

Modeling Mn(II) autocatalytic sorption on MnOx-coated filtration media

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ABSTRACT

This study reports a newly developed kinetic model for predicting manganese (Mn) removal in Mn-coated filtration media. Manganese oxides (MnOx) adsorb and catalyze the oxidation of Mn in the liquid phase to regenerate sorption sites. The most common kinetic models (pseudo-first- and second-order models) do not consider the regeneration of reactive sites, thereby inadequately describing the long-term uptake of Mn(II) by MnOx. We propose a new kinetic model that considers both the rapid initial sorption of Mn(II) onto MnOx and its subsequent slow oxidation to Mn(Ox). This model was generalized to account for different pH, temperatures, and initial Mn concentrations. The enhanced model demonstrated a prediction error of $\pm 1\%$ on the Mn(II) concentration measured in the column effluent of two different MnOx media recovered from industrial filters. Although the contribution of oxidation was found to be 10 times smaller than that of adsorption, it is important to consider if for the prediction of Mn(II) uptake over a 4-h column experiment.

1. Introduction

Manganese (Mn) is a naturally occurring metal that is also produced through anthropogenic activities. It is commonly found in ground, surface, and marine waters in soluble form (Mn(II) or complexed Mn(III)) or particulate forms, such as manganese oxides (Mn(IV)/Mn(III) oxides) [1–3]. Manganese has been associated with the degradation of potable water's aesthetic qualities (color, taste, and odor) [4].

Neurological disorders in children (decreased IQ and hyperactivity, etc.) have been linked to high concentrations of Mn in tap water [5,6]. Therefore, the WHO released a provisional health-based guideline value for Mn in drinking water at 0.08 mg Mn/L while acknowledging that lower concentrations of Mn (0.02 mg Mn/L) can still cause aesthetic problems [4]. Health Canada issued a health-based guideline value of 0.12 mg Mn/L as the Canadian drinking water aesthetic guideline for Mn was lowered from 0.05 to 0.02 mg Mn/L [7]. The USEPA has published a non-enforceable health advisory guideline (0.3 mg Mn/L) and included Mn on its Contaminant Candidate List (CCL5, 2022).

Biofiltration has a long history of application as a cost-effective and sustainable process for removing Mn in its different forms from water. Mn is removed by filtering the aerated water through a granular media (sand naturally coated with Mn oxides and colonized by bacteria). Mn removal through biological filters has been explained by two main mechanisms: the biologically catalyzed oxidation of soluble Mn by biofilms, and the abiotic two-step process involving adsorption and

autocatalytic oxidation of soluble Mn on manganese oxides (MnOx), which coat the filter media [8,9]. Most soluble Mn removal occurs through the abiotic pathway, where Mn(II) is first sorbed on the media surface and subsequently oxidized to progressively form a MnOx coating on the filtration media. The MnOx coating sorbs and oxidizes Mn(II), acting as a catalyst for the subsequent adsorption-oxidation of soluble Mn(II) [9–11].

Abiotic Mn(II) removal may occur via two pathways: 1) homogenous oxidation in the water phase (negligible according to [12], 2) direct adsorption of Mn(II) on the filtration media, followed by heterogeneous oxidation of sorbed Mn(II) with MnOx on the filter media coating to form new MnOx. The second mechanism is also known as autocatalytic oxidation [10,11,13,14]. However, in addition to the Mn(II) adsorption mechanism on the MnOx-coated media, there is a simultaneous heterogeneous oxidation process that continuously decreases the Mn(II) surface loading and maintains the adsorption driving force. Our previous study demonstrated that to properly model the removal of Mn(II) with calcite contactors, the two mechanisms should be taken into consideration [15]. Therefore, any model developed for describing the Mn(II) uptake by biologically mediated MnOx should account for both adsorption and heterogeneous oxidation.

Mn(II) removal by MnOx has most often been described using isotherms and/or pseudo-first- or second-order kinetics models [9,16–18]. However, none of these models considers the autocatalytic properties of the MnOx surfaces, which are needed to: (i) select the best filtration

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media and MnOx media coatings required for a given treatment objective, (ii) explore mechanisms of contaminant removal by MnOx coatings, and (iii) improve our understanding of the fate of Mn in the environment.

Evaluating the reactivity of biologically mediated MnOx as sorbent/oxidant for various other contaminants, such as antibiotics [19,20], arsenic [21], bisphenol A [22], and natural organic matter [23], has garnered an increased scientific interest. However, no research has yet modeled the abiotic reactivity of Mn(II) with biologically mediated MnOx despite the reaction being important in describing the performance of biological filters. Moreover, this reaction helps in understanding the reactivity of MnOx with other contaminants, as similar removal mechanisms (sorption and oxidation) are likely involved [23].

In this study, we developed a new autocatalytic kinetic model based on two mechanisms of Mn(II) removal that allowed discrimination between the adsorption and heterogeneous oxidation of Mn(II). The performance of the autocatalytic model was tested using small-scale column abiotic Mn uptake experiments at different initial Mn(II) concentrations, pH values, and temperatures. Finally, the model was used to describe Mn uptake in media recovered from full-scale biofilters.

