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Electro-assisted Adsorption of Zn(II) on Activated Carbon Cloth in Batch-Flow Mode: Experimental and Theoretical Investigations

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Supporting Information

ABSTRACT: High levels of zinc ion (Zn^{2+}) in environmental scenarios have long been considered to be harmful, and this study was experimentally and theoretically performed to explore the feasibility of electro-assisted adsorption of Zn^{2+} on activated carbon cloth from aqueous solutions in batch-flow mode. The characteristics of carbon cloth were systematically evaluated using cyclic voltammetry and various surface characterization techniques. Effects of operating parameters, including charging voltage, feed Zn^{2+} concentration, solution volume, and flow rate, on the dynamic removal process of Zn^{2+} were examined. Meanwhile, a theoretical model was developed to quantitatively describe the electro-assisted adsorption of Zn^{2+} , and an excellent agreement between the modeling results and the experimental data was observed. The Zn^{2+} removal mechanisms involve both nonelectrostatic interactions (physi- or chemisorption) and electrostatic interactions. Experimental and theoretical results demonstrated a significant enhance-



ment of Zn^{2+} adsorption capacity on the carbon electrodes under the electro-assistance. Moreover, the carbon electrodes exhibited good regeneration performance achieved via a simple short-circuiting method and provided good reproducibility over consecutive runs for the removal of Zn^{2+} . The validated model could be applied to predict the effects of important parameters that are difficult to be experimentally manipulated, and is expected to play an important role in establishing the electro-assisted adsorption as a viable treatment technology for zinc wastewater.

INTRODUCTION

Water pollution from heavy metal ions has become a serious worldwide problem that endangers both the environment and human health.¹⁻⁴ Belonging to the family of heavy metal ions, zinc ion (Zn^{2+}) has been introduced in large quantities into the aqueous environment from zinc manufacturing and other industries such as galvanizing, paints, and pigments.^{5,6} Although Zn²⁺ is an important element for the living organisms and takes part in the metabolism of peptides and nucleic acids, stimulates the activity of various enzymes, high concentrations of Zn^{2+} exceeding permissible levels (5 mg L⁻¹ in drinking water according to the US Environmental Protection Agency) would have detrimental effects on human health, resulting in irritability, muscular stiffness, growth retardation, gastrointestinal distress, lung disorders, and even cancer.⁵⁻⁷ The negative environmental impact of Zn²⁺ has prompted a demand for the purification of industrial zinc wastewater.

Various treatment technologies have been suggested for the removal of Zn^{2+} from wastewater, including chemical precipitation, adsorption, ion-exchange, membrane separation,

and electrochemical methods.^{5–8} Among them, adsorption is considered as one of the most popular measures due to its simple operation, fast response time, and low cost.^{5,9} However, the adsorption method often suffers from limited ion removal efficiency, and a complex and energy-intensive regeneration process. Electrosorption, also called capacitive deionization (CDI), has attracted a great interest and appears to be a promising method for the removal of Zn^{2+} from water due to its key advantages of environmental friendliness, cost-effectiveness, low energy consumption, and facile electrode regeneration.^{10–15}

During the electrosorption process, the ions in the aqueous solution will be attracted to the oppositely charged electrode under the imposed electric field and trapped in the electric double layers (EDLs) formed at the electrode–electrolyte

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Figure 1. Schematic diagram of the CDI cell structure, the experimental setup, and the SEM image of the activated carbon cloth.

interface via electrostatic interactions. Purified water, therefore, can be produced during the electrosorption stage. When a reverse potential or a short circuit is applied, the captured ions will be released from EDLs backing to the solution thereby generating a stream of concentrated water and the saturated electrodes are in situ regenerated.^{11,12,16} In parallel with ion desorption, the energy used to charge the electrodes during electrosorption can be partially recovered.^{10,17,18} Until now, many studies have indicated that the electrosorption method is effective to remove various unwanted ions such us sodium, chloride, fluoride, nitrate, phosphate, and sulfate from water.^{11,13,19–21} The research exploring the electrosorptive removal of heavy metal ions (e.g., Cu²⁺, Ni²⁺, Pb²⁺) from aqueous solutions have also been conducted.^{22–26} However, to the best of our knowledge, no literature has been reported on the electrosorptive removal of Zn²⁺ from water.

