td>0.78 ± 0.19</td>
<td>33.80 ± 11.52</td>
</tr>
</tbody>
</table>

#### Table 2: Major cations and anions of groundwater and seawater samples.
whereas they were between 7 and 12, see Section 2.1) could also correspond to the length of interwell interval in which the groundwater table fluctuates. In general, the topographical and hydrological features observed at the tidal area were similar to those described by other studies in coastal sabkha areas in the Arabian Peninsula [41, 42]. The soil used in this study was attributed to the class of beach sand and sabkha soils [28].

3.2. Kinetics of Sorption and Biodegradation. The results of the biodegradation experiments are shown in Figures 2–4. The measured mean concentrations of Ca^{2+} and Mg^{2+} at the low-salinity condition were slightly higher in the abiotic controls (2.97–4.09 mmol L^{-1} for Ca^{2+} and 0.76–1.19 mmol L^{-1} for Mg^{2+}) than in the biotic microcosms (1.17–2.74 mmol L^{-1} for Ca^{2+} and 0.49–0.89 mmol L^{-1} for Mg^{2+}). The lower concentrations in the biotic microcosms were possibly due to the uptake of Ca^{2+} and Mg^{2+} by bacteria for their metabolism because of the results discussed below (Figures 2 and 3) showing that the benzene and naphthalene were biodegraded in all experiments. Another possible explanation is the sorption of these divalent ions to the soil due to the lower ionic strength in the biotic microcosms [43], which would decrease their concentrations in the aqueous phase. Conversely, the higher ionic strength in the abiotic controls (due to the biocide) could have an important influence on cation exchange and limit the sorption of Ca^{2+} and Mg^{2+}. Because carbonate minerals are among the major constituents of Qatari soils [22], their chemical elements such as Ca^{2+} and Mg^{2+}, therefore, leached from the soil samples during the experiments. As a consequence to the microbial uptake or sorption of Ca^{2+} and Mg^{2+}, all experiments showed a slightly higher pH value in the biotic microcosms than in the controls, because the carbonate ions left in solution led to an increase of the pH. For the experiments with all soil samples at the low-salinity condition, the pH values in the biotic microcosms were between 8.6 ± 0.3 and 8.7 ± 0.2, whereas they were between 8.2 ± 0.2 and 8.4 ± 0.1 in the controls. For the experiments with soil A3 at high salinity, the pH values in the biotic microcosms were between 7.7 ± 0.1 and 7.8 ± 0.2, whereas they were about 7.7 ± 0.2 in the controls. Note that despite the small difference in pH values of the biotic and abiotic samples, their respective pH values were in general stable during the experiments. The low-salinity level in the biotic microcosms containing benzene corresponded to average EC values of 3.2 ± 0.1, 3.3 ± 0.2, and 2.6 ± 0.0 mS cm^{-1} with soils A1, A2, and A3, respectively, and similar values were obtained with naphthalene as they were 3.4 ± 0.1, 3.3 ± 0.1, and 2.6 ± 0.1 mS cm^{-1} with soils A1, A2, and A3, respectively. The higher EC values in soils A1 and A2 are due to the evaporation of water in the vadose zone at the sampling site which increases the salt content. The high-salinity level in the biotic microcosms prepared with only soil A3 corresponded to average EC values of 59.4 ± 0.4 and 60.6 ± 0.8 mS cm^{-1} with benzene and naphthalene, respectively.

Figure 2 shows the time series normalized concentrations of benzene, naphthalene, and SO_{4}^{2−} from the experiments with soils A1, A2, and A3 at low salinity. For the experiments with the deepest soil A3 at high salinity, the results are shown in Figure 3. After 1 day at low salinity, the normalized mean concentrations of benzene in the abiotic controls decreased due to sorption by about 7%, 11%, and 11% on soils A1, A2, and A3, respectively (Figures 2(a), 2(c), and 2(e)), and the concentrations remained relatively stable until 35 days due to equilibrium state with losses of about 7–9%, 7–18%, and 11–19% on soils A1, A2, and A3, respectively. With soil A3 and high salinity, the analysis of the normalized mean concentrations of benzene in the abiotic controls showed that the losses by sorption also stabilized after 1 day between 10 and 17%, and this behavior was similar to the case of soil A3 at low salinity (Figure 3(a)). These results are almost similar to those shown in Ngueleu et al. [28], where a loss by sorption of 12–14% was measured and reached equilibrium after 1 to 2 days for benzene at 25°C and at natural salinity. The slight difference (lower) in loss by sorption on soil A1 at low salinity (7–9%), in this study, is due to the fact that the sorption followed the Langmuir sorption model and Ngueleu et al. [28] used the same mass of sorbent of 35 g (i.e., same number of sorption sites) but a smaller LS of 1.28 ± 0.01 mL g^{-1} and a lower initial concentration (C_{0}) of ~1×10^{-2} mmol L^{-1}, which resulted in slightly lower C/C_{0} values in their study. Note, however, that the Langmuir sorption model (Equation (7)) should not be affected by LS especially that the Langmuir sorption model is limited to one sorption layer.