2. Materials and methods

2.1. Reagents and chemicals

Chemicals used to prepare synthetic water and quantify Mn were purchased from Fisher Scientific (Ottawa, Canada) (NaHCO₃, CaCl₂, NaOH), VWR (Edmonton, Canada) (HCl, Trace metals grade), Sigma-Aldrich (Ontario, Canada) (MnSO₄·H₂O, HNO₃, trace metals grade, imidazole, Na₂B₄O₇·10H₂O), and Frontier Scientific (Newark, USA) (α, β, γ, δ -tetrakis (4-carboxyphenyl) porphyrin also known as T(4-CP)P). All solutions were prepared with ultrapure water (Milli-Q Integral Water Purification System, Millipore, USA) in metal-free plasticware or glassware, which was soaked overnight in a 10 % (by vol.) HNO₃ solution. Subsequently, the solutions were triple-rinsed with deionized water, followed by Milli-Q water, to remove any residue.

2.2. Quantification of Mn in water

Mn(II) in water was quantified according to the optimized porphyrin colorimetric method described by Hatat-Fraile and Barbeau [24] using T(4-CP)P as a reagent. A 0.6 mL of T(4-CP)P solution (0.2 mM), 0.2 mL of CdCl₂ solution (0.6 mM), and 0.2 mL of imidazole buffer were added to a quartz cell with a path length of 2 cm containing 4 mL of the sample. After 5 min of reaction, absorbance was measured at 468 nm using a DR5000 spectrophotometer (HACH, USA). The calibration curve yielded a molar extinction coefficient of 83,845 M⁻¹ cm⁻¹ and exhibited a correlation coefficient of 0.9993.

2.3. Mn column uptake tests

Mn uptake tests were performed by slightly modifying the protocol described by Tobiasson et al. [25]. Briefly, 4 L of a Mn(II) solution was recirculated through a small column containing 20 g of the tested media for 4 h. The media used to develop the model was collected from a pilot-scale Mn biofilter fed with groundwater, the MnOx coating had a biological origin at the beginning of the experiment (characteristics of the media are available in the SI). The solution was circulated at a flow rate $Q = 310$ mL/min for 4 h, corresponding to 625 bed volumes, enabling the treatment of the total liquid volume 18.6 times during the experiment. The experiment was conducted at two different temperatures (4 and 20 °C) in cold/temperate rooms with a temperature variation <0.5 °C throughout the duration of the experiment. The temperature was checked during each sampling.

The feeding solution was prepared using NaHCO₃, CaCl₂, MnSO₄·H₂O, and four different initial concentrations (C_0) of Mn(II) (0.50, 0.75,

1.00, and 1.50 mg Mn/L) in deionized water. To investigate the impact of the solution pH on Mn(II) uptake, the column test was repeated after adjusting the pH of the feeding solution to a value between 6 and 9 by adding 1 M HCl or 1 M NaOH before introducing Mn(II) (details of the solution recipe are available in the SI).

The Mn(II) concentration in the effluent was measured after nine different contact times (0, 5, 15, 30, 45, 60, 120, 180, and 240 min) to evaluate Mn(II) uptake kinetics. A negative control column test was conducted without Mn(II) in the feeding solution to assess potential Mn(II) release from the aged media. The experimental setup is shown in Fig. S1.

2.4. Statistical evaluation of the kinetic model

The traditional pseudo-first- and second-order kinetic models were fitted by linear regression for each condition tested using the Python *sklearn* package. The adsorption–oxidation model was fitted using the module *curve_fit* from the Python *SciPy.optimize* package for each tested pH/temperature condition. The generalized adsorption–oxidation model (integrating pH/temperature effects) was fitted using the BFGS method in *SciPy.optimize* package. The regression procedure consisted of minimizing the squared residuals of the predicted Mn concentration profile $C(t)$ (Eq. (2.1)). The quality of fit of a given kinetic model was evaluated using three criteria: (i) the coefficient of correlation (R^2), (ii) the relative error (in %) between the observed and predicted liquid Mn concentration times ($C(t)_{\text{exp}}$ and $C(t)_{\text{model}}$ respectively) in the effluent of the column during the experiment (Eq. (2.1)), and (iii) the relative error (in %) between the predicted and observed adsorption capacities q_e at the end of the experiment (Eq. (2.2)).

The statistical significance of the operational conditions on the model parameters was determined using the Kruskal–Wallis test (a nonparametric variance analysis), and the model performance was compared using Wilcoxon's test with R (R Core Team, 2023).

$$\text{Relative error on } C(t) = \frac{\sum_i \text{abs} \left(\frac{C(t)_{\text{exp}} - C(t)_{\text{model}}}{C(t)_{\text{exp}}} \right)}{9} \times 100 \quad (2.1)$$

$$\text{Relative error on } q_e = \text{abs} \left(\frac{q(t=4h) - q_{e,\text{model}}}{q(t=4h)} \right) \times 100 \quad (2.2)$$

3. Results and discussion

3.1. Limitations of current sorption kinetic models

The advection-dispersion-reaction (ADR) model (Eq. (3.1)) is commonly used to describe the adsorption of contaminants in a packed bed reactor [26]. For our experimental setup, the dispersion coefficient was calculated using the correlation presented by Delgado [27], with a Peclet number = 9×10^3 and Reynolds number = 6.2. Considering a Mn diffusivity (D) coefficient of 0.688×10^{-9} m²/s [28], a velocity (U) of 23.5 m/h, and an empty bed contact time (EBCT) of 0.13 min, the dispersion and advection terms of the ADR equation were negligible. Therefore, the ADR equation can be simplified to that of a batch or plug-flow reactor (Eq. (3.2)).

