Data Article

Data on removal kinetics of pharmaceutical compounds, artificial sweeteners, and perfluoroalkyl substances from water using a passive treatment system containing zero-valent iron and biochar

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A R T I C L E   I N F O

Article history:
Received 29 June 2019
Received in revised form 9 September 2019
Accepted 19 September 2019
Available online 26 September 2019

Keywords:
Removal kinetics
Pharmaceutical compounds
Artificial sweeteners
Perfluoroalkyl substances
Passive treatment system
Zero-valent iron
Biochar

A B S T R A C T

The data presented in this paper relate to the research paper “Removal of pharmaceutical compounds, artificial sweeteners, and perfluoroalkyl substances from water using a passive treatment system containing zero-valent iron and biochar” [1]. Four columns packed with different ratios of reactive media, including silica sand (SS), zero-valent iron (ZVI), and biochar (BC), were evaluated for simultaneous removal of 14 emerging contaminants from water. The target emerging contaminants included eight pharmaceuticals (carbamazepine, caffeine, sulfamethoxazole, 3,4-methylenedioxymethylamphetamine, 3,4-methylenedioxymethamphetamine, ibuprofen, gemfibrozil, and naproxen), four artificial sweeteners (acesulfame-K, sucralose, saccharin, and cyclamate), and two perfluoroalkyl substances (perfluorooctanoic acid and perfluorooctane sulfonic acid). The samples for target contaminant analysis were collected from the influent, effluent, and profile (along the flow direction) ports of each column. The removal data (concentration vs. residence time) for each target contaminant were fitted to the first-order (exponential decay equation) or zero-order (linear equation) model using SigmaPlot. The removal rate, removal rate constant ($k_{obs}$), mass normalized rate constant ($k_M$), surface area...
normalized rate constant \(k_{SA}\), specific reaction rate constant), and half-life \(t_{0.5}\) of target contaminants in Columns ZVI, BC, and \((ZVI + BC)\) were calculated and summarized in this dataset.

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Specifications Table

| Subject                          | Chemistry            |
|---------------------------------|----------------------|
| Specific subject area           | Organic chemistry, removal kinetics |
| Type of data                    | Table                |
| How data were acquired          | Software SigmaPlot   |
| Data format                     | Analyzed             |
| Parameters for data collection  | The first-order kinetic data were obtained through the exponential decay fitting in the Regression Wizard in SigmaPlot; the zero-order kinetic data were obtained through the linear fitting in Regression Wizard in SigmaPlot. |
| Description of data collection  | The removal kinetic data were collected through the data analysis (Regression Wizard) in SigmaPlot. |
| Data source location            | University of Waterloo, Waterloo, Ontario, Canada |
| Data accessibility              | Data are available in this article |
| Related research article        | YingYing Liu, David W. Blowes, Carol J. Ptacek, and Laura G. Groza |
|                                 | Removal of pharmaceutical compounds, artificial sweeteners, and perfluoroalkyl substances from water using a passive treatment system containing zero-valent iron and biochar |
|                                 | Science of the Total Environment |
|                                 | https://doi.org/10.1016/j.scitotenv.2019.06.450 |

Value of the Data

- The data in this article provide important information on degradation kinetics such as removal rates and half-lives for 14 emerging contaminants treated by zero-valent iron (ZVI) and biochar (BC).
- Researchers working in the field of remediation of emerging contaminants in water can benefit from the data in this article.
- The data present in this article can provide useful information and guidelines for selecting the appropriate types of reactive media to remove specific emerging contaminants.
- The removal kinetic data (removal rate and half-life) can be used to design reactors or permeable reactive barriers (PRBs) for future large-scale field applications.

1. Data

The dataset showed the removal kinetic parameters, including removal rate constant \(k_{obs}\), mass normalized rate constant \(k_M\), surface area normalized rate constant \(k_{SA}\), specific reaction rate constant), and half-life \(t_{0.5}\), for 14 target emerging contaminants in Column ZVI, Column BC, and Column \((ZVI + BC)\). The kinetic parameters for each contaminant are summarized in separate tables (Tables 1–14). The raw data (concentration vs. residence time) of each contaminant can be found in the related research article [1].

2. Experimental design, materials, and methods

2.1. Materials

The native analyte compounds carbamazepine (CBZ), caffeine (CAF), sulfamethoxazole (SMX), ibuprofen (IBU), gemfibrozil (GEM), naproxen (NAP), cyclamate (CYC), and saccharin (SAC) for calibration standards and input stock solution were obtained from Sigma-Aldrich (Oakville, ON, Canada).
Table 1
First-order removal rate constant ($k_{obs}$), mass normalized rate constant ($k_M$), surface area normalized rate constant ($k_{SA}$, specific reaction rate constant), and half-life ($t_{0.5}$) of pharmaceutical carbamazepine in Column ZVI, Column BC, and Column (ZVI + BC). $k_{obs}$ is calculated using least-squares regression during two experimental stages. $C$ is the carbamazepine concentration.

