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Electrosorption for organic pollutants removal and desalination by graphite and activated carbon fiber composite electrodes

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Corresponding Author:	Dayi Zhang Lancaster University UNITED KINGDOM
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Lancaster University
Corresponding Author's Secondary Institution:	
First Author:	Guizhong Zhou
First Author Secondary Information:	
Order of Authors:	Guizhong Zhou
	Wenqian Li
	Zhaofeng Wang
	Xuan Wang
	Shaoxiang Li
	Dayi Zhang
Order of Authors Secondary Information:	
Abstract:	This paper investigated a novel type of carbon-based electrodes, which were equipped with graphite and activated carbon fiber composite, to improve the performance of electrosorption. The results indicated that the highest desalination efficiency achieved 55% and the optimal condition was 1.6 V voltage, 60 minutes retention time and 1.0 cm electrode distance. Freundlich isotherms successfully fitted with the respective behavior of the composite electrode and provided theoretical evidence for the desalination performance improvement. Applied in real black liquor of refined cotton, the graphite and activated carbon fiber composite electrodes achieved high removal efficiency for conductivity (59%) and CODCr (76%). Similar removal performance was also observed in sodium copper chlorophyll wastewater, and removal efficiency were 37% for conductivity and 14% for CODCr respectively. For the first time, this research demonstrated the biodegradability improvement of real industrial wastewater via electrosorption treatment, suggesting a potential pretreatment technique for high salinity wastewater.

Dear Editor,

Thank you very much for the efforts and all the reviewers' comments have been considered and revised in the manuscript modification. All the relative corrections are marked with blue colour in the revised manuscript.

Comment 1

The specific contribution of this paper mainly relies on the treatment of high salinity wastewater, in which salt ions and charge organic molecules were removed. I am not sure whether the title of this paper is appropriate (i.e., electrosorption desalination)?

Answer

The author agreed with reviewer's comments. Desalinating and organic pollutants removal are the two main aims of this research and the title has been changed as "Electrosorption for organic pollutants removal and desalination by graphite and activated carbon fiber composite electrodes"

Comment 2

It is not clear for the reviewer why the authors choose graphite to increase the electrical conductivity of the carbon electrodes, especially as compared to carbon black.

Answer

Due to the large surface area and electrical conductivity of graphite, the author wants to improve the electrosorption performance by carbon surface modification with the help of graphite. More explanation was added in the introduction part.

Comment 3

The authors claimed that they use a novel type of carbon-based electrodes, composed of graphite and activated carbon. Most recently, however, hierarchical ordered porous carbons with macro-, meso-, and micro-pores are recognized as novel electrode materials for capacitive charge storage. The reviewer does not agree with that the graphite and activated carbon composite is a novel electrode material for electrosorption process.

Answer

The author further considered the reviewer's comments and thought it is better to state it is an improved electrode material to enhance the electrosorption efficiency. All the relative texts have been revised in accordance with reviewer's comments.

Comment 4

The authors need to provide the information of pore structure (e.g., specific surface area, pore volume, and pore size distribution) of the composite electrode.

Answer

The author has carried out further adsorption isotherm experiments and added relative data in the supplementary information and the analysis in the main manuscript.

Comment 5

It would be more meaningful if the authors could include the cyclic voltammetry, electrochemical impedance spectra and galvanostatic charge/discharge curves of the composite electrode in the paper.

Answer

The author thanks the reviewer's suggestion and added the cyclic voltammetry graph and relative description in the main text. Due to the time and facility limitation, the other characterization cannot be completed in a short time and further work will be carried out for further publication.

Comment 6

It is suggested to compare the pore structure and electrochemical behaviors of the composite electrode with the other nanoporous carbons reported in literature.

Answer

Thank you for the comments and the author has added some discussion and comparison in the relative sections.

Comment 7

The electrosorption process was conducted in a batch-mode or a single-pass (continuous-flow) experiments?

Answer

The electrosorption process was carried out in a continuous-flow mode, and the parameter has been added in the Materials and Methods section

Comment 8

It is suggested to include the experimental data of electrosorption and regeneration cycles of the process.

Answer

The author has set up a new electrosorption and regeneration for further research on the electrode passivation and electrosorption capacity reduction during the regeneration process. From the current progress, the electrosorption capacity maintained over 75% after 20 generations in artificial wastewater desalination process but did not behave satisfied for real wastewater samples. The results were briefly discussed and illustrated in the main text and supplementary materials. The authors are trying to further improve the electrode manufacturing process for electrode protection and would like to publish relative research in the near future.

Comment 9

The authors intend to discuss the effect of electrode distance on the removal efficiency. The system resistance (equivalent circuit) has dependency on the distance of electrodes, and thereby it would further affect the removal efficiency and current efficiency. The authors should use the same flow rate to investigate the effect of electrode distance. Otherwise, it is not possible to distinguish the effects of electrode distance and flow rate.

Answer

Thank you for the comments and the author agrees with the reviewers that the same flow rate should be applied to distinguish the effects of electrode distance and flow rate. However, the peristaltic pump used in this research cannot achieve the accurate low flow rate when the electrode distance was less than 1.0 cm. It is the reason that the author tries to discuss the impacts of distance and flow rate by models in Section 3.2.4. From the theoretical analysis in this part, the author had the mathematical support to explain the behaviour of conductivity removal with different electrode distance. The authors are purchasing a new peristaltic pump and hope more data will be obtained and published in future paper.

Comment 10

It would be more meaningful of the authors could calculate the specific energy consumption (kWh/m3) for the electrosorption process.

Answer

Thank you for the suggestion. The author has calculated the energy consumption as 0.538 kWh/m^3 when the operation voltage and current is 1.6 V and 6.7 mA respectively (initial chloride concentration 1000 mg/L and the hydraulic retention time 60 min). Relative discussion was added in the main text.

Comment 11

Porada et al. (Prog. Mater. Sci., 58, 1388-1442, 2013) proposed the six electrochemical reactions for the electrosorption process using nanoporous carbon electrodes. For removing the charged organic molecules under an electric field, is there any Faradic reaction, water chemistry, or pH-fluctuations occurring on the electrode surface during the process? The authors should include this for discussion.

Answer

Thank you for the recommendation and the author did not consider these issues in the experimental design and the current experimental data cannot support any evidence for deeper discussion. To address this question, some general discussion on literature was conducted in the manuscript, and it is also good suggestions for the author to further look deeper into the Faradic reaction or other chemical processes on the electrode surface in future experiment.

Comment 12

In the cited reference (Zhou et al., 2014), "Environ Sci Technol" is a incorrect citation. The journal is Environmental Science (in Chinese with English Abstract).

Answer

The author has corrected the mistakes.

Comment 13

The abstract is much similar to the published paper [Zhou et al., Environmental Science , 2014]. So, what is the novelty of this work?