Considering that the carbon electrodes inherently have a certain adsorption capacity for Zn^{2+} in the absence of a charged surface, the electrosorptive removal of Zn²⁺ from water by carbon electrodes is in fact a process involving both nonelectrostatic adsorption (physi- or chemisorption) and electrosorption. It is a complex process affected by a wide range of parameters, such as applied voltage, Zn²⁺ feed concentration, solution volume, electrode area, electrode gap, and electrode pore size distribution. In view of the interconnectivity between parameters and the difficulty in experimentally manipulating some parameters, development of a mathematical model enabling quantitative description and optimization of the electro-assisted adsorption process of Zn²⁺ is of great necessity. Apart from allowing optimization of both operating and design parameters for particular source waters, the theoretical model would also serve as a useful tool to reveal the underlying causes of phenomena, help to gain thorough understanding of the ion removal process, and predict CDI performance under various conditions.^{12,27–31} While classical Langmuir or Freundlich isotherms have been reported to fit the data for the equilibrium Zn^{2+} adsorption onto an uncharged surface,^{5,9} a model capturing both nonelectrostatic adsorption and electrosorption processes of Zn²⁺ at a charged interface is not available.

For these reasons, in the present study, we investigated, both experimentally and theoretically, the feasibility of the electroassisted adsorption of Zn^{2+} from aqueous solutions using activated carbon cloth electrodes operated in a batch-flow mode. A systematic investigation was performed using cyclic voltammetry and surface characterization to elucidate the interaction between Zn^{2+} and the carbon electrode surface. Effects of operating parameters, including applied voltage, Zn^{2+} feed concentration, total water volume, and pump flow rate, were examined and a mathematical model was developed to quantitatively describe the dynamic electro-assisted adsorption process of Zn^{2+} . The model was validated and further applied to predict the effects of other important parameters. To the best of our knowledge, this study is the first to present a mathematical model that enables quantitative capture of both the nonelectrostatic adsorption and the electrosorption processes of one specific ion on the carbon electrodes.

MATERIALS AND METHODS

Reactor Configuration. The CDI cell used in this study is self-made and the structure and composition of the CDI cell is depicted in Figure 1. Activated carbon fiber cloth with a thickness of 300 μ m was purchased from Nantong Senyou Carbon Fiber Cop. China and was used as the binder-free electrodes (9 \times 9 cm² dimension) and each electrode is 0.8 g. Graphite papers with a thickness of 100 μ m were purchased from Heilongjiang Juxiong Import & Export Company, Ltd., China and were used as inert current collectors on the back sides of the electrodes. The carbon electrodes are separated by a middle nonconductive nylon sheet (300-mesh) into anode and cathode pairs at a distance of 200 μ m for fluid flow. All parts are held together with the use of acrylic end plates with holes drilled around the perimeter to allow for fastening with M3 bolts. Inlet and outlet ports of the acrylic end plates are created using luer fittings with an inlet manifold designed for even pressurization of the feed channel so that the solution could be in contact with all sides of the working electrodes. A hole of 1 cm diameter is punched at the center of the upper graphite sheet allowing water running through the spacer to the outer reservoir.

Electro-assisted Adsorption Experiments in Batch-Flow Mode. ACS reagent zinc sulfate ($ZnSO_4$ ·7H₂O, Sigma-Aldrich) was used for the preparation of Zn(II) solution. The stock solution of Zn(II) was prepared with deionized water produced by a Millipore Milli-Q Direct 8/16 water purification system. As can be seen from the schematic diagram of the electro-assisted adsorption test (Figure 1), the feed solution was pumped through the CDI cell by a peristaltic pump (BT-300, Longer Precision Pump Co., Ltd., China) and the effluent

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of CDI cell was sent back to the feed tank. Zn²⁺ removal performance was evaluated with a constant-voltage charging as controlled using a DC power supply (MS155D, Maisheng Electronic Equipment Co., Ltd., China). The changes in conductivity and pH of the solution were continuously monitored in the recycling tank by using conductivity meter (DDS-307, INESA Scientific Instrument Co., Ltd., China) and pH meter (PHS-3C, INESA Scientific Instrument Co., Ltd., China), respectively.