| Column  | Stage | PV | Removal rate, $\mu$mol L$^{-1}$ d$^{-1}$ | $k_{obs}$, d$^{-1}$ | $k_M$, L g$^{-1}$ d$^{-1}$ | $k_{SA}$, L m$^{-2}$ d$^{-1}$ | $t_{0.5}$, d | $R^2$ |
|---------|-------|----|--------------------------------------|-----------------|---------------------|---------------------|-------------|------|
| Column 2 (ZVI) | 1 | 1 | 1.1E+01 | 1.1E+01 | 2.6E-03 | 2.8E-04 | 0.06 | 0.999 |
|          |     | 13 | 4.9 × C | 4.9 | 1.1E-03 | 1.2E-04 | 0.14 | 0.975 |
|          |     | 25 | 4.4 × C | 4.4 | 1.0E-03 | 1.1E-04 | 0.16 | 0.965 |
|          | 2   | 53 | 1.2 × C | 1.2 | 2.9E-04 | 3.0E-05 | 0.56 | 0.931 |
| Column 3 (BC) | 1 | 1 | 5.4 × C | 5.4 | 1.2E-02 | 1.8E-04 | 0.19 | 0.998 |
|          |     | 13 | 2.5 × C | 2.5 | 5.3E-03 | 8.2E-05 | 0.28 | 0.998 |
|          |     | 25 | 1.9 × C | 1.9 | 4.2E-03 | 6.4E-05 | 0.36 | 0.996 |
|          | 2   | 53 | 0.7 × C | 0.7 | 1.5E-03 | 2.3E-05 | 1.0 | 0.970 |
| Column 4 (ZVI + BC) | 1 | 1 | 8.2 × C | 8.2 | 7.2E-03 | 2.1E-04 | 0.09 | 0.999 |
|          |     | 13 | 4.5 × C | 4.5 | 3.9E-03 | 1.2E-04 | 0.16 | 0.966 |
|          |     | 25 | 4.0 × C | 4.0 | 3.5E-03 | 1.0E-04 | 0.17 | 0.970 |
|          | 2   | 53 | 1.3 × C | 1.3 | 1.1E-03 | 3.3E-05 | 0.55 | 0.992 |

Table 2
First-order removal rate constant ($k_{obs}$), mass normalized rate constant ($k_M$), surface area normalized rate constant ($k_{SA}$, specific reaction rate constant), and half-life ($t_{0.5}$) of pharmaceutical caffeine in Column ZVI, Column BC, and Column (ZVI + BC). $k_{obs}$ is calculated using least-squares regression during two experimental stages. $C$ is the caffeine concentration.

| Column  | Stage | PV | Removal rate, $\mu$mol L$^{-1}$ d$^{-1}$ | $k_{obs}$, d$^{-1}$ | $k_M$, L g$^{-1}$ d$^{-1}$ | $k_{SA}$, L m$^{-2}$ d$^{-1}$ | $t_{0.5}$, d | $R^2$ |
|---------|-------|----|--------------------------------------|-----------------|---------------------|---------------------|-------------|------|
| Column 2 (ZVI) | 1 | 1 | 1.6E+01 | 1.6E+01 | 3.7E-03 | 3.9E-04 | 0.04 | 0.999 |
|          |     | 13 | 7.2 × C | 7.2 | 1.7E-03 | 1.8E-04 | 0.10 | 0.998 |
|          |     | 25 | 5.1 × C | 5.1 | 1.2E-03 | 1.2E-04 | 0.14 | 0.982 |
|          | 2   | 53 | 1.5 × C | 1.5 | 3.5E-04 | 3.6E-05 | 0.47 | 0.961 |
| Column 3 (BC) | 1 | 1 | 4.8 × C | 4.8 | 1.0E-02 | 1.6E-04 | 0.14 | 0.999 |
|          |     | 13 | 2.8 × C | 2.8 | 6.0E-03 | 9.4E-05 | 0.25 | 0.999 |
|          |     | 25 | 2.2 × C | 2.2 | 4.8E-03 | 7.4E-05 | 0.31 | 0.996 |
|          | 2   | 53 | 1.0 × C | 1.0 | 2.1E-03 | 3.3E-05 | 0.70 | 0.973 |
| Column 4 (ZVI + BC) | 1 | 1 | 6.9 × C | 6.9 | 6.0E-03 | 1.8E-04 | 0.10 | 0.996 |
|          |     | 13 | 5.5 × C | 5.5 | 4.8E-03 | 1.4E-04 | 0.13 | 0.989 |
|          |     | 25 | 4.5 × C | 4.5 | 3.9E-03 | 1.2E-04 | 0.15 | 0.973 |
|          | 2   | 53 | 1.7 × C | 1.7 | 1.5E-03 | 4.5E-05 | 0.40 | 0.996 |

Table 3
First-order removal rate constant ($k_{obs}$), mass normalized rate constant ($k_M$), surface area normalized rate constant ($k_{SA}$, specific reaction rate constant), and half-life ($t_{0.5}$) of pharmaceutical sulfamethoxazole in Column ZVI, Column BC, and Column (ZVI + BC). $k_{obs}$ is calculated using least-squares regression during two experimental stages. $C$ is the sulfamethoxazole concentration. "---" represents not applicable.