Losses of about 7 to 25% of aqueous concentrations of naphthalene also occurred in the abiotic controls after 1 day due to sorption on the soils at low salinity (Figures 2(b), 2(d), and 2(f)). These concentrations continued to decreased until equilibrium sorption was reached for naphthalene after 7 days (21% loss), 14 days (28% loss), and 7 days (36–40% loss) with soils A1, A2, and A3, respectively. For naphthalene with soil A3 at high salinity (Figure 3(b)), although the decrease in the controls of 31% at 1 day is almost similar to the case of soil A3 at low salinity (Figure 2(f)), losses by sorption kept increasing until 14 days when an equilibrium was reached at a loss of 47 to 49%. Similarly to the case of benzene with soil A1 at low salinity, the above equilibrium sorption rate and time of naphthalene were also different from those shown in Ngueleu et al. [28] at 25°C and at natural salinity where the rate was measured as 75% at the equilibrium time of 2 days. These differences were due to the same reason given above for benzene and suggest
Figure 2: Sorption and biodegradation kinetics of benzene (Benz.) and naphthalene (Naph.) with soils A1 (a and b), A2 (c and d), and A3 (e and f) at low salinity. In Figures 2–4, the symbols are mean concentrations while the error bars are intervals between maxima and minima and they are within the width of the symbols when not visible. Aqueous concentrations at sampling time (C) are normalized by their respective initial concentrations (C₀).
that sorption kinetics on the Qatari soil varies with LS and $C_0$, especially for naphthalene in which the highest difference in the sorption rate at equilibrium was observed.

Overall, the above results on sorption show that naphthalene sorbed stronger than benzene for all the scenarios considered and this was due to its higher affinity to organic carbon, reported in [28] for similar soils at 0.84 ± 0.47% dry, and to its higher hydrophobicity (see Table 1). Sorption at low salinity for benzene was in general similar and slightly stronger with soils A2 (7-18%) and A3 (11-19%) than with soil A1 (7-9%). For naphthalene, the loss by sorption at the low salinity was the strongest with soil A3 (36-40%). At the low-salinity level, the increase of sorption with depth cannot be attributed to salinity because the EC of the deepest soil A3 was slightly smaller than those of soils A1 and A2. Ngueleu et al. [28] also showed that the sorption of naphthalene was not affected by salinity at the low-salinity level. A probable reason for the increase of sorption with depth is the

![Figure 3](image1.png)

**Figure 3:** Sorption and biodegradation kinetics of benzene (a) and naphthalene (b) with soil A3 at high salinity (seawater).

![Figure 4](image2.png)

**Figure 4:** Summary of normalized aqueous concentration losses of benzene (Benz.) and naphthalene (Naph.) due to simultaneous sorption and biodegradation in biotic microcosms as a function of depth and salinity. The horizontal gray lines represent the limits between the soils A1, A2 and A3 from the top.
heterogeneous physicochemical properties of the soil samples. However, when the results of the low- and high-salinity levels are considered, the higher concentration losses at the high salinity of only naphthalene suggest that the sorption of this compound could increase with salinity (36-40% to 47-49% with soil A3 at low- and high-salinity levels, respectively).