Answer

In the previous publication [Zhou et al., Huanjing Kexue , 2014], the author only reports the electrosorption of different electrode materials and its performance in real wastewater treatment. To further discuss the mechanism and optimize the electrosorption performance, this work introduced detailed discussion of adsorption

isotherms and different restricted factors to further explain and improve the electrosorption process. All these new discussions were not in the previous publication.

Electrosorption for organic pollutants removal and desalination by graphite and activated carbon fiber composite electrodes

Short title

Carbon electrode electrosorption

Guizhong Zhou[1], Wenqian Li[1], Zhaofeng Wang[1], Xuan Wang[1], Shaoxiang Li[1], Dayi Zhang[2,*]

1 College of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao, 266042, P. R. China

2 Lancaster Environment Centre, Lancaster University, Lancaster, LA1 2YQ, UK

Corresponding author

Dr Dayi Zhang

Lancaster Environment Centre, Lancaster University, Lancaster, LA1 2YQ, UK

E-mail: d.zhang@lancaster.ac.uk

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Abstract: This paper investigated a new type of carbon-based electrodes, which were equipped with graphite and activated carbon fiber composite, to improve the performance of electrosorption. The results indicated that the highest desalination efficiency achieved 55% and the optimal condition was 1.6 V voltage, 60 minutes retention time and 1.0 cm electrode distance. Freundlich isotherms successfully fitted with the respective behavior of the composite electrode and provided theoretical evidence for the desalination performance improvement. Applied in real black liquor of refined cotton, the graphite and activated carbon fiber composite electrodes achieved high removal efficiency for conductivity (59%) and COD_{Cr} (76%). Similar removal performance was also observed in sodium copper chlorophyll wastewater, and removal efficiency were 37% for conductivity and 14% for COD_{Cr} respectively. For the first time, this research demonstrated the biodegradability improvement of real industrial wastewater via electrosorption treatment, suggesting a potential pretreatment technique for high salinity wastewater.

Keywords: electrosorption; graphite and activated carbon fiber composite electrodes; saline wastewater; desalination efficiency

1. Introduction

Water pollution is one of the major concerns in water supply and wastewater management (Huang and Xia 2001). Different from domestic wastewater, industrial wastewater aggravated the actuality due to the intensive discharge and threats of toxic compounds, such as heavy metals (Boening 2000), crude oil (Chen et al. 2013, Zhang et al. 2013) and pesticide (Kolpin et al. 2002). It therefore caused serious ecological challenges (Burkholder et al. 2007) and human health risk (Cantor 1997). Particularly, industrial salinity wastewater contained high salt content and was reported with increasing discharge. The intensive attention has been drawn due to its composition of poisonous and hardly-decomposed organic pollutants (Lefebvre and Moletta 2006). Since the high salinity damaged the cytomembrane and enzymes of microbes, industrial salinity wastewater inhibited the growth and activities of degrading microorganisms, consequently resulting in the failure of the biological treatment (GuetaDahan et al. 1997). Such challenges have brought difficulties in industrial wastewater treatment plant, raising the practical demand of pretreatment technique of desalination for further biological process.

To achieve effective desalination, many physical and chemical methods have been widely investigated, including thermal dynamic method, chemical method, and membrane method (Greenlee et al. 2009, Jing et al. 2009, Mtombeni et al. 2013, Zhao et al. 2011). As a novel method for seawater and industrial wastewater desalination, electrosorption has the unique features of low cost, high anti-pollution ability, environmentally friendly and simple operation (Wang et al. 2012). Trapped by the opposite charge on the electrode surface, the ions in wastewater were adsorbed and fixed in the electrical double layer, and subsequently removed from the aqueous phase (Choi and Choi 2010, Nadakatti et al. 2011). Generally, activated carbon (Chang et al. 2011), activated carbon fiber (ACF) (Li et al. 1997), carbon nanotubes (Li et al. 2008) and carbon aerogel (Rasines et al. 2012) were the most applied electrode materials. Though carbon aerogel and carbon nanotube had the best desalination performance (Farmer et al. 1995, Farmer et al. 1996, Rasines et al. 2012), they suffered from the

high cost and were not appropriate for industrial application. Alternatively, surface modified carbon or carbon-based materials had become the cutting edge for the improvement of electrosorption performance (Ahn et al. 2007, Avraham et al. 2011, Chang et al. 2011, Lee et al. 2009). Since the large specific area and high conductivity are the two key factors affecting electrosorption performance, it is meaningful to develop integral electrode of carbon materials with respective advantages for electrosorption enhancement. Considering the higher electrical conductivity of graphite and the high adsorption efficiency of activated carbon fiber (Ahn et al. 2007, Ishikawa et al. 1996, Jannakoudakis et al. 1993, Kim 2005, Porada et al. 2013b), the integral electrode with the two elements therefore drew many research and industrial interests, viewed as suitable engineering device for practical desalination of industrial salinity wastewater.

In this study, the combination of graphite and activated carbon fiber was applied for desalination and organic pollutants removal as an improved composite electrode material. The determinants affecting the desalting efficiency were analyzed as the operation voltage, initial chloride concentration, pH value and electrode distance. Applied in real industrial wastewater with high salinity, the graphite and activated carbon fiber composite electrodes had good performance to achieve high removal efficiency of conductivity and improve the biodegradability of the water sample, suggested as a practical pretreatment technique for refined cotton and sodium copper chlorophyll wastewater before further advanced biological treatment.

2. Materials and methods

2.1 Wastewater sample

Artificial wastewater and real industrial wastewater samples were investigated in this study. Artificial salinity wastewater contained different level of NaCl concentration as 100, 200, 500, 1,000, 2,000, 5,000, 10,000 and 20,000 mg/L. The organic matters were consisted of glucose and the concentration was from 4000 to 5000 mg/L. The real black liquor of refined cotton wastewater was taken from Shangdong

Guangtongbao Pharmaceuticals Co. Ltd. located in Weifang city, China. The sodium copper chlorophyll wastewater was the discharge of Shandong Shengwei Biotech Co. Ltd. located in Heze city, China.

2.2 Graphite and activated carbon fiber composite electrodes

The preparation of graphite and activated carbon fiber composite electrodes followed potassium hydroxide cleaning. Briefly, the graphite and activated carbon fiber (m:m=3:2) were blended as the raw electrode material, subsequently mixed with phenolic resin (0.25 g/mL, ethanol as the solvent) with 2:1 mass ratio. Afterwards, the mixture was pressed and carbonized at 750°C, 850°C and 950°C for 60 min respectively in nitrogen atmosphere. Finally, the composite electrode was treated in boiling KOH solution (1 mol/L) for 3 h, washed by deionized water thoroughly and kept storage in deionized water for further experiment.