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - U \frac{\partial C}{\partial z} - \text{kinetic reaction model} \quad (3.1)$$

$$\frac{dC}{dt} = -\text{kinetic reaction model} \quad (3.2)$$

Considering adsorption as the only Mn(II) removal mechanism, Eq. (3.2) is transformed into Eq. (3.3) and Eq. (3.4) after integration.

$$\frac{dC}{dt} = -\frac{m_*}{V} \frac{dq}{dt} \quad (3.3)$$

$$C(t) = C_0 - \frac{m}{V} q(t) \quad (3.4)$$

The quantity of Mn sorbed on the media ($q(t)$) was first modeled using the common adsorption kinetics models that have already been used to describe Mn(II) adsorption [18], that is, the pseudo-first- (Eq. (3.5) and Eq. (3.6)) and second-order (Eq. (3.7) and Eq. (3.8)) models.

$$\frac{dq}{dt} = k_1(q_e - q(t)) \quad (3.5)$$

$$\ln(q_e - q(t)) = \ln(q_e) + k_1 t \quad (3.6)$$

$$\frac{dq}{dt} = k_2(q_e - q(t))^2 \quad (3.7)$$

$$\frac{1}{q(t)} = \frac{1}{k_2 q_e^2 t} + \frac{1}{q_e} \quad (3.8)$$

For the pseudo-first-order model, defining the adsorption capacity at equilibrium is necessary, which was calculated using either (i) the Freundlich isotherms or (ii) considering that the adsorption capacity at equilibrium is equivalent to the total Mn sorbed at the end of the experiment: $q_e = q(t = 4 \text{ h})$. Freundlich isotherms, instead of Langmuir isotherms, were selected for the remaining analysis because the former provided better correlation coefficients for most of the tested conditions (Table S1). The correlation coefficients were higher when $q_e = q(t = 4 \text{ h})$ (data not shown). This approach was selected for the remainder of the analysis.

The parameters of the pseudo-first- and second-order models for the Mn(II) uptake experiments are presented in Table S2. Fig. 1A shows the correlation between the Mn (II) concentrations predicted based on these two models and the actual concentrations measured in the column effluent. The correlation coefficients were not statistically different ($p > 0.05$). However, the prediction errors for q_e (Eq. (2.2)) and $C(t)$ (Eq. (2.1)) were lower in the pseudo-first-order model. The mean relative prediction errors of $C(t)$ calculated for the pseudo-first-order model (1 %) indicated that this model is a better fit for estimating the Mn(II) concentration than the pseudo-second-order model (5.4 %). Most of the previous studies have used a pseudo-second-order kinetic model to model Mn(II) uptake [16–18,29]. However, these studies were conducted using batch experiments rather than column tests. The observed discrepancy in the fitting of the kinetic models in the column versus batch uptake experiments might be explained by differences in hydrodynamics and contact with the atmosphere of the experimental setup. The latter can affect oxygen diffusion on the surface and, consequently, the oxidative reactivity of MnOx. With this consideration, we conclude that column uptake experiments are more appropriate than batch experiments for modeling the reactivity of MnOx media in the context of packed-bed applications, as suggested by Tobiason et al. [25].

Fig. 1B shows the relative prediction errors (%) for Mn(II) concentration in the column effluent for the two kinetic models. Both models suffer from an increase in the prediction error with longer contact times, which is more evident in the case of the pseudo-second-order fit. Fig. 1C and D show the residuals of the pseudo-first-order model for a contact time of 5 and 240 min. As discussed above, for short contact times, the average residual of the normalized concentration is close to 0, while for longer contact times, it is -33 %. This indicates that, despite a good prediction error, the pseudo-first-order model increasingly underestimates Mn removal by MnOx as contact time increases. Accordingly, we suggest that the pseudo-first- and second-order models did not capture the catalytic effect of the newly formed MnOx during the Mn sorption-oxidation experiments [13]. Two uptake tests ($C_0 = 0.5$ and 1.5 mg Mn/L) were conducted over a 33-h period (Fig. 1E and F) for further investigations. As observed with the 4 h tests, the prediction errors of the pseudo-first-order model remained fairly low for short filtration durations but remarkably increased as the filtration time increased (i.e., starting at 24 h of filtration). Therefore, the pseudo-first-

order mechanism is inadequate for describing the operation of a catalytic filter over a filtration cycle (that lasts for several days). We propose the use of a model that considers both oxidation and adsorption to better predict Mn(II) removal. The proposed model is presented in the next section.

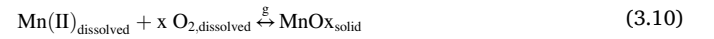
3.2. Including autocatalytic effect of Mn(II) sorption kinetic on biogenic MnOx

Different mechanisms have been proposed to explain Mn(II) removal using MnOx. This involves an initial step of Mn (II) adsorption on MnOx, followed by autocatalytic oxidation [17,30–32]. Fig. 2 shows a schematic of the two mechanisms involved in the removal of Mn (II) by MnOx.

Based on our previous isotherm and kinetic studies, we propose that Step 1, that is, the adsorption of Mn(II), can be described by the following pseudo-first-order kinetic model (Eq. (3.9)).

$$\frac{dC}{dt} = -\frac{m}{V} k_{ad} (q_{Mn(II),e} - q_{Mn(II)}(t)) \quad (3.9)$$

However, it is important to consider that during the entire adsorption process, Mn(II) undergoes progressive oxidation to MnOx, making the sorption sites available for more Mn(II) adsorption. This implies that while the Mn(II) loading $q_{Mn(II)}(t)$ increases due to adsorption, it simultaneously decreases because of the oxidation step, which regenerates the media. For the oxidation of Mn(II) adsorbed onto MnOx by dissolved oxygen (Eq. (3.10)), the dissolved oxygen was in excess in our experiment (the water was in contact with atmosphere during the experiment with an initial dissolved oxygen value of 9.3 mg O₂/L); therefore, dissolved oxygen concentration was disregarded in the model. The oxidation of Mn(II) sorbed onto MnOx was described by a first-order reaction (Eq. (3.11)).