Unless otherwise stated, prior to each experiment, the CDI cell was flushed thoroughly using Milli-Q water with shortcircuiting mode applied to ensure that no residual charge and no ions remained on the electrodes. Then the water in the CDI cell was drained. The feed solution with a certain Zn²⁺ concentration and a certain volume was prepared in the feed tank and, subsequently, was pumped into the CDI cell and recycled many times under zero voltage until the reading of the conductivity meter became stable. We named this recycling process in the absence of electric field as the nonelectrostatic adsorption (physi- or chemisorption) of Zn²⁺. The electrosorption of Zn^{2+} started with a constant voltage applied to the CDI cell. The solution in the recycling vessel was stirred throughout the test to ensure a homogeneous composition. No pH adjustment was carried out during the whole operation. Samples were collected at predetermined time intervals from the feed tank. Zn²⁺ concentrations were measured using the Atomic Absorption Spectrophotometer (AAS, PerkinElmer, U.S.A.) with Zn²⁺ Hollow Cathode Lamp at 213.9 nm wavelength.

The desorption efficiency for spent activated carbon cloths was investigated using three methods, i.e., short-circuiting, reverse constant voltage (-0.4 V) and reverse square-wave pulsed voltage (5 s of -0.4 V and 5 s of open circuit). Desorption ended when the potential difference between the two electrodes reached 0 V. Experiments of consecutive adsorption–desorption cycles were carried out by treating 100 mL of feed solution containing 80 mg L⁻¹ Zn²⁺ at a pump flow rate of 44 mL min⁻¹. Electrosorption was conducted at a charging voltage of 1.2 V followed immediately by short-circuiting desorption. Upon completion of the electrode regeneration, the cell was charged again to initiate the next same treatment cycle.

Material Characterization. The morphology and size analyses were performed by scanning electron microscopy (SEM) using a JSM-5600 LV microscope (JEO, Ltd., Japan). The specific surface area and pore size distribution of the activated carbon cloth were determined using a Micromeritics ASAP-2020 Accelerated Surface Area and Porosimetry Analyzer (Micromeritics Instrument Corporation, U.S.A.) based on the N₂ adsorption/desorption isotherm. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The pore size distribution spanning the micropore range was determined by the Density Functional Theory (DFT) method while the pore size distribution spanning the mesopore and macropore ranges was determined by the Barrent-Joyner-Halenda (BJH) method. The surface elemental composition and chemical state analyses were based on the results of X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, U.K.).

The electrochemical characteristics of Zn^{2+} on the activated carbon cloth electrode were determined using cyclic voltammetry (CV) (CHI 627D, CH Instruments, Inc., U.S.A.) with a conventional three-electrode cell. The three-

electrode cell consisted of a standard calomel electrode as the reference electrode, a platinum mesh as the counter electrode, and the activated carbon cloth electrode as the working electrode. CV measurements were undertaken in 80 mg L^{-1} zinc solution at room temperature. The potential scan rate was set at 100 mV s⁻¹, and the potential range was between -1.2 V and +1.2 V.

Theoretical Model. The electro-assisted adsorption of Zn(II) on activated carbon cloths in the batch-flow mode is specifically divided into two processes. First, a certain volume of feed solution with a predetermined Zn^{2+} concentration was pumped into a CDI cell with fresh or completely regenerated carbon electrodes and was recycled under zero voltage until the reading of the conductivity meter became stable (Zn^{2+}) concentration would drop to a certain value during this process). We named this recycling process in the absence of electric field as the nonelectrostatic adsorption (physi- or chemisorption) of Zn^{2+} . Then, the electrosorption process of Zn²⁺ started with a constant voltage applied to the CDI cell. A theoretical model was developed and employed to fit the experimental data related to the whole electro-assisted adsorption process. During the nonelectrostatic adsorption process, Zn²⁺ concentrations between the aqueous phase and the solid phase would reach equilibrium. During electrosorption process, the model only considers transport of ions in the direction perpendicular to the fluid flow and ion concentration gradients are neglected throughout the cell system (i.e., spacer channel, pipes, and recycling vessel), which is a reasonable approximation when the extent of ion electrosorption "per pass" is relatively low. The ions are preferentially stored in the electrical double layers (EDLs) inside the micropores (i.e., pores smaller than 2 nm) of activated carbon cloth. The modified Donnan (mD) model that can properly capture the strongly overlapping EDLs' structure along electrodes' pore walls is employed to relate the ion concentration inside the micropores to that outside the micropores. The mD model includes an extra term describing adsorption of ions into micropores due to forces separate from the applied electric field. The details of the model derivation are provided in the Supporting Information (SI).