2.3 Electrosorption desalination device

The design of electrosorption desalination device was illustrated in Fig. 1. The electrode working voltage was 1.6 V without specific description and the influent rate was 10 mL/min. To evaluate and optimize the desalting and COD_{Cr} removal efficiency, the number of the composite electrodes was set as 1, 2, 4, 6, 8 and 10. Further improvement was carried out with the adjustment of distance between the two electrodes as 0.5, 1.0, 1.5 and 2.0 cm. To evaluate the energy consumption during the electrosorption process, the electrosorption desalination device was operated for 1 hour with the 1.6 V operation voltage. During the desalination process, the initial chloride concentration was 1000 mg/L and the hydraulic retention time was 60 min.

2.4 Wastewater treatment

For the operation voltage optimization, artificial wastewater with 5,000 mg/L NaCl was applied and the voltages were set up as 1.2, 1.4, 1.6, 1.8 and 2.0 V, respectively. Throughout the experiment, all the wastewater treatments were undertaken for one hour. The pH value of artificial wastewater was adjusted to 2, 4, 6, 8 and 10, with separate addition of 20% H_2SO_4 and 30% NaOH.

2.5 Analytical method

The existence and behavior of functional groups on the graphite and activated carbon fiber composite electrodes were measured and analysed by Fourier Transform Infrared Spectroscopy (FTIR). The surface structure of the electrode was analysed by ISM-6700F (JEOL Limited, Japan), and the operation voltage was 10 kV. An ASAP2000 automatic adsorption system (Micromeritics, USA) was used to determine the specific surface area, pore volume and pore size of the graphite and activated carbon fiber composite electrodes. With N_2 gas as the adsorbent and 12 hours completed adsorption-desorption at 77 K, the BET method calculated the specific surface from the sorption isotherm, and the pore volume and pore size were predicted by the density functional formalism (DFF). The cyclic voltammetry of the graphite and activated carbon fiber composite electrodes was measured by CHI660C electrochemical workstation (CH Instrument, USA) with 10 mV/s scan rate.

Chemical oxygen demand (COD_{Cr}) followed fast digestion-spectrophotometric method, analysed by COD analyzer (DR 2700, Hach, USA). COD was determined according to APHA Standard Methods (APHA 2005). The 2.0 mL water sample was mixed and digested with 1.0 mL digestion solution (10.22 g/L $K_2Cr_2O_7$, 67 mL/L H_2SO_4 and 33.3 g/L $HgSO_4$) at 150°C for 2 h in DR4000 digester (Hach, USA). The solution was then cooled down and measured at 420 nm with UV2501PC spectrophotometer (SHIMADZU, Japan). The 425 mg potassium hydrogen phthalate was dissolved in 1.0 L deionized water and series diluted as standard COD solution. The chloride measurement followed silver nitrate titration method (Chinese 2002). The pH value was determined by pH meter (PHS-2, Xi'an Yima Opto-electrical Technology, China). The biodegradability of wastewater after electrosorption was evaluated by the specific oxygen uptake rate, and the dissolved oxygen (DO) in wastewater sample was measured with a fluorescent DO meter (HQ30d, Hach, USA).

3. Results and discussion

3.1 Surface structure analysis of graphite and activated carbon fiber composite electrodes

The KOH treated electrode had significantly different morphological structure with different treatment temperatures, as shown in Fig. 2. The electrode surface was smooth with low specific surface area (Fig. 2a) before any treatment, and the adsorption is not of high efficiency. Different from the acid treatment effects on the mesoporous carbon (Li et al. 2006), no clear and ordered carbon structure was observed on the electrode surface. The adsorption capacity was improved by increasing surface area with KOH alkaline treatment. Fig. 2 b-d illustrated that the electrode surface had more porous microstructure with the increasing KOH treatment temperature. Further pore structure (Table S1) proved the increasing BET specific surface area from 1050.3 m^2/g (original activated carbon fiber before treatment) to 1263.6-1367.4 m^2/g (KOH treatment under different temperatures), and 850°C treatment has the highest value. The pore volume and size also increased from 1.165 cm^3/g and 1.88 nm (original activated carbon fiber before treatment) to 1.337 cm^3/g and 1.99 nm (850°C KOH treatment). Similar as previous study (Bleda-Martinez et al. 2006), the KOH activation caused certain structural rearrangement on the carbon surface, and the temperature was the restriction factor affecting the activation process. More evidence from infrared spectrum also showed stronger stretching vibration of hydroxyl (-OH, 3440 cm^{-1}), carbonyl (C=O, 1,650 cm^{-1}) and carboxyl (-COOR, 1,200 cm^{-1}) after KOH treatment (Zhou et al. 2014), indicating higher ion exchange ability to improve the ion adsorption capacities of the composite electrodes. Furthermore, the carbonyl group also had the characteristics to accelerate the electron transfer, and the desalting efficiency of the composite electrodes might be further enhanced. Compared to nanostructures of other carbon materials, the surface morphologies illustrated that KOH treatment effectively improve the porosity of the graphite and activated carbon fiber (Bleda-Martinez et al. 2006), with higher surface area than carbon cloth (Ahn et al. 2007) or direct active carbon coating electrode (Choi and Choi 2010). Nevertheless,

the graphite treatment increased the pore size and decreased the number of pores smaller than 1 nm, which might negatively affect the desalination efficiency due to the positive relationship between desalination and the volume of pores < 1 nm (Porada et al. 2013a). Fig. 3 illustrated the cyclic voltammetry of the graphite and activated carbon fiber composite electrodes and each CV curve has a smooth increasing and declining pattern, suggesting the reversible desalination process. There was no obvious peak current, showing no oxidation-reduction reaction during the electrosorption process. Determined by other two variables as chemical impregnation ratio and activation time (Hameed et al. 2008), the optimal KOH treatment condition was evaluated as 850°C, 1 mol/L and 1 hour for the highest desalination and organic pollutants removal efficiency. The results of cyclic voltammetry also revealed that the composite electrode with 850°C KOH treatment has the highest current capacity.