$$\frac{dq_{ox,Mn(II)}}{dt} = -k_{ox} q_{Mn(II)}(t) \quad (3.11)$$

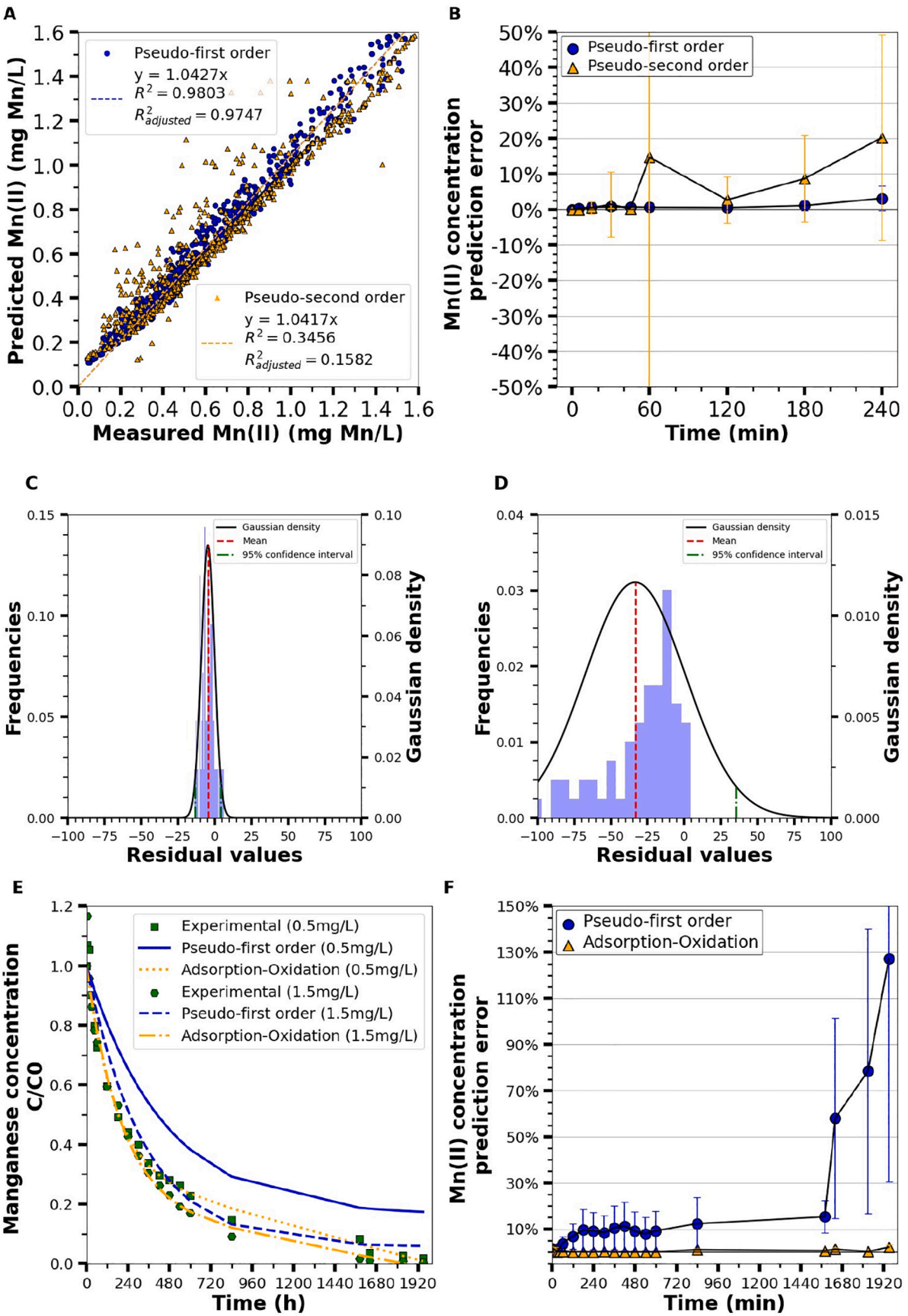
To describe these two simultaneous mechanisms (adsorption and oxidation), we performed a mass balance of Mn(II) in the solid phase (Eq. (3.12)) while including a first-order term to describe the autocatalytic oxidation of Mn(II) adsorbed on MnOx.

$$\frac{dq_{Mn(II)}}{dt} = -\frac{dC}{dt} \times \frac{V}{m} - k_{ox} q_{Mn(II)}(t) \quad (3.12)$$

The combination of Eqs. (3.9) and (3.12), followed by their integration, yields Eq. (3.13), which describes the evolution of Mn(II) in the liquid phase as a function of time. This equation is denoted as the adsorption-oxidation model in the remainder of this paper. It is noteworthy that no mass balance was conducted with respect to the total mass of Mn inside the column, as the complete removal of 1.5 mg Mn (II)/L would result in a maximum increase of 0.07 % (assuming the formation of MnO₂), which is a negligible amount. Therefore, we argue that the catalytic effect is not caused by the addition of new Mn(II) sorption sites but rather by the regeneration of existing ones present on the MnOx media. This process involves covering the existing site with a new reactive site possessing similar properties.