| Column  | Stage | PV | Removal rate, $\mu$mol L$^{-1}$ d$^{-1}$ | $k_{obs}$, d$^{-1}$ | $k_M$, L g$^{-1}$ d$^{-1}$ | $k_{SA}$, L m$^{-2}$ d$^{-1}$ | $t_{0.5}$, d | $R^2$ |
|---------|-------|----|--------------------------------------|-----------------|---------------------|---------------------|-------------|------|
| Column 1 (Control) | 1 | 25 | 0.2 × C | 0.2 | --- | --- | 3.6 | 0.877 |
|          |     | 53 | 0.4 × C | 0.4 | --- | --- | 1.8 | 0.984 |
| Column 2 (ZVI) | 1 | 1 | 4.5E+02 | 4.5E+02 | 1.1E-01 | 1.1E-02 | 0.002 | 1.000 |
|          |     | 13 | 4.7E+02 | 4.7E+02 | 1.1E-01 | 1.1E-02 | 0.001 | 1.000 |
|          |     | 25 | 4.6E+02 | 4.6E+02 | 1.1E-01 | 1.1E-02 | 0.001 | 1.000 |
|          | 2   | 53 | 1.5E+02 | 1.5E+02 | 3.5E-02 | 3.7E-03 | 0.005 | 1.000 |
| Column 3 (BC) | 1 | 1 | 1.6 × C | 1.6 | 3.5E-03 | 5.4E-05 | 0.43 | 0.999 |
|          |     | 13 | 1.2 × C | 1.2 | 2.5E-03 | 3.8E-05 | 0.60 | 0.999 |
|          |     | 25 | 1.1 × C | 1.1 | 2.4E-03 | 3.8E-05 | 0.61 | 0.993 |
|          | 2   | 53 | 0.5 × C | 0.5 | 1.1E-03 | 1.7E-05 | 1.4 | 0.991 |
| Column 4 (ZVI + BC) | 1 | 1 | 4.5E+02 | 4.5E+02 | 4.0E-01 | 1.2E-02 | 0.002 | 1.000 |
|          |     | 13 | 4.7E+02 | 4.7E+02 | 4.1E-01 | 1.2E-02 | 0.001 | 1.000 |
|          |     | 25 | 4.6E+02 | 4.6E+02 | 4.1E-01 | 1.2E-02 | 0.001 | 1.000 |
|          | 2   | 53 | 1.5E+02 | 1.5E+02 | 1.3E-01 | 3.9E-03 | 0.005 | 1.000 |
### Table 4
First-order removal rate constant ($k_{obs}$), mass normalized rate constant ($k_M$), surface area normalized rate constant ($k_{SA}$, specific reaction rate constant), and half-life ($t_{0.5}$) of pharmaceutical 3,4-methylenedioxymethamphetamine (MDA) in Column ZVI, Column BC, and Column (ZVI + BC). $k_{obs}$ is calculated using least-squares regression during two experimental stages. ^c is the MDA concentration.

| Column   | Stage | PV     | Removal rate$^a$, ($\mu$mol L$^{-1}$ d$^{-1}$) | $k_{obs}$, d$^{-1}$ | $k_M$, L g$^{-1}$ d$^{-1}$ | $k_{SA}$, L m$^{-2}$ d$^{-1}$ | $t_{0.5}$, d | $R^2$ |
|----------|-------|--------|-----------------------------------------------|---------------------|----------------------------|-------------------------------|--------------|-------|
| Column 2 (ZVI) | 1 | 1 | 1.9E+02 × C | 1.9E+02 | 4.3E-02 | 4.6E-03 | 0.004 | 1.000 |
| Column 2 (ZVI) | 13 | 1.3E+01 × C | 1.3E+01 | 3.0E-03 | 3.1E-04 | 0.06 | 0.999 |
| Column 2 (ZVI) | 25 | 7.8 × C | 7.8 | 1.8E-03 | 1.9E-04 | 0.09 | 0.998 |
| Column 3 (BC) | 2 | 53 | 2.4 × C | 2.4 | 5.5E-04 | 5.8E-05 | 0.29 | 0.996 |
| Column 4 (ZVI + BC) | 1 | 1 | 2.0E+01 × C | 2.0E+01 | 1.8E-02 | 5.3E-04 | 0.03 | 1.000 |
| Column 4 (ZVI + BC) | 13 | 1.2E+01 × C | 1.2E+01 | 1.0E-02 | 3.0E-04 | 0.06 | 0.999 |
| Column 4 (ZVI + BC) | 25 | 8.7 × C | 8.7 | 7.6E-03 | 2.3E-04 | 0.08 | 0.999 |

### Table 5
First-order removal rate constant ($k_{obs}$), mass normalized rate constant ($k_M$), surface area normalized rate constant ($k_{SA}$, specific reaction rate constant), and half-life ($t_{0.5}$) of pharmaceutical 3,4-methylenedioxymethamphetamine (MDMA) in Column ZVI, Column BC, and Column (ZVI + BC). $k_{obs}$ is calculated using least-squares regression during two experimental stages. ^c is the MDMA concentration.

| Column   | Stage | PV     | Removal rate$^a$, ($\mu$mol L$^{-1}$ d$^{-1}$) | $k_{obs}$, d$^{-1}$ | $k_M$, L g$^{-1}$ d$^{-1}$ | $k_{SA}$, L m$^{-2}$ d$^{-1}$ | $t_{0.5}$, d | $R^2$ |
|----------|-------|--------|-----------------------------------------------|---------------------|----------------------------|-------------------------------|--------------|-------|
| Column 2 (ZVI) | 1 | 1 | 3.0E+02 × C | 3.0E+02 | 6.9E-02 | 7.3E-03 | 0.002 | 1.000 |
| Column 2 (ZVI) | 13 | 3.5E+02 × C | 3.5E+02 | 8.2E-02 | 8.7E-03 | 0.002 | 1.000 |
| Column 2 (ZVI) | 25 | 1.4E+01 × C | 1.4E+01 | 3.2E-03 | 3.4E-04 | 0.05 | 1.000 |
| Column 3 (BC) | 2 | 53 | 4.0 × C | 4.0 | 9.3E-04 | 9.8E-05 | 0.17 | 1.000 |
| Column 3 (BC) | 1 | 1 | 1.1E+01 × C | 1.1E+01 | 2.3E-02 | 3.6E-04 | 0.07 | 0.999 |
| Column 3 (BC) | 13 | 7.7 × C | 7.7 | 1.7E-02 | 2.6E-04 | 0.09 | 0.998 |
| Column 3 (BC) | 25 | 5.2 × C | 5.2 | 1.1E-02 | 1.7E-04 | 0.13 | 0.997 |
| Column 4 (ZVI + BC) | 1 | 1 | 2.3E+01 × C | 2.3E+01 | 2.2E-02 | 6.6E-04 | 0.03 | 1.000 |
| Column 4 (ZVI + BC) | 13 | 1.6E+01 × C | 1.6E+01 | 1.4E-02 | 4.1E-04 | 0.04 | 1.000 |
| Column 4 (ZVI + BC) | 25 | 1.0E+01 × C | 1.0E+01 | 9.0E-03 | 2.7E-04 | 0.07 | 0.999 |
| Column 4 (ZVI + BC) | 2 | 53 | 4.3 × C | 4.3 | 3.8E-03 | 1.1E-04 | 0.16 | 1.000 |