RESULTS AND DISCUSSION

Characterization. From the SEM images presented in Figure 1, it can be seen that the activated carbon cloth shows a long, uniform, and cylindrical morphology. The average diameter was determined to be 8.6 μ m. The BET specific surface area of the activated carbon cloth was measured to be 1118 m² g⁻¹. The pore size distributions of the activated carbon cloth obtained using the DFT method and BJH method are shown in Figure S1 in the SI. The results clearly indicate that most of the pores of the activated carbon cloth are in the microporous range (≤ 2 nm). XPS analysis was conducted to obtain further information on the surface chemical composition of the activated carbon cloth (Figure S2). The survey scan revealed that the carbon cloth is composed of three elements, i.e., carbon (89.9%), oxygen (6.6%), and nitrogen (3.5%). From Figure S2b, it was observed that the C 1s spectrum was deconvoluted into four peaks. The peak at 284.6 eV was attributed to C-C/C=C, which was assigned to graphitic sp² carbons. The other three peaks at 286.3, 288.2, and 289.7 eV indicated the existence of the oxygen-containing groups of hydroxyl (C-O), carbonyl (C=O), and carboxyl (O-C=O).³² The O 1s spectrum was

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deconvoluted into two component peaks (Figure S2c). The peak at 531.5–531.7 eV corresponds to the carbonyl oxygen atoms in esters, amides, anhydrides, and oxygen atoms in hydroxyls or ethers, while the peak at 532.8 eV corresponds to the oxygen atoms in carboxyl groups.²⁵ These oxygen surface groups suggest the ability of activated carbon cloth to coordinate Zn^{2+} which promotes the nonelectrostatic adsorption. Cyclic voltammetry (CV) was conducted to evaluate the capacitive characteristics of the carbon cloth electrodes (see Figure S3). The CV curve exhibited a typical capacitor-like characteristic with a symmetric cyclic shape. No evident oxidation/reduction peaks appeared in the selected potential range, indicating that the zinc ions were mainly removed from the solution by the formed electrical double layers rather than through the electrochemical redox reactions.

Effects of Operating Parameters and Model Validation. First, we investigated the effects of charging voltage on the electro-assisted adsorption process of Zn^{2+} . Figure 2



Figure 2. Effects of charging voltage on the dynamic electro-assisted adsorption process of Zn(II). Experimental conditions: $C_{\text{Zn,feed}} = 80 \text{ mg L}^{-1}$, $\phi_{\rm p} = 44 \text{ mL min}^{-1}$, and $V_{\rm tot} = 100 \text{ mL}$. Symbols: experimental data; Lines: modeling results.

presents the dynamic variation in Zn²⁺ concentration with time at different applied voltages (0.6 V, 0.9 V, 1.2 V) for a fixed pump flow rate of 44 mL min⁻¹, a feed Zn²⁺ concentration of 80 mg L^{-1} and a total water volume of 100 mL. Here, it should be noted that the first data point at time zero at a certain charging voltage represents the feed Zn²⁺ concentration, while the second data point at time zero represents the steady-state Zn^{2+} concentration after the feed Zn^{2+} solution filled the CDI cell and was recycled multiple times at open circuit (i.e., the initial Zn^{2+} concentration before charging). As such, the length of the vertical line indicates the extent of Zn²⁺ adsorption on the activated carbon cloth due to nonelectrostatic interactions (physi- or chemisorption). Upon applying a fixed charging voltage, Zn²⁺ concentration declined quickly and then tended to be stable, suggesting the gradual saturation of ion electrosorption on the carbon electrodes. Additionally, it is apparent that, as the applied charging voltage increased, the final equilibrium Zn²⁺ concentrations decreased. On the basis of Figure 2, it can be calculated that, at a charging voltage of 1.2 V, 13% of the total adsorbed Zn^{2+} were retained via physior chemisorption while 87% of the total adsorbed Zn²⁺ were