$$C(t) = C_0 + \frac{m}{V} k_{ad} q_{Mn(II),e} \left(-t + \frac{k_{ad}}{k_{ad} + k_{ox}} \left(t + \frac{(e^{-(k_{ad}+k_{ox})t} - 1)}{k_{ad} + k_{ox}} \right) \right) \quad (3.13)$$

The parameters of Eq. (3.13) were fitted to the results of the 63-column tests (see Table S3 for the fitted values of k_{ad} , k_{ox} , $q_{Mn(II),e}$). Fig. 3A compares the Mn(II) predicted in the column effluent using the adsorption-oxidation model with the traditional pseudo-first-order model. The mean relative prediction errors for $C(t)$ were calculated to be very low: 0.05 % for the adsorption-oxidation model, indicating its superior performance (Wilcoxon's test, $p < 0.05$) compared to that of the



(caption on next page)

Fig. 1. A) Measured vs predicted Mn concentrations in the column effluent for the pseudo-first- and second-order models ($n = 567$ for each model). B) Prediction errors for the pseudo-first- and second-order models as a function of uptake duration. Marks and error bars represent the mean and standard deviation, respectively, considering all testing conditions ($n = 63$ for each time for the pseudo-first-order model; $n = 62$ for each time for the pseudo-second-order model: an outlier value was removed with an error of 2300 %). C) Residue distribution of the pseudo-first-order model for a contact time of 5 min. D) Residue distribution of the pseudo-first-order model for a contact time of 240 min. E) Evolution of the experimental and predicted normalized Mn concentration with respect to time for a 33-h preliminary test at an initial Mn concentration of 0.5 and 1.5 mg Mn/L. F) Prediction errors for the pseudo-first-order and adsorption–oxidation models as a function of uptake duration. Marks and error bars represent the mean and standard deviation, respectively, considering the two testing conditions.

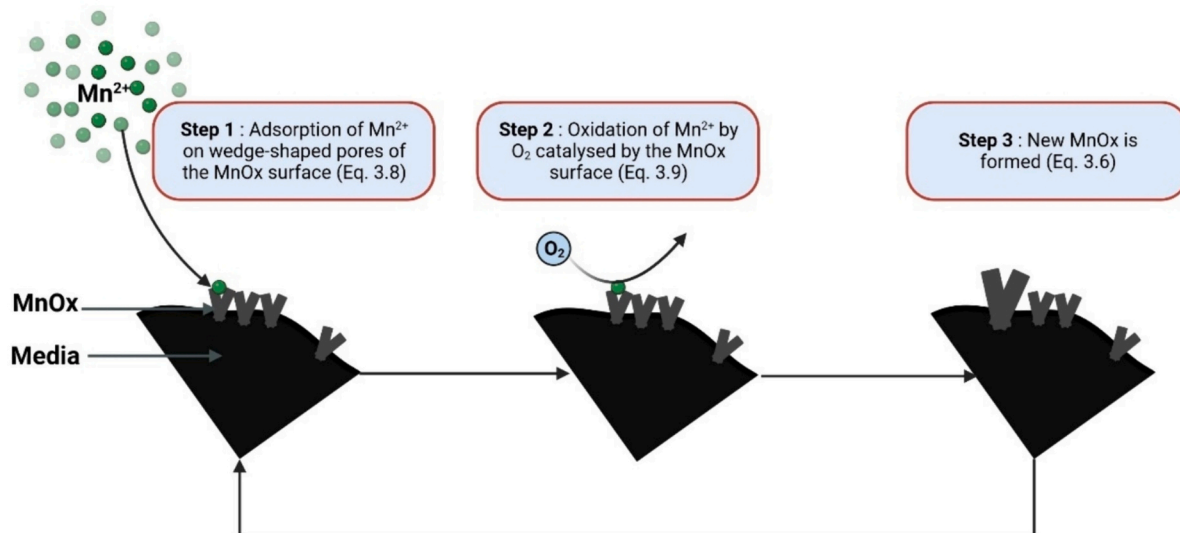


Fig. 2. Schematic of the mechanism of adsorption–autocatalytic oxidation of Mn(II) by MnOx loaded media during column uptake tests (created with [Biorender.com](https://www.biorender.com)).

pseudo-first-order model (1 %). More importantly, [Fig. 3B](#) demonstrates that the prediction error of the adsorption–oxidation model was not dependent on the uptake duration, as opposed to the pseudo-first-order model, in which the prediction error increased up to a maximum of 15 % after 4 h of filtration. [Fig. 3C](#) and [D](#) show the residuals of the adsorption–oxidation model as a function of contact time. In contrast to the pseudo-first-order model, the residuals in the adsorption–oxidation model followed a Gaussian distribution, including the residual obtained for longer filtration times. The average prediction error for the longest contact time (4 h) was 4.5 %. This value is closer to zero than that of the pseudo-first-order model (–33 %). Given that industrial filters typically operate from 2 to 14 days before backwashing, it is essential to consider oxidative MnOx media regeneration.

3.3. Generalization of the model to variations in operating conditions

Although the sorption–oxidation model accurately predicts individual uptake experiments, it must be calibrated to predict Mn(II) uptake under variable operating conditions, such as pH and temperature. For this purpose, a statistical analysis (Kruskal-Wallis test) was first performed to determine the impact of operating conditions on the three model parameters. [Fig. S3](#) presents the effects of pH, temperature, and initial concentration of Mn on the values of k_{ad} , k_{ox} , and $q_{Mn(II),e}$, respectively. The impact of pH was significant only for sorption (k_{ad} , $p = 0.01$), whereas temperature significantly affected the oxidation (k_{ox} , $p = 0.0008$) and media capacity ($q_{Mn(II),e}$, $p = 0.009$). As expected, the initial concentration (C_0) affected the media capacity $q_{Mn(II),e}$ (p -value = 1.10^{-6}). However, increasing C_0 did not impact k_{ad} and k_{ox} ($p > 0.05$).