3.2 Restriction factors of electrosorption treatment for artificial wastewater

3.2.1 Initial chloride concentration

Negative relationship was observed between chloride initial concentration and its removal efficiency, as shown in Fig. 4. The removal efficiency dropped dramatically from 64% (100 mg/L) to 15% (20,000 mg/L) in artificial salinity wastewater samples. However, the total amount of chloride removal increased with the initial chloride concentration, which was from 36 mg/L (initial concentration 100 mg/L) to 3,000 mg/L (initial concentration 20,000 mg/L). The adsorption isotherms were simulated by linearized Langmuir equation (Equation (1)) and Freundlich equation (Equation (2)).

$$Q = Q_{max} \frac{K_L C}{1 + K_L C} \quad (1)$$

$$Q = K_F C^{1/n} \quad (2)$$

Here, Q represents the chloride equilibrium concentration (mg/L), and C is the mount of adsorbed chloride ion on the carbon electrode (mg/g). Q_{max} is the maximum adsorption capacity in accordance with the complete monolayer coverage. K_L is Langmuir constant (L/mg) determined by binding energy, whereas K_F and n

are the Freundlich constants referring to the adsorption capacity and the absorption tendency, respectively. As simulated in Fig. 4 and Table 1, both two isotherms models match the experimental data with high regression coefficient (Supplementary material Fig. S1 and S2). Freundlich isotherms predicted the behavior of NaCl adsorption more accurately than the Langmuir model. Of different isotherm dynamics investigated previously (Ban et al. 1998, Hoda et al. 2006, Hou et al. 2013, Li et al. 2009), Langmuir isotherms fitted with the desalination behavior well when the initial NaCl concentration was low (Wang et al. 2012), whereas Freundlich isotherms interpreted better behavior under high salt conditions (Ayranci and Hoda 2005, Li et al. 2010). Table 1 also demonstrated that the $1/n$ value (0.622) was between 0.1 and 1, indicating the favorable adsorption process on the surface of fiber composite electrodes.

3.2.2 Operation voltage

Fig. 5 illustrated the conductivity removal curve, and the absorption equilibrium was observed after 60 minutes when the removal efficiency became constant. The final conductivity removal efficiency was 29% when the operation voltage was 1.2 V, and the adsorption capacity gradually increased with the operation voltage. With limited electrolysis reaction when the voltage was below 1.8 V, the highest conductivity removal efficiency was 55% (1.8 V).

Adsorption kinetics of NaCl is important for the desalination process, and the operation voltage significantly affect the adsorption dynamics. The kinetics of electrosorption under different operation voltage (1.2, 1.4, 1.6, 1.8 and 2.0 V) was determined and simulated by the pseudo-first-order adsorption process (Wang et al. 2012), as shown in the following Equation (3) and (4).

$$dC/dt = -k(C - C_e) \tag{3}$$

$$\log(C - C_e) = \log(C_0 - C_e) - \frac{k}{2.303} \cdot t \tag{4}$$

where t is the reaction time (min) and k refers to the adsorption rate constant

(min^{-1}). C is the dynamic NaCl concentration (mg/L), whereas C_0 and C_e represent the initial and equilibrium concentration of NaCl (mg/L), respectively. Table 2 listed the values of adsorption rate constant and equilibrium NaCl concentration. It was obvious that C_e has positive relationship with the increase of operation voltage, whereas k reached the maximal value of 0.036 when operation voltage was 1.8 V and dropped at 2.0 V. This phenomenon was caused by the electrolysis of sodium chloride occurring at high operation voltage as stated previously (Cho et al. 2010), consequently resulting in dramatic conductivity removal efficiency jumped to 78%. Considering the energy consumption and operation safety, the optimal operation voltage was suggested as 1.6 V and applied in further experiments.

3.2.3 pH value

As illustrated in Fig. 6, pH had limited impacts on the desalting performance. Chloride removal efficiency dropped slightly with the increase of pH value. The electrostatic repulsion on the surface of composite electrodes led to a larger amount of positive charges at low pH (Ayranci and Duman 2005), causing higher desalination efficiency to some extent. Though pH was observed as sensitive parameters for fluoride electrosorption removal (Lounici et al. 1997), chloride had higher ion strength and was limited affected by the hydroxide ion during the electrosorption process. pH was not the restriction factor for the desalination efficiency of industrial wastewater with high sodium chloride concentration.

3.2.4 Electrode distance

Electrode distance showed unique impacts on chloride removal efficiency (Fig. 7a). The highest chloride removal efficiency (48%) was achieved when the electrode distance was 1.0 cm. When the distance was too small (0.5 cm), the high flow rate led to shorter contact time between the wastewater and the electrode, consequently resulting in insufficient adsorption, though the shorter distance could improve the capacity of electrical adsorption.

Based on the pseudo-first-order adsorption process demonstrated in Equation (3) and

(4), the adsorption rate constant per unit volume of fluid (k', where $k = \frac{w \cdot l \cdot d}{v_i} \cdot k'$) was introduced to evaluate the integral impacts of electrode distance and flow rate, and the following Equation (5) showed the modified electrosorption dynamics.

$$\log(C - C_e) = \log(C_0 - C_e) - \frac{w \cdot l}{2.303 \times v_i} \cdot k' \cdot d \quad (5)$$

Here, w, l and d represent the width (cm), length (cm) and distance (cm) of the electrodes. v_i is the influent flow rate (cm^3/min). The adsorption rate constant per unit area, k', changes with the electrode distance (d). Electrodes with the same length and width but shorter distance have higher electro-capacities (Porada et al. 2013b), consequently leading to higher adsorption rate constant. The model simulation also fitted with the experimental results when the electrode distance was above 1.0 cm (Fig. 7b). The decreasing electronic force had superiority to the increasing contact time, and the optimal electrode distance was therefore suggested as 1.0 cm. Though electrical double layer has suggested smaller distance for higher capacitance (Simon and Gogotsi 2008), the conclusion in this work gave more evidence on the desalination efficiency with variable distance and flow velocity determined by constant flow rate.

3.2.5 Regeneration and energy consumption

With initial 1000 mg/L sodium chloride as the influent, the desalination performance of the graphite and activated carbon fiber composite electrodes after regeneration was evaluated (Fig. S3). The electrosorption efficiency was initially 77.9% and maintained from 77.7% to 78.0% within 10 cycles of regeneration. After 20 cycles of regeneration, the desalination performance still maintained over 77.0%, showing the stability of the composite electrodes in engineering application. From the results of energy consumption during electrosorption process, the operation current was 6.7 mA (1.6 V operation voltages) and the energy consumption was 0.538 kWh/m^3 when initial chloride concentration was 1000 mg/L and the hydraulic retention time was 60 min. Compared to the energy consumption from 1.06 kWh/m^3 to 1.80 kWh/m^3 by reverse osmosis treatment (Elimelech and Phillip 2011), the graphite and activated

carbon fiber composite electrodes in this study had the advantages in energy saving. However, this work was only conducted in small scale and its practical energy consumption needed further investigation.

3.3 Performance of electrosorption treatment for real salinity wastewater

3.3.1 Black liquor from refined cotton wastewater

After acidification, the COD_{Cr} and conductivity of black liquor from refined cotton wastewater were 8,040 mg/L and 26,000 μs/cm, respectively. Under optimal operation condition obtained above, the COD_{Cr} and conductivity removal were shown in Fig. 8. More removal efficiency was achieved with higher number of composite electrodes, and the highest removal efficiency for conductivity and COD_{Cr} was achieved when the number of electrodes was 10. The COD_{Cr} removal could be explained by the adsorption of electronic charged organic molecules in the black liquor of refined cotton wastewater, with similar mechanisms as chloride ion.