held via electrostatic interactions. The model described in the theory section to quantitatively capture the electro-assisted adsorption of Zn²⁺ in the batch-flow mode include three categories of parameters: theoretical parameters $(V_{\rm T}, F)$, experimental parameters (V_{charge} , V_{tot} , V_{mi} , A, $C_{Zn,feed}$) and fitting parameters (D_{Zn} , D_{SO4} , L_{eff} , C_{St} , μ_{att}). V_T (V) represents the thermal voltage equal to 25.7 mV at room temperature, and F represents the Faraday's constant (96,485 C mol⁻¹); V_{charge} (V), V_{tot} (m³), and $C_{\text{Zn,feed}}$ (mM) refer to the charging voltage, total treated water volume and feed Zn²⁺ concentration, respectively, while $V_{\rm mi}$ (m³) and A (m²) refer to the micropore volume and the projected area, respectively, for all electrodes of the same sign (i.e., all anodes, or all cathodes); D_{Zn} (m² s⁻¹) is the diffusion coefficient of Zn^{2+} , D_{SO4} (m² s⁻¹) is the diffusion coefficient of SO_4^{2-} , L_{eff} (m) describes the total effective resistance of the spacer and both electrodes, C_{St} (F m⁻³) is the volumetric Stern layer capacity, and μ_{att} (kT) is the nonelectrostatic attraction term. More detailed information about the meaning of each parameter used in the model is provided in the model development section of the SI. The experimental data obtained in Figure 2 were fitted with simulated results from the model and the following values of fitting parameters were derived: $D_{Zn} = 3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $D_{SO4} = 3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $L_{\text{eff}} = 1 \text{ mm}$, $C_{\text{St}} = 5.45 \times 10^7 \text{ F m}^{-3}$, $\mu_{\text{att}} = 2.3 \text{ kT}$. From Figure 2, it was observed that the proposed model agrees well with the experimental data and provides a good description of the Zn^{2+} removal profiles at all the three applied charging voltages, though some slight deviations exist between the measured data and modeling results.

The pH changes during the whole adsorption process at different charging voltages were recorded to examine the possibility of Zn(II) precipitation. As can be seen from Figure 3, the pH decreased rapidly and then leveled off during



Figure 3. pH variation during adsorption and desorption steps under different charging voltages. Experimental conditions: $C_{Zn,feed}$ = 80 mg L^{-1} , $Ø_p$ = 44 mL min⁻¹, V_{tot} = 100 mL, and $V_{discharge}$ = 0 V.

electrosorption, followed by a gradual increase approaching to the initial value during desorption. These profiles of pH variation are quite similar to those reported by Tang et al.³³ and could be attributed to the Faradaic reactions occurring on the surfaces of and/or within carbon electrodes. The pH fluctuations when the CDI cell was charged at a voltage of 0.6 V-1.2 V were not significant and within the pH range of 4.05.8, suggesting that the change of pH exerted a marginal effect on the treated water quality and Zn(II) precipitation is unlikely to happen during the batch-flow mode operation. In addition, to ensure that Zn^{2+} was not reduced to the element Zn at the cathode surface, SEM characterization of the cathode was performed after Zn²⁺ electrosorption experiments. Figure S4 shows the SEM images of the cathode after 30 min of Zn²⁺ electrosorption tests at 0, 0.6, 0.9, and 1.2 V with an image magnification factor of 1000. When a charging voltage of 0.6-1.2 V was applied, no apparent change on the cathode surface could be observed compared to that at 0 V, which indicates that electrostatic interaction based on EDLs primarily occurred between Zn²⁺ and the cathode during the process of electrosorption while no reduction reaction of Zn²⁺ occurred. This feature is also consistent with the experimentally measured cyclic voltammetry curves.

In addition to the effects of charging voltage, we also investigated the effects of other operating parameters, including feed Zn^{2+} concentration, total treated water volume and pump flow rate, on the electro-assisted adsorption process of Zn^{2+} . In the meantime, the obtained experimental data were used to further validate the developed model. Figure 4 presents



Figure 4. Effects of feed Zn^{2+} concentration on the dynamic electroassisted adsorption process of Zn(II). Experimental conditions: V_{charge} = 1.2 V, ϕ_p = 44 mL min⁻¹, and V_{tot} = 100 mL. Symbols: experimental data; Lines: modeling results.

the removal process of Zn^{2+} at different feed Zn^{2+} concentrations (60 mg L⁻¹, 80 mg L⁻¹, 100 mg L⁻¹) for a fixed charging voltage of 1.2 V, a pump flow rate of 44 mL min⁻¹, and a total water volume of 100 mL. In light of the length of the vertical lines at time zero, one can easily know the amount of Zn^{2+} adsorbed on the activated carbon cloths at different feed Zn^{2+} concentrations due to physi- or chemisorption. A higher feed Zn^{2+} concentration led to a larger physi- or chemisorption amount of Zn^{2+} . Specifically, when the feed Zn^{2+} concentrations were 60 mg L⁻¹, 80 mg L⁻¹ and 100 mg L⁻¹, the physi- or chemisorption amount of Zn^{2+} were 0.424 mg, 0.565 mg, and 0.707 mg, respectively. The physi- or chemisorption amount of Zn^{2+} is almost linear with the feed Zn^{2+} concentration since the ratio of physichemisorbed Zn^{2+} to the feed Zn^{2+} concentration is around 0.00707 mg per mg L⁻¹ feed Zn^{2+} . During the electrosorption process, the Zn^{2+} concentration dropped rapidly within the first 10 min and then leveled off with a higher initial Zn^{2+} concentration resulting in a higher steady-state Zn^{2+} concentration. Additional experiments were conducted to probe the effects of two common coexisting cations (Na⁺ and Mg²⁺) on the electro-assisted removal of Zn^{2+} (see Figure S5). Results revealed that Zn^{2+} removal efficiency decreased with a higher initial concentration of both Na⁺ and Mg²⁺, and the presence of Mg²⁺ had a greater interference with Zn^{2+} removal. Figure 5 presents the removal process of Zn^{2+} at different total