Once the significant effects were identified, empirical expressions were developed to describe their influence on the model parameters (see [Text S1](#)). The generalized model was then recalibrated using 48 of the 63 randomly chosen uptake column tests (chosen randomly). The remaining 15 tests (24 % of the data shown in bold in [Table S3](#)) were used to

validate the prediction accuracy of the models.

[Fig. 4A](#) shows the Mn(II) concentrations predicted in the column effluent using the generalized adsorption–oxidation model for the calibration and validation datasets. The mean relative prediction errors for $C(t)$ were identical (1.0 %) for both the calibration and validation datasets. [Fig. 4B](#) shows an increase in the prediction error for the longest contact time (up to 21 %). [Fig. 4C](#) and [D](#) present the residuals of the adsorption–oxidation generalized model as a function of contact time. The residuals of the model were centered close to zero, which remained true for long contact times.

The use of the generalizable model did not significantly reduce the relative error of $C(t)$ compared to the pseudo-first-order model fitted to individual uptake experiments. However, the generalized model allows the prediction of Mn(II) uptake using variable water matrices (C_0 , pH, and temperature). It also helps to identify the respective roles of sorption and heterogeneous oxidation as Mn(II) removal mechanisms.

3.4. Application of the generalized adsorption–oxidation model to another aged media

To verify the applicability of this model to other aged media, we performed 12 additional column uptake experiments using a 6-year-old media. The media used in this study were collected from a full-scale biofilter treating Mn-laden groundwater. These media are shown in [Fig. S4](#). The sorption–oxidation model was first fitted to the 12-column uptake experiments to find new equations describing the effects of pH, temperature, and initial Mn(II) concentration ([Table S4](#) and [Text S2](#)). Subsequently, the generalized sorption equation was fitted to the new dataset. [Fig. 5A](#) and [B](#) show the Mn(II) removal predictions for the adsorption–oxidation and the generalized adsorption–oxidation models. As for the first studied media, the adsorption–oxidation model fitted to individual uptake experiments provided accurate Mn predictions (with a mean prediction error of 0.11 % and a maximum error of only 0.31 %).