In Figure 2, the decrease of the normalized mean concentration of benzene in the biotic microcosms at low salinity was the same as in the controls after 4, 1, and 4 days with soils A1, A2, and A3, respectively. The concentration of benzene in soil A1 then deviated from the sorption equilibrium level with a constant slope from the 7th to the 35th day at reductions of 12% and 31%, respectively. The latter observation indicates that the biodegradation of benzene occurred in the biotic microcosms after a lag phase of about 7 days, and indicates that the biodegradation of benzene occurred in biotations of 12% and 31%, respectively. The latter observation due to biodegradation were observed from the 4th day, but as in the controls. With this soil, di biotic microcosms decreased in general in the same manner as in the controls. With this soil, differences in concentration due to biodegradation were observed from the 4th day, but due to fluctuating concentrations in the controls, a clear difference was noticeable after 21 days. Without considering the fluctuations, biodegradation alone accounted for about 8% of concentration loss on the 35th day. The lag phase of biodegradation of naphthalene with soils A2 and A3 at low salinity was about 14 days because clear differences in concentration were observed afterwards, with the highest reductions due to biodegradation of 21% and 17% on the 35th day, respectively.

In Figure 3, the results for soil A3 at high salinity showed that the maximum mean losses of about 39% and 58% at 21 days of the combined sorption and biodegradation in biotic microcosms were similar to those measured at low salinity at 35 days (about 40% and 54%) for benzene and naphthalene, respectively. The total significant reduction of naphthalene from the aqueous phase at high salinity was mostly due to sorption not biodegradation. The lag phases of biodegradation were about 4 and 7 days for benzene and naphthalene, respectively. The losses due to biodegradation of benzene and naphthalene at high salinity were about 22% and 11%, while the corresponding losses at 21 days with soil A3 at low salinity were 19% and 10%, respectively. The above results indicate that the coastal indigenous bacteria were capable of metabolizing the hydrocarbons in soil A3 in both low- and high-salinity conditions and at similar rates.

For all the scenarios considered, the normalized mean concentrations of SO$_4^{2-}$ were quite similar in abiotic and biotic samples (Figures 2 and 3) and they were in general equal to approximately 1.0 with some exceptions. The exceptions include for example the normalized mean concentration of SO$_4^{2-}$ of about 1.3 from the experiment with benzene in soil A1 at low salinity (Figure 2(a)). Normalized SO$_4^{2-}$ concentrations higher than 1.0 suggest that it leached from the soil during the experiment as observed by Nguelou et al. [28]; the difference in concentrations at different times is indicative of the nonuniform distribution of SO$_4^{2-}$ in the coastal soil. Serum bottles could have indeed received fractions of the coastal soil with slightly different SO$_4^{2-}$ concentrations since the homogenization of the soil prior to filling the serum bottles was not done.

For the low-salinity condition, nitrate (NO$_3^-$) was also detected at low concentrations but generally higher in controls than in biotic samples, and this finding suggests that NRB are also among the microbial groups in the coastal soil because nitrate was not added in the background solutions. The ability of NRB to biodegrade benzene and naphthalene is well documented (e.g., [44-47]). For the experiments with benzene, the absolute mean concentrations of NO$_3^-$ in the abiotic and biotic samples were, respectively, 0.073 ± 0.013 and 0.0 ± 0.0 mmol L$^{-1}$ with soil A1, 0.0 ± 0.0 and 0.0 ± 0.0 mmol L$^{-1}$ with soil A2, and 0.039 ± 0.027 and 0.02 ± 0.028 mmol L$^{-1}$ with soil A3. For the experiments with naphthalene, these concentrations of NO$_3^-$ in the abiotic and biotic samples were, respectively, 0.072 ± 0.009 and 0.005 ± 0.007 mmol L$^{-1}$ with soil A1, 0.027 ± 0.024 and 0.004 ± 0.005 mmol L$^{-1}$ with soil A2, and 0.024 ± 0.033 and 0.005 ± 0.013 mmol L$^{-1}$ with soil A3. Due to low NO$_3^-$ concentrations in the soil, it was not detected in samples from the high-salinity condition because the dilution of the corresponding IC samples was high in order to determine the major anion SO$_4^{2-}$ which was prepared at an elevated concentration.