### Table 6
First-order removal rate constant ($k_{obs}$), mass normalized rate constant ($k_M$), surface area normalized rate constant ($k_{SA}$, specific reaction rate constant), and half-life ($t_{0.5}$) of pharmaceutical ibuprofen in Column ZVI, Column BC, and Column (ZVI + BC). $k_{obs}$ is calculated using least-squares regression during two experimental stages. ^c is the ibuprofen concentration.

| Column   | Stage | PV     | Removal rate$^a$, ($\mu$mol L$^{-1}$ d$^{-1}$) | $k_{obs}$, d$^{-1}$ | $k_M$, L g$^{-1}$ d$^{-1}$ | $k_{SA}$, L m$^{-2}$ d$^{-1}$ | $t_{0.5}$, d | $R^2$ |
|----------|-------|--------|-----------------------------------------------|---------------------|----------------------------|-------------------------------|--------------|-------|
| Column 2 (ZVI) | 1 | 1 | 2.6 × C | 2.6 | 6.0E-04 | 6.3E-05 | 0.27 | 0.943 |
| Column 2 (ZVI) | 13 | 1.2 × C | 1.2 | 2.9E-04 | 3.0E-05 | 0.56 | 0.926 |
| Column 2 (ZVI) | 25 | 0.9 × C | 0.9 | 2.2E-04 | 2.3E-05 | 0.74 | 0.932 |
| Column 3 (BC) | 2 | 53 | 0.2 × C | 0.2 | 4.7E-05 | 4.9E-06 | 3.5 | 0.864 |
| Column 3 (BC) | 1 | 1 | 1.9 × C | 1.9 | 4.2E-03 | 6.5E-05 | 0.36 | 0.992 |
| Column 3 (BC) | 13 | 1.2 × C | 1.2 | 2.6E-03 | 4.0E-05 | 0.57 | 0.997 |
| Column 3 (BC) | 25 | 1.1 × C | 1.1 | 2.4E-03 | 3.7E-05 | 0.63 | 0.996 |
| Column 4 (ZVI + BC) | 2 | 53 | 0.4 × C | 0.4 | 8.9E-04 | 1.4E-05 | 1.7 | 0.992 |
| Column 4 (ZVI + BC) | 1 | 1 | 2.9 × C | 2.9 | 2.5E-03 | 7.6E-05 | 0.24 | 0.978 |
| Column 4 (ZVI + BC) | 13 | 1.7 × C | 1.7 | 1.5E-03 | 4.5E-05 | 0.41 | 0.958 |
| Column 4 (ZVI + BC) | 25 | 1.6 × C | 1.6 | 1.4E-03 | 4.1E-05 | 0.44 | 0.952 |
| Column 4 (ZVI + BC) | 2 | 53 | 0.5 × C | 0.5 | 4.0E-04 | 1.2E-05 | 1.5 | 0.941 |
USA). The native analytes per isotope-labeled MDA-d5 and MDMA-d5 were obtained from Cerilliant Corporation (Round Rock, TX, USA). 3,4-methylenedioxyamphetamine (MDA), 3,4-methylenedioxymethamphetamine (MDMA), and their isotope-labeled standards SMX-d4, CYC-d11, SAC-13C6, ACE-K-d4, and SCL-d6 were obtained from Toronto Research Chemicals Inc. (Toronto, ON, Canada). The native analytes acesulfame-K (ACE-K), sucralose (SCL), and the isotope-labeled standards CBZ-d10, CAF-d3, IBU-d3, GEM-d6, and [13C]-NAP were obtained from Cambridge Isotope Laboratory Inc. (Tewksbury, MA, USA). The isotope-labeled standards [13C]-PFOA and [13C]-PFOS were obtained from Wellington Laboratories Inc. (Guelph, ON, Canada). The analytes PFOA and PFOS as dry powder for preparation of the input stock solution were obtained from Sigma-Aldrich, Canada. The silica sand (SS; 0.6–0.8 mm) was obtained from US Silica Company Inc. (Ottawa, IL, USA). The biochar (BC; oak hard wood; 0.50–2.26 mm) was obtained from Cowboy Charcoal Co. (Brentwood, TN, USA).