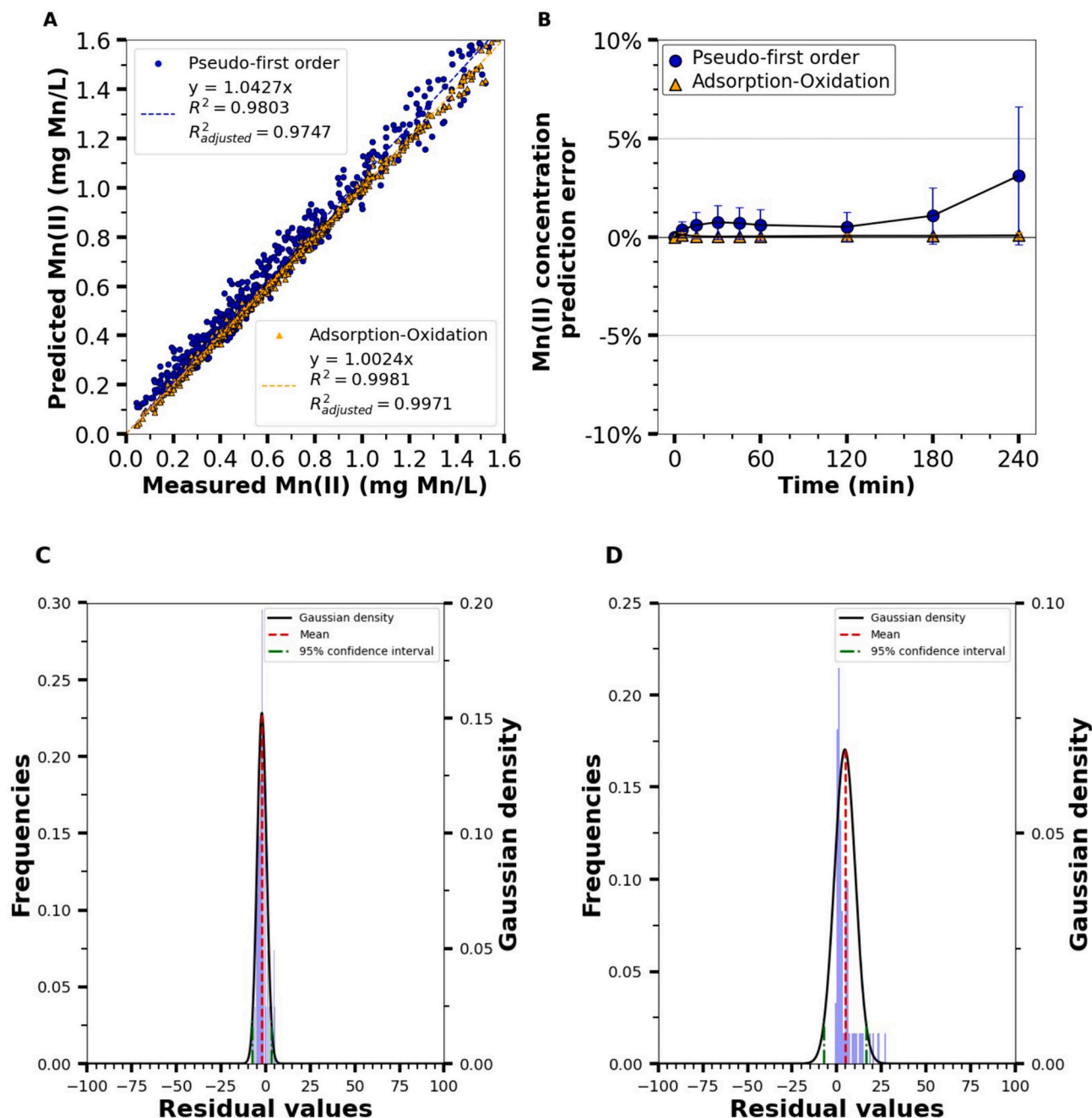


Fig. 3. A) Measured vs. predicted Mn(II) concentrations for the pseudo-first-order and adsorption–oxidation models ($n = 567$ for each model). B) Prediction errors for the pseudo-first-order and adsorption–oxidation models as a function of uptake duration. Marks and error bars represent the mean and standard deviations, respectively ($n = 63$ for each reported contact time). C) Residuals distribution of the adsorption-oxidation model for a contact time of 5 min. D) Residuals distribution of the adsorption-oxidation model for a contact time of 240 min.

The generalized adsorption–oxidation model yielded a mean prediction error of 0.95 % (with a maximum of 7.3 %), a performance similar to the fit on the 6-month-old media. In the next section, the fitted parameters obtained for both media are compared.

3.5. Comparison of filter media

The adsorption–oxidation model was fitted to the 6-month and 6-year-old filtration media. In Fig. S5, we compare the impact of the operational conditions (pH, temperature, and C_0) on the fitted parameters (k_{ad} , k_{ox} , and q_e). As anticipated from the literature [9], the adsorption kinetics were at least 10 times faster than the oxidation kinetics. Therefore, oxidation is the limiting step for Mn(II) removal via

the adsorption–oxidation process with MnOx. Interestingly, the kinetic constants, k_{ad} , and k_{ox} , were significantly higher ($p < 0.05$) for the 6-year-old media in the range of operational testing conditions ($6 < \text{pH} < 9$ and $4^\circ\text{C} < T < 20^\circ\text{C}$). Under the same conditions, the capacity at equilibrium q_e was higher for the 6-month-old media.

Fig. S5-D shows the predicted Mn(II) concentration in solution during Mn(II) uptake in both media. The model predicted that, for a short filtration duration, both media provide identical Mn(II) removal. After 3 h of uptake, progressively better Mn(II) removal was observed in the aged media because of its higher oxidation rate. Similarly, Sahabi et al. [9] concluded that 15-year-old media exhibited enhanced performance compared to 3-year-old media. Our modeling effort suggests that the improved performance of the aged media probably originates from its