Regarding the positive relationship between the increasing number of electrodes and the contacting distance for the influent (Porada et al. 2012), the electrosorption kinetic was expressed in Equation (6), where n represented the number of electrodes.

$$\log(C - C_e) = \log(C_0 - C_e) - \frac{d \cdot w \cdot l \cdot k}{2.303 \times V} \cdot n \quad (6)$$

Dynamic model simulation successfully predicted the behavior of conductivity removal with different number of electrodes (Fig. 8). As the determinant factor, more electrodes improved the high salinity wastewater treatment performance in terms of longer electrosorption contact time. The impacts were significant when the number of electrodes were less than 4, where the conductivity removal efficiency increased significantly from 39% to 53%. When the number of electrodes was higher, the increase of removal efficiency dropped. Taking both efficiency and cost into account, the suggested number of electrodes was 8, and the conductivity and COD_{Cr} removal efficiency was 59% and 76%, respectively.

The significant improvement of oxygen consumption rate, from 0.090 mg/(L·min) to

0.381 mg/(L·min), was also observed after the electrosorption treatment (Zhou et al. 2014). Due to the inhibition effects of salinity on the growth and activities of microbes, the electrosorption treatment could encourage the biodegradation capacity through salinity mitigation (Fan et al. 2006). Besides, electrosorption treatment might also remove some other macromolecules or toxic chemicals, which further contributed to the biodegradability enhancement (Fan et al. 2008). There was only limited research investigating the biodegradability change after electrosorption treatment (Donnaperna et al. 2009), and only artificial wastewater samples were tested (Fan et al. 2006). From the six possible electrochemical effects on the electrode surface for organic matter removal, the biodegradability improvement might be explained by the capacitive ion storage in the electrical double layer or Faradaic reactions on the electrode surface (Porada et al. 2013b). The capacitive ion storage could effective capture the polar organic molecule in the double layer, and the Faradaic reaction could quinone into hydroquinone, which is easier for biodegradation (Jensen et al. 2002). In this research, the author did not observe the hydroquinone formation or organics polarity change due to the complexity and high concentration of organic molecules in the real black liquor from refined cotton wastewater. The results in study were the first time to prove that the biodegradability of real industry wastewater could be improved by electrosorption treatment but the main mechanisms required further investigation.

3.3.2 Sodium copper chlorophyll wastewater

For sodium copper chlorophyll wastewater, the values of COD_{Cr} and conductivity in water sample were 6,600 mg/L and 16,250 μs/cm, respectively. As illustrated in Fig. 9, different conductivity removal efficiency was achieved in the treatments with respective electrodes numbers. Similar to the results of refined cotton wastewater treatment, higher conductivity removal efficiency was achieved with the increasing number of electrodes. Simulated by the adsorption model, the relationship between the conductivity removal and electrode number was also obtained in Fig. 9, where the highest removal efficiency was 37% when the number of electrodes was 10. However,

COD_{Cr} removal had significant change from 11% (1 pair of electrode) to 14% (10 pairs of electrodes), possibly due to less charged organic matters in sodium copper chlorophyll wastewater (Ferruzzi and Schwartz 2005). 8 pairs of electrodes were also suggested as the practical operation condition for sodium copper chlorophyll wastewater desalination. It is similar that the biodegradation capacity of the sodium copper chlorophyll wastewater was also improved, in which the oxygen consumption rate after electrosorption was 0.219 mg/(L·min), higher than 0.077 mg/(L·min) in the original wastewater.

3 Conclusions

In this study, we optimized the electrosorption desalination device, with the graphite and activated carbon fiber composite electrodes, to improve the treatment efficiency of refined cotton and sodium copper chlorophyll wastewater. The three key factors affecting the salinity and organic matter removal efficiency were identified as retention time, electrode voltage and electrode distance. The optimal condition for desalination was 60 min, 1.6 V and 1.0 cm respectively. pH showed limited impacts on the removal efficiency of chloride and COD_{Cr}. Compared to Langmuir model, Freundlich isotherms fitted better with the desalination performance of the composite electrodes under respective conditions. With optimal 8 pairs of electrodes for practical desalting, this technique successfully achieved high conductivity removal efficiency for real refined cotton and sodium copper chlorophyll wastewater. The further improvement of biodegradability also suggested that the graphite and activated carbon fiber composite electrodes have promising application prospects for industrial salinity wastewater as an appropriate pretreatment to encourage advanced biological treatment.

4 Acknowledgements

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6 Figure

Fig. 1. The design of electrosorption desalination device.

Fig. 2. SEM images of electrode surface with different KOH treatment. (a) no KOH treatment; (b) KOH treatment at 750°C for 1 hour; (c) KOH treatment at 850°C for 1 hour; (d) KOH treatment at 950°C for 1 hour.

Fig. 3. The cyclic voltammetry of the graphite and activated carbon fiber composite electrodes under different treatment temperature.

Fig. 4. The impacts of initial chloride concentration on desalination efficiency (black dots) and isotherm model simulation (Langmuir and Freundlich, red and blue line) for chloride adsorption on the composite electrode.

Fig. 5. Desalination performance at different operation voltage (dot) and Freundlich isotherm dynamic simulation (line) for ion adsorption on the composite electrode.

Fig. 6. Desalination efficiency against pH value.

Fig. 7. Desalination performance with different electrode distance (dot) and Freundlich isotherm dynamic simulation (line) for ion adsorption on the composite electrode (a). The isotherm model demonstrated the impacts of electrode distance on desalination efficiency (b).

Fig. 8. The experimental conductivity removal efficiency (column) and Freundlich isotherm simulation (dot and line) of refined cotton wastewater by electrosorption desalination.

Fig. 9. The experimental conductivity removal efficiency (column) and Freundlich isotherm simulation (dot and line) of sodium copper chlorophyll wastewater by electrosorption desalination.

7 Table

Table 1

Determined parameters of K_L, K_F and n of Langmuir and Freundlich isotherms model.

Isotherm	Model equation	Parameter	Value
Langmuir	$Q = Q_{max}\frac{K_L C}{1 + K_L C}$	Q_{max}	1.89
		K_L	0.544
		R^2	0.9850
Freundlich	$Q = K_F C^{1/n}$	K_F	7.56
		$1/n$	0.622
		R^2	0.9882

Table 2

Adsorption rate constant and equilibrium NaCl concentration under different operation voltage.