### 2.2. Column experimental design

Four acrylic columns were used, each column was 30 cm in length and 5 cm inner diameter. Influent and effluent ports were installed on the bottom and top of each column, respectively, for introducing...
Table 9
Zero- or first-order removal rate constant ($k_{obs}$), mass normalized rate constant ($k_M$), surface area normalized rate constant ($k_{SA}$), specific reaction rate constant, and half-life ($t_{0.5}$) of artificial sweetener acesulfame-K in Column ZVI, Column BC, and Column (ZVI + BC). Removal rate constant $k_{obs}$ is calculated using least-squares regression during two experimental stages. "--" represents no removal of acesulfame-K was observed.

| Column | Stage | PV | $k_{obs}$ | $k_M$ | $k_{SA}$ | $t_{0.5}$ | $R^2$ |
|--------|-------|----|-----------|-------|----------|----------|-------|
| Column 2 (ZVI) | 1 | 1 | 2.3E-01 x C | 2.3E-01 | 5.3E-05 | 5.6E-06 | 3.1 | 0.749 |
| | 13 | | 1.0E-01 x C | 1.0E-01 | 2.4E-04 | 2.6E-04 | 6.6 | 0.906 |
| | 25 | | 9.8E-02 x C | 9.8E-02 | 2.3E-04 | 2.4E-04 | 7.0 | 0.874 |
| | 2 | 53 | 1.1E-01 x C | 1.1E-01 | 2.7E-04 | 2.8E-04 | 6.1 | 0.870 |
| Column 3 (BC) | 1 | 1 | 1.6 E+01 | 1.6 E+01 | 3.4E-02 | 5.3E-04 | 3.2 | 0.864 |
| | 13 | | -- | -- | -- | -- | -- |
| | 25 | | -- | -- | -- | -- | -- |
| | 2 | 53 | -- | -- | -- | -- | -- |
| Column 4 (ZVI + BC) | 1 | 1 | 5.9 | 5.8 | 5.1E-03 | 1.5E-04 | 8.3 | 0.976 |
| | 13 | | 4.2 | 4.2 | 3.7E-03 | 1.1E-04 | 12 | 0.634 |
| | 25 | | 4.9 | 4.9 | 3.3E-03 | 1.3E-04 | 10 | 0.835 |
| | 2 | 53 | | 3.2 | 3.2 | 2.8E-03 | 8.3E-05 | 17 | 0.866 |

$^a$ Removal of acesulfame-K followed a first-order reaction rate, unit of $k_{obs}$ is d$^{-1}$, unit of $k_M$ is L g$^{-1}$ d$^{-1}$, unit of $k_{SA}$ is L m$^{-2}$ d$^{-1}$.

$^b$ Removal of acesulfame-K followed a zero-order reaction rate, unit of $k_{obs}$ is µmol acesulfame-K L$^{-1}$ d$^{-1}$ (µg acesulfame-K L$^{-1}$ d$^{-1}$), unit of $k_M$ is µmol acesulfame-K d$^{-1}$ g$^{-1}$ (µg acesulfame-K d$^{-1}$ g$^{-1}$), unit of $k_{SA}$ is µmol acesulfame-K d$^{-1}$ m$^{-2}$ (µg acesulfame-K d$^{-1}$ m$^{-2}$).

input solution and discharging effluent. Seven sampling ports were installed along the length of each column at 3.75-cm intervals for profile sampling. Column Control was packed with 100% SS. Column ZVI and Column BC were packed with 50% (vol%) of ZVI and BC, respectively, and balanced with SS. Column (ZVI + BC) was packed with 10% (vol%) of ZVI, 40% (vol%) of BC, and balanced with SS.

Input solution contained 10 µg L$^{-1}$ of pharmaceuticals CBZ, CAF, SMX, MDA, MDMA, IBU, GEM, and NAP; 100 µg L$^{-1}$ of artificial sweeteners ACE-K, CYC, SAC, and SCL; and 50 µg L$^{-1}$ of PFOA and 20–100 µg L$^{-1}$ of PFOS. The input solution was pumped through four columns from bottom to top at a flow rate of 0.3 pore volume (PV) d$^{-1}$ before 50 PV during the first stage of the experiment; the flow rate was decreased to 0.1 PV d$^{-1}$ after 50 PV during the second stage of the experiment. Three profile samplings (along the length of the columns) were performed during the first stage of the experiment after 1, 13, and 25 PV of flow through the columns; one profile sampling was conducted during the second stage of the experiment after 53 PV of flow.

All the emerging contaminant samples were spiked with isotopically-labeled internal standards before analysis. The pharmaceutical, PFOA, and PFOS samples were then concentrated through a solid phase extraction (SPE) process; their concentrations were determined using liquid chromatography (LC) followed by tandem mass spectrometry (MS). The concentrations of artificial sweeteners were directly analyzed by ion chromatography (IC) followed by MS without SPE. Detailed information on column experimental setup and analytical procedures for target emerging contaminants are summarized by Liu et al. [1].

2.3. Removal kinetics of target emerging contaminants by ZVI, BC, and (ZVI + BC)

The removal rates ($k_{obs}$) for target emerging contaminants during two experimental stages were calculated using least-squares regression in SigmaPlot. The removal of target pharmaceuticals within Columns ZVI, BC, and (ZVI + BC) followed a first-order rate model reported by Liu et al. [1] that can be described by equation (1). $k_M$ and $k_{SA}$ were calculated according to equations (2) and (3) which are defined by Johnson et al. [2]. The half-life ($t_{0.5}$) of the first-order rate for target pharmaceuticals was calculated following equation (4).

$$- \frac{dC}{dt} = k_{obs} \ C$$

(1)
Table 10
Zero-order removal rate constant ($k_{\text{obs}}$), mass normalized rate constant ($k_{\text{M}}$), surface area normalized rate constant ($k_{\text{SA}}$, specific reaction rate constant), and half-life ($t_{0.5}$) of artificial sweetener cyclamate in Column ZVI, Column BC, and Column (ZVI + BC). Removal rate constant $k_{\text{obs}}$ is calculated using least-squares regression during two experimental stages. "-" represents no removal of cyclamate was observed.