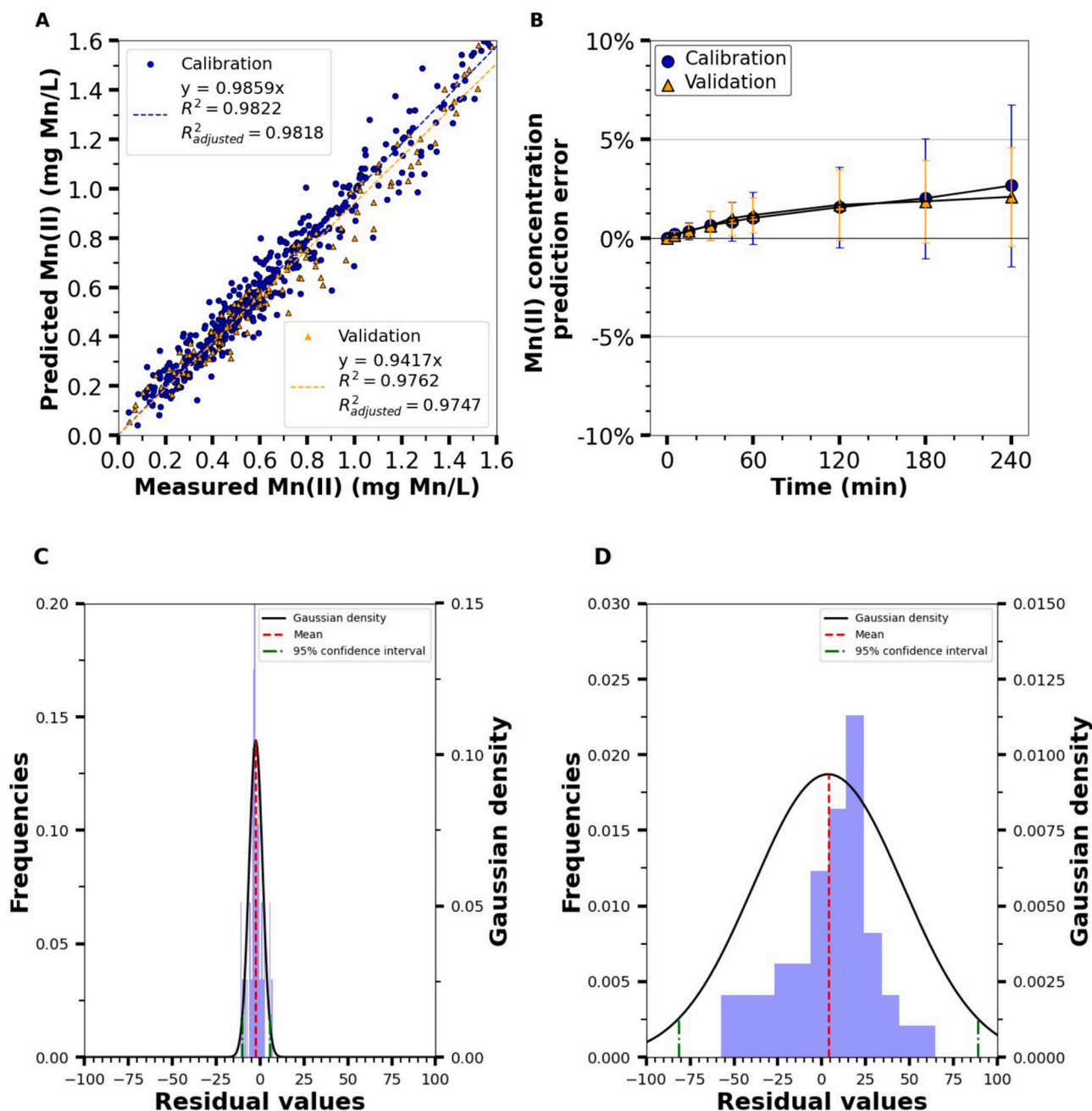


Fig. 4. A) Measured vs predicted Mn concentrations in the column effluents using the generalized adsorption-oxidation model for the calibration and validation datasets ($n = 432$ for calibration, $n = 135$ for validation). B) Prediction errors for the generalized adsorption-oxidation model for the calibration and validation datasets as a function of filtration duration. Marks and error bars represent the mean values and standard deviations ($n = 48$ for calibration and $n = 15$ for validation for each contact time), respectively. C) Residuals distribution of the generalized adsorption-oxidation model for a contact time of 5 min. D) Residuals distribution of the generalized adsorption-oxidation model for a contact time of 240 min.

superior autocatalytic properties. Additional work is required to study the influence of media aging on the kinetics and equilibrium model parameters.

4. Conclusion

We demonstrated that the traditional kinetic models underestimated Mn(II) removal for longer filtration times (4 h and beyond), given that these models do not consider media regeneration, that is, the oxidation of Mn(II) to form new MnOx, which delays equilibrium. Therefore, a new kinetic model (adsorption-oxidation) was proposed to describe the Mn(II) uptake by MnOx by considering both adsorption and oxidation.

This model has been proven to successfully account for different pH values, temperatures, and initial Mn(II) concentrations. It was also well-fitted to compare media of different ages. The adsorption kinetics were at least 10 times faster than the oxidation kinetics. Significant differences in the fitted parameters were observed between the two media, indicating that the older medium is more reactive than the newer one.

Future studies should consider a wider range of filtration media to validate the applicability of the proposed model. In addition, mechanistic equations (rather than empirical equations) should be developed to describe the role of O_2 in medium oxidation and pH during sorption.

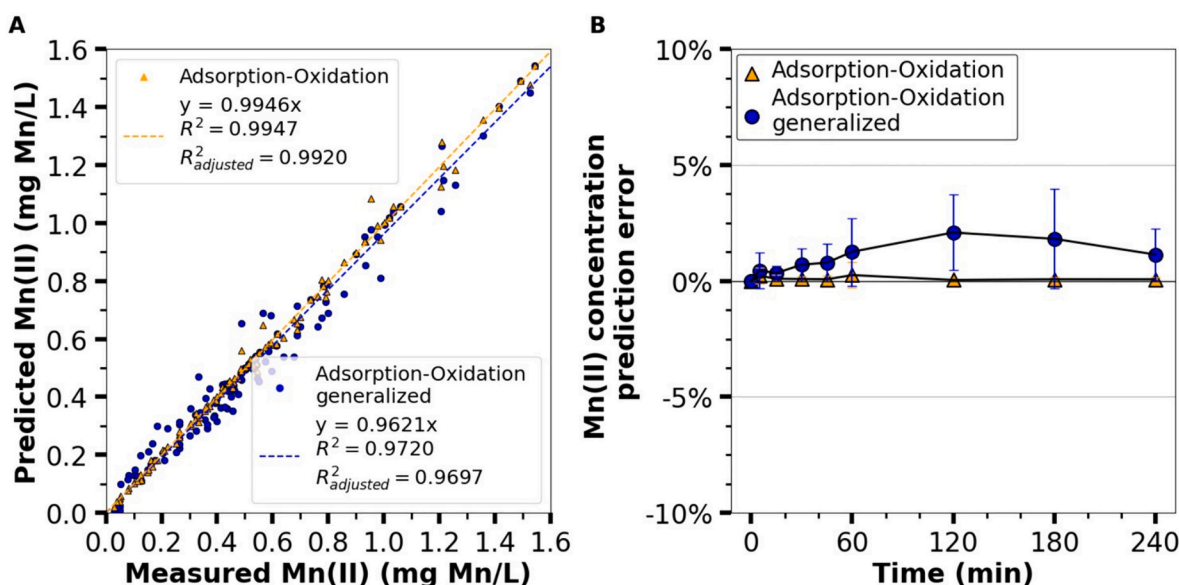


Fig. 5. A) Measured vs predicted effluent Mn(II) concentrations for the adsorption–oxidation and the generalized adsorption–oxidation models for the 6-year-old media ($n = 108$). B) Prediction errors for the adsorption–oxidation and the generalized adsorption–oxidation models for the 6-year-old media as a function of uptake duration. Marks and error bars represent the mean values and standard deviations ($n = 12$ for each time), respectively.

CRedit authorship contribution statement

Jérôme Ducret: Writing – original draft, Visualization, Software, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Benoît Barbeau:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing 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 paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2024.105408>.

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