Figure 5. Effects of total treated water volume on the dynamic electro-assisted adsorption process of Zn(II). Experimental conditions: $V_{\text{charge}} = 1.2 \text{ V}$, $C_{\text{Zn,feed}} = 80 \text{ mg L}^{-1}$, and $\mathcal{O}_{\text{p}} = 44 \text{ mL min}^{-1}$. Symbols: experimental data; Lines: modeling results.

treated water volume (100 mL, 200 mL, 300 mL) for a fixed charging voltage of 1.2 V, a pump flow rate of 44 mL min⁻¹, and a feed Zn^{2+} concentration of 80 mg L^{-1} . It was found that the total treated water volume also had an influence on the physi- or chemisorption amount of Zn²⁺ when the other parameters were kept constant. The physi- or chemisorption amount of Zn²⁺ at total treated water volume of 100 mL, 200 mL, and 300 mL were 0.565 mg, 0.614 mg, and 0.622 mg, respectively. Moreover, it is obvious that use of a large total water volume in batch-flow mode is not suitable for the treatment of zinc wastewater as the change in Zn²⁺ concentration is low when the treated total water volume is large. In fact, Zn²⁺ electrosorption amount Q (mg) can be calculated according to $Q = (c_0 - c_e) \cdot V_{tot}$, where c_0 is the initial Zn^{2+} concentration before charging (mg L⁻¹), c_e is the equilibrium Zn^{2+} concentration (mg L⁻¹), and V_{tot} is the total treated water volume (L). Therefore, $c_e = c_0 - Q/V_{tot}$. We can reasonably assume that Q remains constant when only the parameter $V_{\rm tot}$ is changed, which could then explain the nature of the results obtained in Figure 5. In Figures 4 and 5, we fit the experimental data using the same set of values of fitting parameters as those in Figure 2, and it turned out that the theoretical model could generate simulation results that fit the experimental measurements with excellent precision (as indicated by the coefficient of determination in Table S1), covering both the nonelectrostatic adsorption and the electrosorption processes.

Figure 6 presents the removal process of Zn^{2+} as a function of pump flow rate (32 mL min⁻¹, 44 mL min⁻¹, 56 mL min⁻¹) for a fixed charging voltage of 1.2 V, a feed Zn^{2+} concentration



Figure 6. Effects of pump flow rate on the dynamic electro-assisted adsorption process of Zn(II). Experimental conditions: $V_{\text{charge}} = 1.2 \text{ V}$, $C_{\text{Zn,feed}} = 80 \text{ mg L}^{-1}$, and $V_{\text{tot}} = 100 \text{ mL}$. Symbols: experimental data; Lines: modeling results.

of 80 mg L^{-1} and a total water volume of 100 mL. At a flow rate of 32 mL min⁻¹, about 1000 s were needed to reach the electrosorption equilibrium. Increasing the flow rate to 44 mL min⁻¹ and 56 mL min⁻¹ enhanced the adsorption rate and it took only about 800 s to reach the electrosorption equilibrium. Similar behavior has been observed in using O-doped BN nanosheets and N-doped graphene nanosheets as the CDI electrode for removal of other heavy-metal ions.34,35 It was believed that the high flow rate enabled rapid ion diffusion within the activated carbon cloths and increased the amount of ions available for electrosorption in the next cycle of usage. Furthermore, it was observed that the two different flow rates of 44 mL min⁻¹ and 56 mL min⁻¹ exerted little influence on the complete removal process of Zn^{2+} . In the aspect of theory, the model simulation successfully matched with the experimental results at flow rates of 44 mL min⁻¹ and 56 mL min⁻¹. In fact, in our model, the parameter of flow rate is not included, which implicitly determines the lack of effect of flow rate on ion removal. We assumed that at every moment in time, the specific ion concentration throughout the cell (i.e., spacer channel, pipes and recycling vessel) was the same. The results presented in Figure 6 indicate that the low flow rate of 32 mL min⁻¹ affects the validity of the assumption to some

degree and thereby the accuracy of the model simulation. Apart from the ion adsorption rate and equilibrium ion concentration, energy consumption is another important performance indicator. Generally, a lower flow rate means a lower pumping energy requirement. Through comprehensive consideration, it can be concluded that the appropriate pump flow rate in this study is likely to be 44 mL min⁻¹.