Voltage (V)	**1.2**	**1.4**	**1.6**	**1.8**	**2.0**
$\boldsymbol{k}$	0.024	0.028	0.032	0.036	0.025
$\boldsymbol{C_e}$ **(mg/L)**	1800	2400	2800	2900	4400

Figure

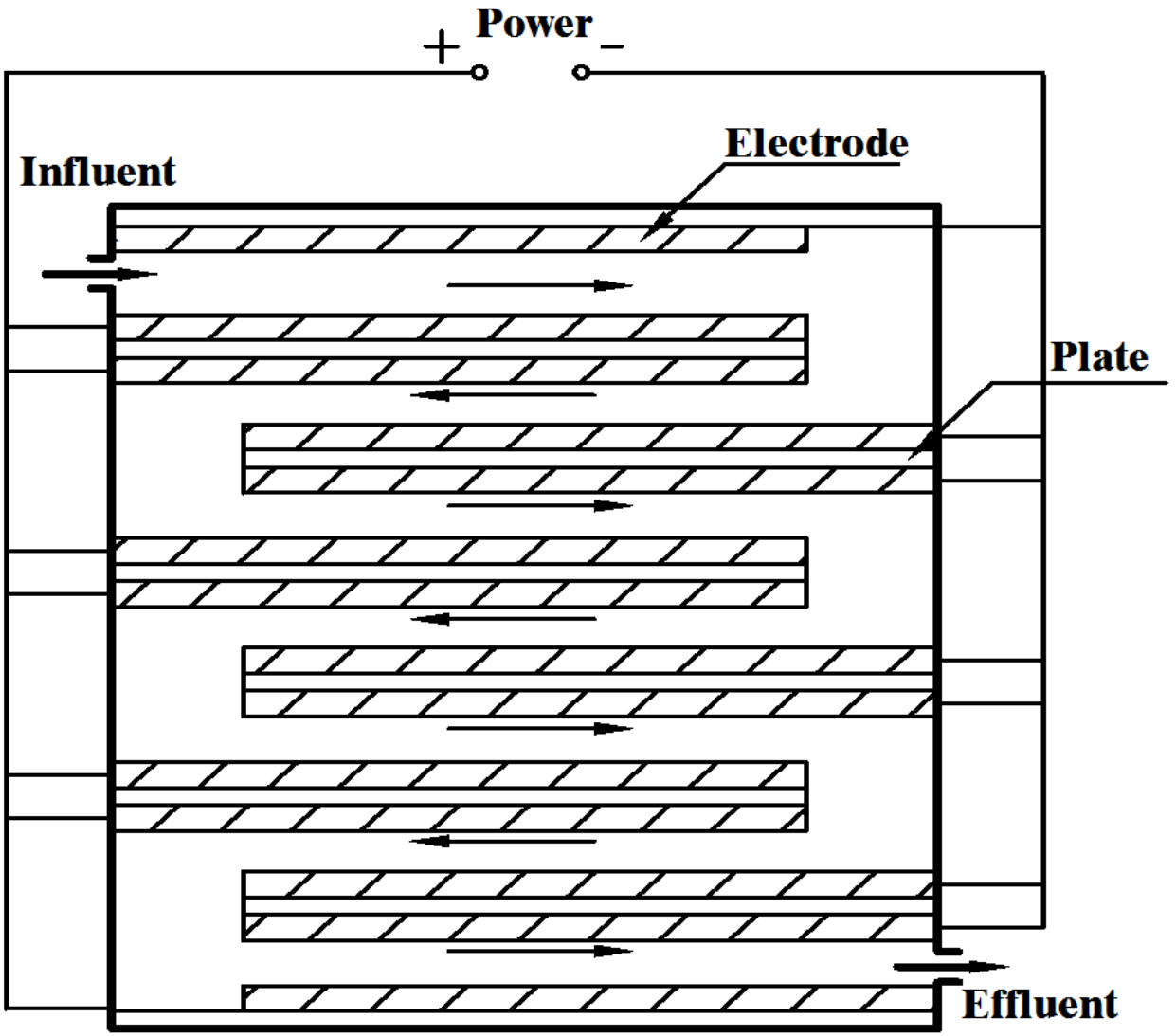
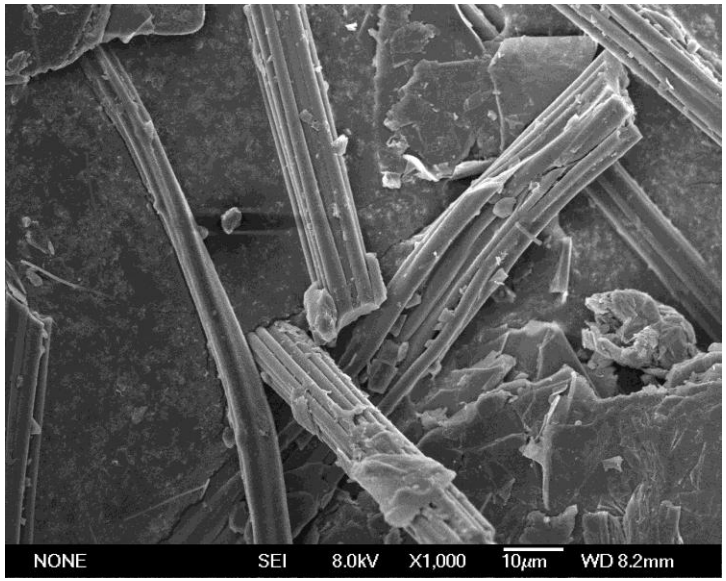