| Column           | Stage | PV | Removal rate, µmol L$^{-1}$ d$^{-1}$ (µg L$^{-1}$ d$^{-1}$) | $k_{\text{obs}}$, µmol L$^{-1}$ d$^{-1}$ (µg L$^{-1}$ d$^{-1}$) | $k_{\text{M}}$, µmol g$^{-1}$ d$^{-1}$ (µg g$^{-1}$ d$^{-1}$) | $k_{\text{SA}}$, µmol m$^{-2}$ d$^{-1}$ (µg m$^{-2}$ d$^{-1}$) | $t_{0.5}$, d | $R^2$ |
|------------------|-------|----|-------------------------------------------------|--------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-----------|-------|
| Column 2 (ZVI)   | 1     | 1  | 1.5E+01                                        | 1.5E+01                                          | 3.6E-03                                         | 3.8E-04                                         | 3.3       | 0.697 |
|                  | 13    |    | -                                             | -                                               | -                                              | -                                              | -         | -     |
|                  | 25    |    | -                                             | -                                               | -                                              | -                                              | -         | -     |
|                  | 2     | 53 | -                                             | -                                               | -                                              | -                                              | -         | -     |
| Column 3 (BC)    | 1     | 1  | 8.4                                           | 8.4                                             | 1.8E-02                                         | 2.8E-04                                         | 5.8       | 0.839 |
|                  | 13    |    | -                                             | -                                               | -                                              | -                                              | -         | -     |
|                  | 25    |    | -                                             | -                                               | -                                              | -                                              | -         | -     |
|                  | 2     | 53 | -                                             | -                                               | -                                              | -                                              | -         | -     |
| Column 4 (ZVI + BC) | 1    | 1  | 2.0                                           | 2.0                                             | 1.8E-03                                         | 5.2E-05                                         | 23        | 0.624 |
|                  | 13    |    | -                                             | -                                               | -                                              | -                                              | -         | -     |
|                  | 25    |    | -                                             | -                                               | -                                              | -                                              | -         | -     |
|                  | 2     | 53 | -                                             | -                                               | -                                              | -                                              | -         | -     |

Note: The poor $R^2$ values at 1 PV in this table are likely due to little removal of cyclamate in the three treatment columns.
Table 11
Zero- or first-order removal constant ($k_{obs}$), mass normalized rate constant ($k_M$), surface area normalized rate constant ($k_{SA}$), specific reaction rate constant, and half-life ($t_{0.5}$) of artificial sweetener saccharin in Column ZVI, Column BC, and Column (ZVI + BC). Removal rate constant $k_{obs}$ is calculated using least-squares regression during two experimental stages. $^a$ is the saccharin concentration. $^c$ is zero removal of saccharin was observed.

| Column 2 (ZVI) | Stage | PV | $k_{obs}$ | $k_M$ | $k_{SA}$ | $t_{0.5}$ | $R^2$ |
|---------------|-------|----|-----------|-------|---------|-------|------|
| 1             | 1     | 3.5E+01 | 8.1E-03 | 8.6E-04 | 1.5    | 0.898 |
| 13            | 4.7   | 1.1E-03 | 1.2E-04 | 9.3    | 0.804 |
| 25            | 1.3   | 3.9E-04 | 4.1E-05 | 32     | 0.583 |
| 2             | 53    | 2.4E+01 | 5.2E-02 | 2.2    | 0.983 |
| 2             | 53    | 2.6   | 5.6E-03 | 21     | 0.828 |
| 2             | 53    | 3.4E+01 | 3.0E-02 | 1.3    | 0.969 |
| 13            | 1.4E+01 | 1.2E-02 | 3.4E-04 | 3.1    | 0.960 |
| 25            | 1.1E+01 | 9.4E-03 | 2.8E-04 | 4.9    | 0.845 |
| 2             | 53    | 2.1   | 1.9E-03 | 25     | 0.701 |

$^a$ Removal of saccharin followed a first-order reaction rate, unit of $k_{obs}$ is $d^{-1}$, unit of $k_M$ is $Lg^{-1}d^{-1}$, unit of $k_{SA}$ is $Lm^{-2}d^{-1}$.

$^b$ Removal of saccharin followed a zero-order reaction rate, unit of $k_{obs}$ is $mol$ saccharin $L^{-1} d^{-1}$ ($mg$ saccharin $L^{-1} d^{-1}$), unit of $k_M$ is $mol$ saccharin $d^{-1} g^{-1}$ ($mg$ saccharin $d^{-1} g^{-1}$), unit of $k_{SA}$ is $mol$ saccharin $d^{-1} m^{-2}$ ($mg$ saccharin $d^{-1} m^{-2}$).