The measurement of dissolved O$_2$ was performed in biotic microcosms and the observed lowest and consumed absolute concentrations of this electron acceptor along with those of NO$_3^-$ are shown in Table 3. Based on the observed maximum concentrations of O$_2$ and NO$_3^-$ consumed, the maximum concentrations of the two PHCs that could be mineralized by aerobic bacteria and NRB are also presented in Table 3. The calculations of PHC concentrations were performed by using the stoichiometry ratios between the PHCs and O$_2$ (7.5 : 1 and 12 : 1 for benzene and naphthalene, respectively) and between the PHCs and NO$_3^-$ (15 : 1 and 24 : 1 for benzene and naphthalene, respectively) (Equations (1) and (2) and (5) and (6), respectively). Mass balance calculations were not performed with SO$_4^{2-}$ because considerable leaching of this anion occurred during the experiments that did not enable to clearly determine losses associated with biodegradation by SRB. For the low-salinity condition, the results in Table 3 show that the calculated PHC concentrations biodegraded by both aerobic bacteria and NRB vary between about 11% and 85% of the actually observed maximum concentrations of PHCs biodegraded in the experiments, with the highest microbial contribution being for the case of naphthalene in soil A1.

An estimate of the remainder of PHC concentrations not associated to O$_2$ and NO$_3^-$ losses in all scenarios can be determined by neglecting the contribution of NRB at the high-salinity condition due to the lack of NO$_3^-$ data (Table 3). This remainder varies between 0.038 and 0.055 mmol L$^{-1}$ for benzene and between 0.001 and 0.021 mmol L$^{-1}$ for naphthalene. The calculated concentration losses of SO$_4^{2-}$ needed to
<table>
<thead>
<tr>
<th>Compound</th>
<th>Soil and environmental condition</th>
<th>Electron acceptor</th>
<th>Observed lowest concentration of an electron acceptor in biotic samples (mmol L⁻¹)</th>
<th>Observed maximum consumption of an electron acceptor* (mmol L⁻¹)</th>
<th>Maximum concentration of PHCs biodegraded based on maximum electron acceptor consumed† (mmol L⁻¹)</th>
<th>Observed actual maximum concentration of PHCs biodegraded in the experiment including an assumed contribution of SRB (mmol L⁻¹)</th>
</tr>
</thead>
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<td>Benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>A1 (low salinity)</td>
<td></td>
<td>O₂</td>
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<td>0.053</td>
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<td>0.008</td>
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<td>0.003</td>
<td>0.008</td>
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<td>A2 (low salinity)</td>
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<td>0.022</td>
<td>0.002</td>
<td>0.012</td>
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<td>NO₃⁻</td>
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<td>0.012</td>
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<td>0.005</td>
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<td>0.033</td>
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<td></td>
<td>NO₃⁻</td>
<td>No data</td>
<td>No data</td>
<td>No data</td>
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</tbody>
</table>

The evaluation was performed with the mean concentrations of triplicate biotic samples and duplicate controls. *The consumption or losses of O₂ and NO₃⁻ are reductions from the initial concentration of O₂ and concentrations of NO₃⁻ in controls, respectively. †The calculations were based on the stoichiometry ratios in Equations (1) and (2) and (5) and (6).
mineralize these concentrations of benzene, based on the stoichiometry ratio of 3.75:1 (Equation (3)), are between 0.144 and 0.208 mmol L⁻¹; and naphthalene, based on the stoichiometry ratio of 6:1 (Equation (4)), are between 0.008 and 0.127 mmol L⁻¹. These losses of SO₄²⁻ are less than 3% of its initial concentrations (10 and 43.9 mmol L⁻¹ at the low- and high-salinity conditions, respectively). These results suggest that aerobic bacteria, NRB and most likely SRB biodegraded benzene and naphthalene in the biotic microcosms for the period investigated. The expected losses of SO₄²⁻ (<3%) were very low that they could explain why a clear decreasing trend of the concentration of SO₄²⁻ in the biotic microcosms could not be seen in Figures 2 and 3. If oxygen inhibited the activity of the anaerobic bacteria at some time during the experiment [34], it would imply that the performance of the anaerobic bacteria observed in this study is among the best because groundwater at the site could continuously be supplied by oxygen due to frequent groundwater table fluctuation. Dobson et al. [48], who conducted laboratory thin-slab sandy aquifer experiments in water-fluctuating and non-fluctuating conditions and using a solution containing O₂, NO₃⁻, and SO₄²⁻, also observed both aerobic and anaerobic biodegradations in their experiments as indicated by minor losses of SO₄²⁻ for a short period and significant losses of O₂ and NO₃⁻.