Fig. 1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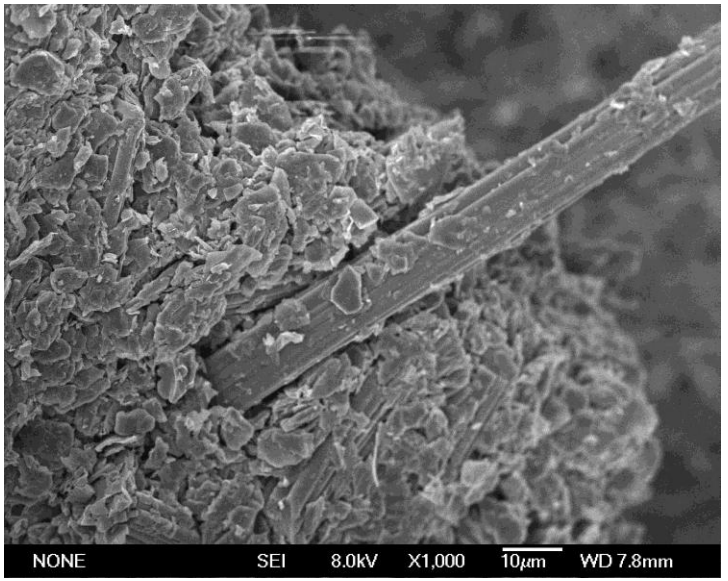
(a)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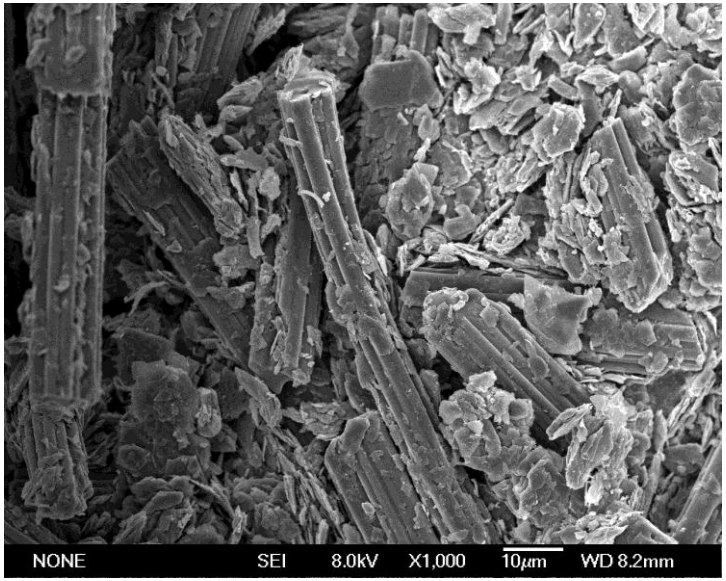
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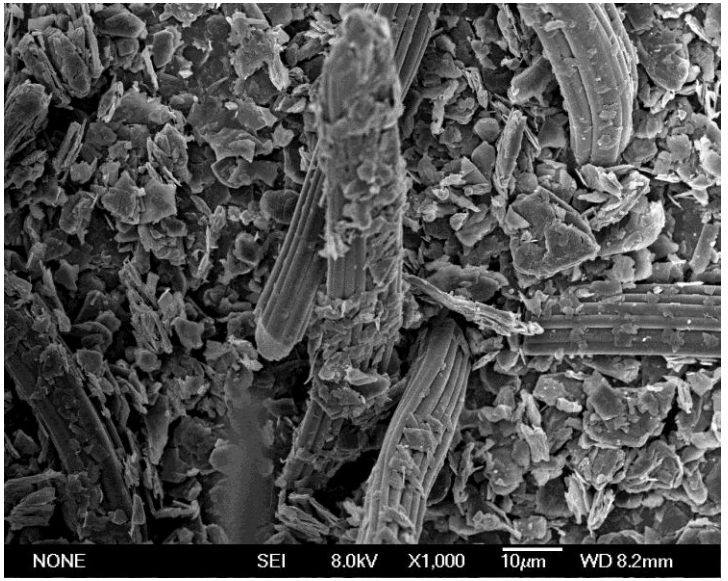
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(d)

Fig. 2

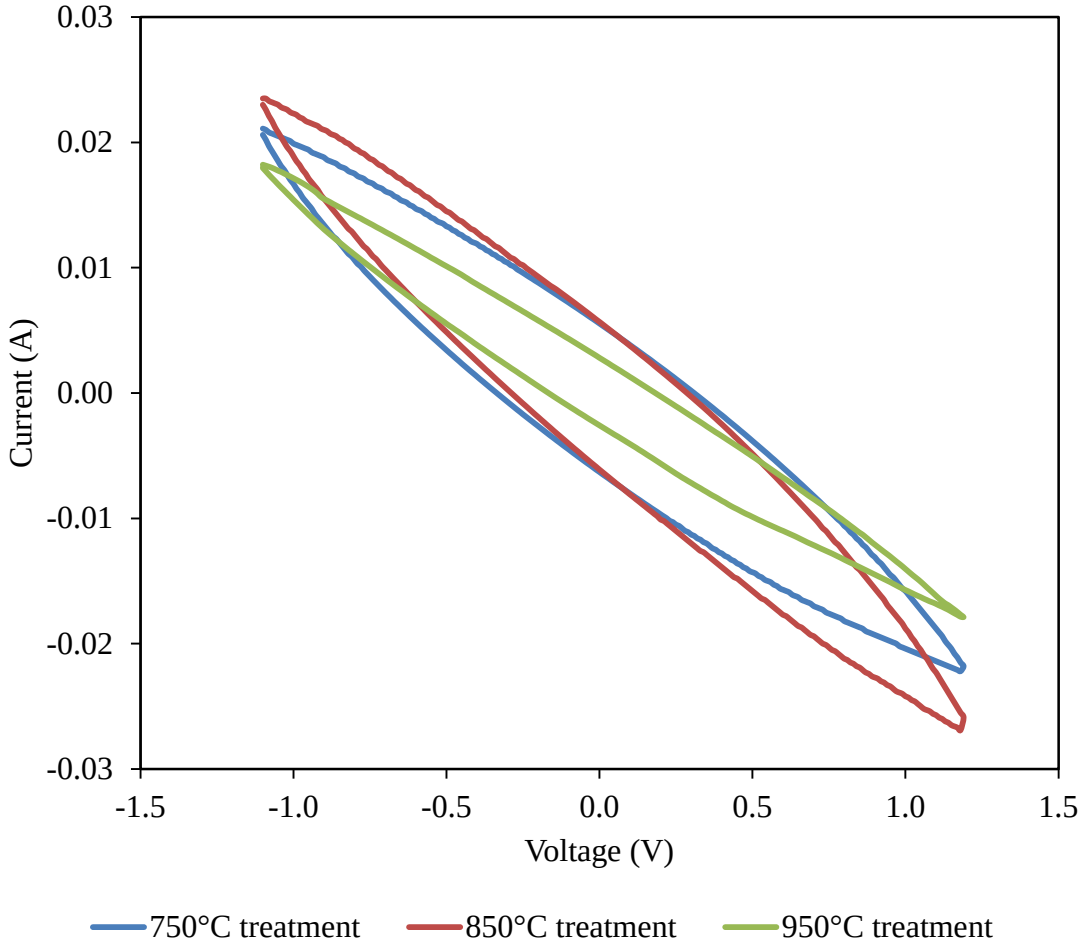
0.03
0.02
0.01
0.00
-0.01
-0.02
-0.03
Current (A)
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
Voltage (V)
750°C treatment
850°C treatment
950°C treatment