Model Application. On the basis of the above validated model, it is evident that, in addition to the parameters of charging voltage (V_{charge}), total treated water volume (V_{tot}), and feed Zn^{2+} concentration ($C_{\text{Zn,feed}}$), the parameters of micropore volume (V_{mi}), nonelectrostatic attraction term (μ_{att}), and electrode projected area (A) also play an important role in the electro-assisted adsorption of Zn^{2+} . As mentioned previously, difficulties exist in experimentally analyzing the effects of each parameter. As such, herein, the effects of V_{mi} , μ_{att} and A are examined by use of the developed mathematical tool.

The effects of micropore volume (V_{mi}) and nonelectrostatic attraction term (μ_{att}) on the batch-mode equilibrium Zn^{2+} concentrations after physi- or chemisorption and after electrosorption are shown in Figure 7a, b, respectively. It can be seen from Figure 7a that, when the other parameters are kept constant, the equilibrium Zn²⁺ concentration after physior chemisorption decreases linearly with increasing V_{mi} at a slow rate while the equilibrium Zn²⁺ concentration after electrosorption decreases linearly with increasing $V_{\rm mi}$ at a fast rate. It is worth noting that the difference between the feed Zn²⁺ concentration and the equilibrium Zn²⁺ concentration after physi- or chemisorption represents the concentration difference caused by physi- or chemisorption, while the difference between the equilibrium Zn²⁺ concentration after physi- or chemisorption and the equilibrium Zn²⁺ concentration after electrosorption represents the concentration difference caused by electrosorption. The concentration difference caused by physi- or chemisorption and by electrosorption steadily increase with $V_{\rm miv}$ suggesting that the increase in $V_{\rm mi}$ favorably contributes to the enhancement of Zn²⁺ adsorption amount via both physi- or chemisorption and electrosorption. Moreover, the significantly larger concentration difference caused by electrosorption than that caused by physi- or chemisorption indicates that the increase in $V_{\rm mi}$ would bring about a much greater and more positive influence on the electrosorption than the physi- or chemisorption process. From Figure 7b, it was found that, as μ_{att} increases when the other parameters remain unchanged, the equilibrium



Figure 7. Effects of (a) micropore volume V_{mi} and (b) nonelectrostatic attraction term μ_{att} on the batch-mode equilibrium Zn^{2+} concentrations after physi- or chemisorption and after electrosorption at assumed conditions of $V_{charge} = 1.2$ V, $C_{Zn,feed} = 80$ mg L⁻¹, and $V_{tot} = 100$ mL.



Figure 8. (a) Effects of electrode projected area *A* on the batch-mode equilibrium Zn^{2+} concentrations after physi- or chemisorption and after electrosorption in one CDI cell at assumed conditions of $V_{charge} = 1.2$ V, $C_{Zn,feed} = 100$ mg L⁻¹, and $V_{tot} = 300$ mL; and (b) schematic illustration of the equivalence of one cell to a stack of cells in parallel.

Zn²⁺ concentration after physi- or chemisorption drops exponentially while the equilibrium Zn²⁺ concentration after electrosorption decreases slowly and subsequently drops quickly. Furthermore, the gradual increase in the concentration difference caused by physi- or chemisorption along with the gradual decrease in the concentration difference caused by electrosorption imply that the increase in μ_{att} has a huge positive impact on the Zn²⁺ physi- or chemisorption but has a negative effect on the Zn²⁺ electrosorption.