In general, the experimental results from the biotic microcosms and abiotic controls show that sorption was the dominant process for naphthalene whereas biodegradation was the main process controlling the fate of benzene. Regarding biodegradation at low salinity, the losses of aqueous concentration for benzene after 35 days were slightly higher in soil A2 (28 ± 2%) than in soils A1 (22 ± 4%) and A3 (21 ± 2%). This conclusion cannot be drawn for naphthalene because of the large standard deviation obtained with soil A3 (8 ± 3%, 21 ± 1%, and 17 ± 9% for soils A1, A2, and A3, respectively). Since soil A2 was located across the groundwater table at the time of sampling, the latter rates would suggest that the interface between the vadose zone and the groundwater system could be a hot spot for the biodegradation of at least benzene at low salinity. However, due to the possible good hydraulic connection between the shallow aquifer and the sea, as suggested by the type of coastal soil (sandy) and by the rise of the groundwater table during sampling, soils A1 and A3 would also frequently intersect with the groundwater table similarly to soil A2. That being said, microbial activities in these three soil samples would in general be similar.

A summary of the combined contribution of sorption and biodegradation on the kinetic removal of benzene and naphthalene from the aqueous phase as a function of depth and salinity is shown in Figure 4. Visually, the plots clearly show that the removal increased with depth and salinity, and as stated before, the dominant removal process was biodegradation for benzene and sorption for naphthalene. It is possible that the weaker sorption of benzene, as compared to naphthalene, made it easily bioavailable to bacteria in the aqueous phase. The fact that benzene also has a smaller molecular weight than naphthalene, it could have also facilitated its relatively faster biodegradation because the lighter PHCs are generally more susceptible to microbial degradation than the heavier ones [5, 14]. A statistical regression analysis of the percent losses of PHCs (\(1 - C / C_0\) × 100) due to sorption and biodegradation versus depth and salinity as EC (separately) was performed for selected sampling times. These times corresponded to the results showing stronger visual relationships with depth and EC separately. The data sets selected were then those obtained at 21 and 35 days when using depth data (i.e., means of soil intervals of 7.5, 22.5, and 35 cm), and only at 21 days when using salinity data (i.e., mean of EC data of 3.2, 3.3, 2.6, and 59.4 mS cm⁻¹ for benzene and 3.4, 3.3, 2.6, and 60.6 mS cm⁻¹ for naphthalene). This analysis was carried out using the Microsoft Office Excel Program Analysis ToolPak which provided the square of the Pearson correlation coefficient \(R^2\) and the \(p\) value between two variables. As shown in Table 4, \(R^2\) values of 1.0 indicate good linear correlations between percent loss (\(y\)) and depth (\(x\)) after 21 days for benzene \((y = 0.36x + 21.43)\) and naphthalene \((y = 0.98x + 15.71)\) and, based on a significance level (\(\alpha\)) of 0.05, these relationships were statistically significant \((p < 0.05)\). Good linear correlations also existed after 35 days for benzene \((y = 0.33x + 29.14)\) and naphthalene \((y = 0.77x + 28.29)\), but they were not statistically significant because \(p\) values were greater than 0.05. No statistically reasonable relationship was obtained between the percent losses and EC data at 21 days but this could somehow be due to the fact that three of the four EC data were fairly similar, therefore not providing any possible trend. However, the lack of relationship with the EC would support the interpretation previously mentioned that the indigenous bacteria metabolized the two PHCs at low- and high-salinity conditions and at similar rates (using soil A3).

The best fits of the models M1 and M2 are plotted in Figures 2 and 3, and the model parameters are presented in Table 5 along with RMSE values which reflect the very good