Table 12
Zero- or first-order removal constant ($k_{obs}$), mass normalized rate constant ($k_M$), surface area normalized rate constant ($k_{SA}$), specific reaction rate constant, and half-life ($t_{0.5}$) of artificial sweetener sucralose in Column ZVI, Column BC, and Column (ZVI + BC). Removal rate constant $k_{obs}$ is calculated using least-squares regression during two experimental stages. $^c$ is the sucralose concentration.

| Column 2 (ZVI) | Stage | PV | $k_{obs}$ | $k_M$ | $k_{SA}$ | $t_{0.5}$ | $R^2$ |
|---------------|-------|----|-----------|-------|---------|-------|------|
| 1             | 1     | 2.1E+01 | 4.8E-04 | 5.1E-05 | 0.3    | 0.922 |
| 13            | 1.3E+01 | 2.4E-04 | 2.5E-05 | 0.7    | 0.927 |
| 25            | 4.4E+01 | 1.0E-02 | 1.1E-03 | 1.4    | 0.963 |
| 2             | 53    | 1.2E+01 | 2.8E-03 | 2.9E-04 | 4.9    | 0.995 |
| 1             | 1     | 1.3E+01 | 2.7E-03 | 4.2E-05 | 0.5    | 0.999 |
| 13            | 0.9E+01 | 1.9E-03 | 2.9E-05 | 0.8    | 0.983 |
| 25            | 0.7E+01 | 1.4E-03 | 2.2E-05 | 1.1    | 0.983 |
| 2             | 53    | 0.2E+01 | 4.3E-04 | 6.6E-06 | 3.5    | 0.981 |
| 1             | 1     | 1.6E+01 | 1.4E-03 | 4.2E-05 | 0.4    | 0.948 |
| 13            | 0.9E+01 | 8.1E-04 | 2.4E-05 | 0.8    | 0.961 |
| 25            | 0.7E+01 | 6.4E-04 | 1.9E-05 | 1.0    | 0.942 |
| 2             | 53    | 0.2E+01 | 1.6E-04 | 4.7E-06 | 3.9    | 0.995 |

$^a$ Removal of sucralose followed a first-order reaction rate, unit of $k_{obs}$ is $d^{-1}$, unit of $k_M$ is $Lg^{-1}d^{-1}$, unit of $k_{SA}$ is $Lm^{-2}d^{-1}$.

$^b$ Removal of sucralose followed a zero-order reaction rate, unit of $k_{obs}$ is $mol$ sucralose $L^{-1} d^{-1}$ ($mg$ sucralose $L^{-1} d^{-1}$), unit of $k_M$ is $mol$ sucralose $d^{-1} g^{-1}$ ($mg$ sucralose $d^{-1} g^{-1}$), unit of $k_{SA}$ is $mol$ sucralose $d^{-1} m^{-2}$ ($mg$ sucralose $d^{-1} m^{-2}$).

\[
k_M = \frac{k_{obs}}{\rho_m}
\]

\[
k_{SA} = \frac{k_{obs}}{\rho_a} = \frac{k_M}{a_s}
\]

\[
t_{0.5} = \frac{0.693}{k_{obs}}
\]
Table 13
Zero- or first-order removal constant (kobs), mass normalized rate constant (kM), surface area normalized rate constant (kSA, specific reaction rate constant), and half-life (t0.5) of perfluorooctanoic acid (PFOA) in Column ZVI, Column BC, and Column (ZVI + BC). Removal rate constant kobs is calculated using least-squares regression during two experimental stages. 0.7 is the PFOA concentration. “—” represents no removal of PFOA was observed.

| Column          | Stage | PV | Removal rate1, μmol L−1 d−1 (μg L−1 d−1) | kobs          | kM            | kSA           | t0.5, d | R²  |
|-----------------|-------|----|----------------------------------------|---------------|---------------|---------------|--------|-----|
| Column 2 (ZVI)  | 1     | 1  | 2.2E+01b                               | 2.2E+01b      | 5.5E-04b      |               | 1.3    | 0.821|
|                 | 13    |    | —                                       | —             | —             |               | —      | —   |
|                 | 25    |    | —                                       | —             | —             |               | —      | —   |
|                 | 2     | 53 | —                                       | —             | —             |               | —      | —   |
| Column 3 (BC)   | 1     | 1  | 1.0 × C1a                               | 1.0a          | 2.1E-03a      | 3.3E-05a      | 0.7    | 0.980|
|                 | 13    |    | 0.5 × C1a                               | 0.5a          | 1.1E-03a      | 1.8E-05a      | 1.3    | 0.987|
|                 | 25    |    | 1.2E+01b                               | 1.2E+01b      | 2.5E-02b      | 3.9E-04b      | 2.3    | 0.956|
|                 | 2     | 53 | 0.9b                                   | 0.9b          | 1.9E-03b      | 3.0E-05b      | 25     | 0.780|
| Column 4 (ZVI + BC) | 1   | 1  | 2.0E+01b                               | 2.0E+01b      | 1.8E-02b      | 5.3E-04b      | 1.3    | 0.935|
|                 | 13    |    | 7.7b                                   | 7.7b          | 6.7E-03b      | 2.0E-04b      | 3.3    | 0.933|
|                 | 25    |    | 2.0b                                   | 2.0b          | 1.7E-03b      | 1.5E-05b      | 13     | 0.725|
|                 | 2     | 53 | —                                       | —             | —             |               | —      | —   |

a Removal of PFOA followed a first-order reaction rate, unit of kobs is d−1, unit of kM is L g−1 d−1, unit of kSA is L m−2 d−1.
b Removal of PFOA followed a zero-order reaction rate, unit of kobs is μmol PFOA L−1 d−1 (μg PFOA L−1 d−1), unit of kM is μmol PFOA d−1 g−1 (μg PFOA d−1 g−1), unit of kSA is μmol PFOA d−1 m−2 (μg PFOA d−1 m−2).