Assuming that the same carbon cloth electrodes are used, the effects of electrode projected area (A) on the batch-mode equilibrium Zn²⁺ concentrations after physi- or chemisorption and after electrosorption are displayed in Figure 8a. It is noteworthy that, when plotting the figure, $V_{\rm mi}$ would vary in direct proportion to A while the other parameters remain constant. The predicted results turn out that A has similar effects to $V_{\rm mi}$ on the equilibrium Zn^{2+} concentrations after physi- or chemisorption and after electrosorption. It should be pointed out that all the above results are based on one CDI cell. To bring CDI to large-scale practical applications, many cells need to be pressed together in parallel to construct a stack. As a matter of fact, for batch-mode operation, one CDI cell with the electrode area of $N \times A$ is equivalent to a stack of N CDI cells in parallel with each electrode area of A (see Figure 8b). That is to say, there is no difference in the electroassisted adsorption kinetics of Zn²⁺ between the two CDI configurations if the operating conditions (e.g., charging voltage, feed Zn²⁺ concentration, total treated water volume, and flow rate) remain identical.

Consecutive Adsorption-Desorption Cycles. Recovering used adsorbents is crucial to the practical use of adsorption process because the feasibility of an industrial adsorption process depends largely on the cost of regenerating the spent adsorbent.³⁶ In this work, the desorption efficiency for spent activated carbon cloths was investigated using three methods, i.e., short-circuiting, reverse constant voltage, and reverse square-wave pulsed voltage. It turned out that short-circuiting was the most efficient among the three examined desorption methods. Figure 9 shows the dynamic variation in Zn²⁺ concentration over 100 consecutive cycles using the simple short-circuiting desorption method. Prior to the charging step in the first cycle, Zn²⁺ feed concentration dropped from 80 mg L^{-1} to about 75 mg L^{-1} attributed to the physi- or chemisorption. During charging, Zn²⁺ concentration decreased from 75 mg L^{-1} to around 42 mg L^{-1} , which was caused by electrostatic interactions. During discharging, Zn²⁺ concentration increased and finally returned back to 72 mg L⁻¹, indicating that almost all the Zn²⁺ ions held by electrostatic interactions (87% of the total adsorbed Zn^{2+}) could be released from the electrodes while the Zn²⁺ ions retained by physi- or chemisorption (13% of the total adsorbed Zn^{2+}) appeared to be difficult to desorb from the electrodes through the simple short-circuiting method. The following second and third cycles saw the readsorption of Zn²⁺ and the near complete desorption of Zn²⁺ via electrostatic interactions. After a long period of successive runs, during the 99^{th} and 100^{th} cycles, the carbon electrodes still possessed good repeatability and exhibited good regeneration performance for the removal



Figure 9. Dynamic variation in Zn²⁺ concentration over one hundred consecutive adsorption–desorption cycles. Experimental conditions: $V_{\text{charge}} = 1.2 \text{ V}$, $C_{\text{Zn,feed}} = 80 \text{ mg L}^{-1}$, $\emptyset_{\text{p}} = 44 \text{ mL min}^{-1}$, $V_{\text{tot}} = 100 \text{ mL}$, and $V_{\text{discharge}} = 0 \text{ V}$.

of Zn^{2+} , though a slight loss in the Zn^{2+} electrosorption capacity was observed compared to the initial cycles.

Environmental Implications. In this work, both experimental and modeling approaches have been employed to systematically investigate the feasibility of electro-assisted adsorption of Zn²⁺ on activated carbon cloth from aqueous solutions operated in the batch-flow mode. The electroassisted adsorption of Zn²⁺ on activated carbon cloths is specifically divided into two processes: nonelectrostatic adsorption (i.e., physi- or chemisorption) and electrostatic adsorption (i.e., electrosorption). On the basis of characterization of the activated carbon cloth, evaluation of the electrochemical characteristics of Zn²⁺ on the carbon electrode and investigation of the effects of multiple operating parameters on the dynamic removal process of Zn²⁺, a mathematical model proposed to enable quantitative description of both the nonelectrostatic adsorption step and the electrosorption step was validated. Experimental and theoretical results demonstrated a significant enhancement of Zn²⁺ adsorption capacity on the carbon electrodes under the electroassistance. The model developed here not only appropriately captured the experimental results obtained and showed how change in the operating parameters affected the adsorption kinetics of Zn²⁺, but also allowed for prediction of Zn²⁺ treatment performance over a range of operating conditions, cell arrangements, and feedwater compositions. The model favorably contributed to a better understanding of the separation process and could provide valuable guidance to the selection of particular design and operating parameters suited to achieving suitable treated water quality. Considering the ability of the model to satisfactorily describe zinc ion removal, it is very likely that the model could be extended to other cases such as copper ion, magnesium ion, and, with some further modifications, even nitrate and perchlorate ions, though the zinc ion case considered here may be a simplification of real water conditions and scope for model improvement exists.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b05909.

Ancillary experimental results and details of the model development (PDF)

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Notes

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