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percent losses at low salinity by sorption and biodegradation versus depth</th>
<th>Percent losses by sorption and biodegradation versus salinity as EC</th>
<th>(k_b) values at low salinity versus depth</th>
<th>(k_b) values versus salinity as EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>(R^2)</td>
<td>(p) value</td>
<td>(R^2)</td>
<td>(p) value</td>
</tr>
<tr>
<td>21 days</td>
<td>1.00</td>
<td>0.04</td>
<td>0.93</td>
<td>0.16</td>
</tr>
<tr>
<td>35 days</td>
<td>1.00</td>
<td>0.007</td>
<td>0.96</td>
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agreement of the fits. For their batch sorption experiments at 25°C and natural salinity, Ngueleu et al. [28] determined that the ranges of \( S_{\text{max}} \) and \( K \) for benzene were 0.031-0.050 mmol kg\(^{-1}\) and 0.091-0.193 mmol L\(^{-1}\), whereas for naphthalene they were 0.236-0.464 mmol kg\(^{-1}\) and 0.070-0.163 mmol L\(^{-1}\), respectively. The values of \( S_{\text{max}} \) and \( K \) in Table 5 are all within these ranges. The values of \( f_{\text{eq}} \) and \( \lambda \) indicate that equilibrium sorption dominated over kinetic sorption for benzene (\( f_{\text{eq}} > 0.5 \) and higher \( \lambda \)) whereas except for the experiment with soil A3 at low salinity, kinetic sorption was dominant for naphthalene. The magnitudes of \( k_b \) values suggest that biodegradation occurred at very slow rates. The lowest biodegradation rates were for naphthalene with soils A1 and A2 at the low-salinity condition. The slow rates could represent cases of first microbial exposure to PHCs since the soil was not contaminated at the site because cases of prior microbial exposure could exhibit faster biodegradation rates [46]. Suarez and Rifai [49] conducted a comprehensive review of biodegradation rates of fuel hydrocarbons from 133 field and laboratory studies which were conducted under either aerobic, anaerobic, or mixed aerobic/anaerobic conditions. From their statistical analysis of the results, median rate coefficients for benzene, ethylbenzene, and xylenes of (3 to 4) \( \times 10^{-3} \) day\(^{-1}\) were estimated from all the studies. These values are similar or close to the values estimated in this study. It is relevant to remind that aerobic and anaerobic bacteria mineralized benzene and naphthalene in this study, and therefore, the observed losses of these PHCs (Figures 2 and 3) and the simulated kinetic rate coefficients (Table 5) represent their combined contribution. These results should then not be extrapolated to other studies with differing availability of electron acceptors (e.g., studies with single redox conditions). A statistical regression analysis of \( k_b \) versus depth and salinity as EC (separately) was also performed and the results are presented in Table 4. Similarly to the analysis using the percent losses, good linear correlations were also obtained between \( k_b \) (y) and depth (x) for benzene (\( y = 2 \times 10^{-4}x + 8 \times 10^{-3} \)) and naphthalene (\( y = 2 \times 10^{-4}x + 1.1 \times 10^{-3} \)), but they were not statistically significant since \( p \) values were greater than 0.05. No statistically reasonable relationship was also obtained between the \( k_b \) and EC data. 4. Conclusions The findings of this study indicated that the dominant process in the batch experiments was sorption for naphthalene and biodegradation for benzene. It was suggested that the increase of sorption of these two PHCs with depth is likely due to the heterogeneous physicochemical properties of the coastal soil. Biodegradation at the low \( O_2 \) and high \( SO_4^{2-} \) concentrations could be attributed to aerobic bacteria, NRB, and most likely SRB for the period investigated, with the contribution of NRB deduced from losses of \( NO_3^- \) during the experiments. The lag phases of benzene and naphthalene biodegradation were between 1 and 4 days and between 4 and 14 days, respectively. In general, the 0.2 mmol L\(^{-1}\) benzene was degraded faster than the 0.1 mmol L\(^{-1}\) naphthalene, and similar biodegradation rates were determined at low- and high-salinity conditions for the soil sample collected below the groundwater table. The biodegradation of benzene and naphthalene was, however, very slow as their simulated first-order biodegradation rate coefficients varied between 8.99 \( \times 10^{-3} \) and 1.77 \( \times 10^{-2} \) day\(^{-1}\) and between 2.53 \( \times 10^{-3} \) and 1.19 \( \times 10^{-2} \) day\(^{-1}\), respectively. Overall, sorption and biodegradation together, which were statistically found to increase with depth at selected times when combined, can help to achieve remediation goals at PHC-contaminated coastal soil and groundwater environments in Qatar. These findings also add up to the limited quantitative information on biodegradation kinetics of PHCs at (semi-)arid saline coastal soil environments. Data Availability The data used to support the findings of this study are available from the corresponding author upon request. Disclosure The findings achieved herein are solely the responsibility of the authors. Conflicts of Interest The authors declare that they have no conflicts of interest.
Acknowledgments

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