Table 14
Zero- or first-order removal constant (kobs), mass normalized rate constant (kM), surface area normalized rate constant (kSA, specific reaction rate constant), and half-life (t0.5) of perfluorooctane sulfonic acid (PFOS) in Column ZVI, Column BC, and Column (ZVI + BC). Removal rate constant kobs is calculated using least-squares regression during two experimental stages. 0.7 is the PFOS concentration.

| Column          | Stage | PV | Removal rate1, μmol L−1 d−1 (μg L−1 d−1) | kobs          | kM            | kSA           | t0.5, d | R²  |
|-----------------|-------|----|----------------------------------------|---------------|---------------|---------------|--------|-----|
| Column 2 (ZVI)  | 1     | 1  | 2.0 × C1a                               | 2.0a          | 4.6E-04a      | 4.9E-05a      | 0.4    | 0.911|
|                 | 13    |    | 0.9 × C1a                               | 0.9a          | 2.1E-04a      | 2.3E-05a      | 0.8    | 0.834|
|                 | 25    |    | 2.2E+01b                               | 2.2E+01b      | 5.1E-03b      | 5.4E-04b      | 1.5    | 0.929|
|                 | 2     | 53 | 2.6b                                   | 2.6b          | 6.2E-04b      | 6.5E-05b      | 16     | 0.734|
| Column 3 (BC)   | 1     | 1  | 1.8 × C1a                               | 1.8a          | 3.9E-03a      | 6.0E-04a      | 0.4    | 0.989|
|                 | 13    |    | 0.5 × C1a                               | 0.5a          | 1.2E-03a      | 1.8E-05a      | 1.3    | 0.511|
|                 | 25    |    | 0.9 × C1a                               | 0.9a          | 1.8E-03a      | 2.8E-05a      | 0.8    | 0.961|
|                 | 2     | 53 | 0.2 × C1a                               | 0.2a          | 4.6E-04a      | 7.2E-06a      | 3.2    | 0.967|
| Column 4 (ZVI + BC) | 1   | 1  | 2.2 × C1a                               | 2.2a          | 1.9E-03a      | 5.7E-05a      | 0.3    | 0.974|
|                 | 13    |    | 0.7 × C1a                               | 0.7a          | 5.8E-04a      | 1.7E-05a      | 1.1    | 0.881|
|                 | 25    |    | 1.1 × C1a                               | 1.1a          | 9.6E-04a      | 2.9E-05a      | 0.6    | 0.962|
|                 | 2     | 53 | 7.0b                                   | 7.0E+01b      | 6.1E-03b      | 1.8E-04b      | 5.9    | 0.966|

a Removal of PFOS followed a first-order reaction rate, unit of kobs is d−1, unit of kM is L g−1 d−1, unit of kSA is L m−2 d−1.
b Removal of PFOS followed a zero-order reaction rate, unit of kobs is μmol PFOS L−1 d−1 (μg PFOS L−1 d−1), unit of kM is μmol PFOS d−1 g−1 (μg PFOS d−1 g−1), unit of kSA is μmol PFOS d−1 m−2 (μg PFOS d−1 m−2).

where C is the contaminant concentration (μmol L−1 or μg L−1), kobs is the first-order removal rate constant (d−1), kM is the mass normalized first-order rate constant (L g−1 d−1), kSA is the specific first-order reaction rate constant or surface area normalized first-order rate constant (L m−2 d−1), ρs is the mass concentration of reactive media (g L−1 of solution), ρs is the surface area concentration of reactive media (m² L−1 of solution), αs is the specific surface area of reactive media (m² g−1), and t0.5 is the half-life of contaminant (d). The specific surface areas of the reactive media ZVI, BC, and (ZVI + BC) used are 9.5, 64.5, and 33.6 m² g−1 which are reported previously [3,4].

The removal of artificial sweeteners, PFOA, and PFOS within three treatment columns followed a first- or zero-order rate model or followed a first-order rate in the early stage of the experiment followed by a zero-order rate in the late stage of the experiment [1]. The kobs, kM, kSA, and t0.5 for the first-order rate of artificial sweeteners, PFOA, and PFOS were calculated following the equations (1)–(4). The
zero-order rate model can be described by equation (5). \( k_M \) and \( k_{SA} \) for the zero-order reaction can also be calculated according to equations (2) and (3). However, the half-life \( t_{0.5} \) of the zero-order reaction for target artificial sweeteners, PFOA, and PFOS was calculated following equation (6).

\[
\frac{dC}{dt} = k_{obs} \tag{5}
\]

\[
t_{0.5} = \frac{C_0}{2k_{obs}} \tag{6}
\]

where \( C_0 \) is the initial contaminant concentration (\( \mu \text{mol} \text{ L}^{-1} \) or \( \mu \text{g} \text{ L}^{-1} \)). The units of \( k_{obs} \), \( k_M \), and \( k_{SA} \) for the zero-order rate were different from that for the first order rate. For the zero-order rate, the unit of \( k_{obs} \) is \( \mu \text{mol contaminant} \text{ L}^{-1} \text{ d}^{-1} \) (\( \mu \text{g contaminant} \text{ L}^{-1} \text{ d}^{-1} \)), the unit of \( k_M \) is \( \mu \text{mol contaminant} \text{ d}^{-1} \text{ g}^{-1} \) (\( \mu \text{g contaminant} \text{ d}^{-1} \text{ g}^{-1} \)), and the unit of \( k_{SA} \) is \( \mu \text{mol contaminant} \text{ d}^{-1} \text{ m}^{-2} \) (\( \mu \text{g contaminant} \text{ d}^{-1} \text{ m}^{-2} \)).

**Conflict of Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

**Acknowledgments**

The authors thank the Natural Sciences and Engineering Research Council of Canada for providing funding for this article through a Discovery Grant awarded to C. Ptacek.

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