Fig. 3

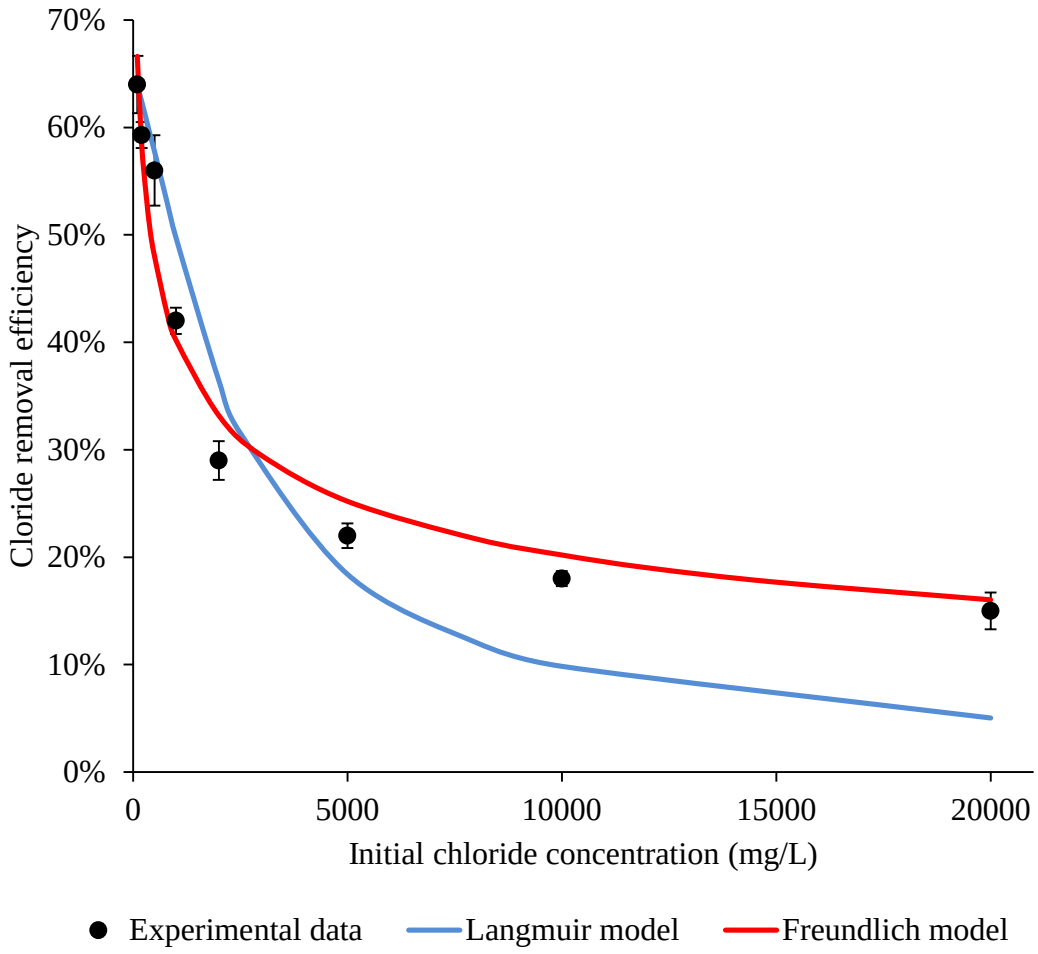
70%
60%
50%
40%
30%
20%
10%
0%
Cloride removal efficiency
0
5000
10000
15000
20000
Initial chloride concentration (mg/L)
Experimental data
Langmuir model
Freundlich model

Fig. 4

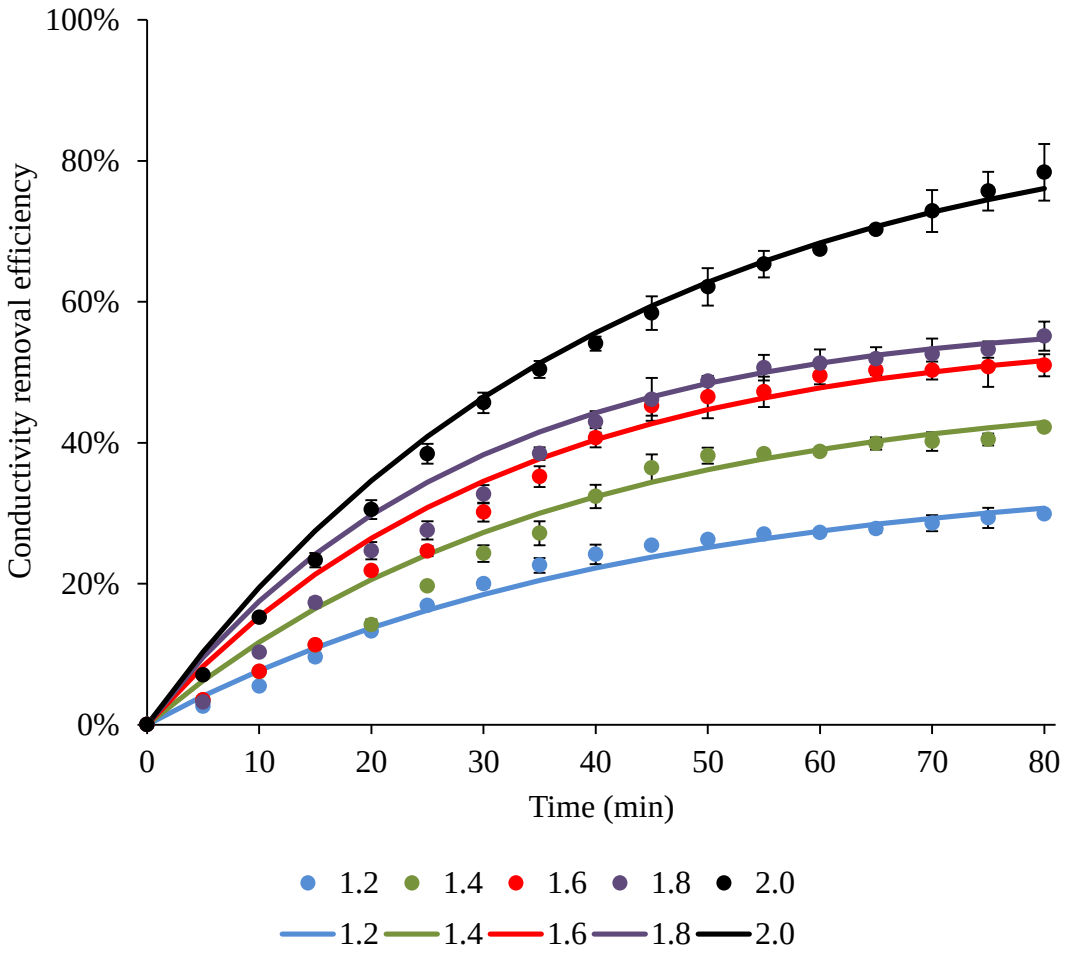
100%
80%
60%
40%
20%
0%
Conductivity removal efficiency
0
10
20
30
40
50
60
70
80
Time (min)
1.2
1.4
1.6
1.8
2.0
1.2
1.4
1.6
1.8
2.0

Fig. 5

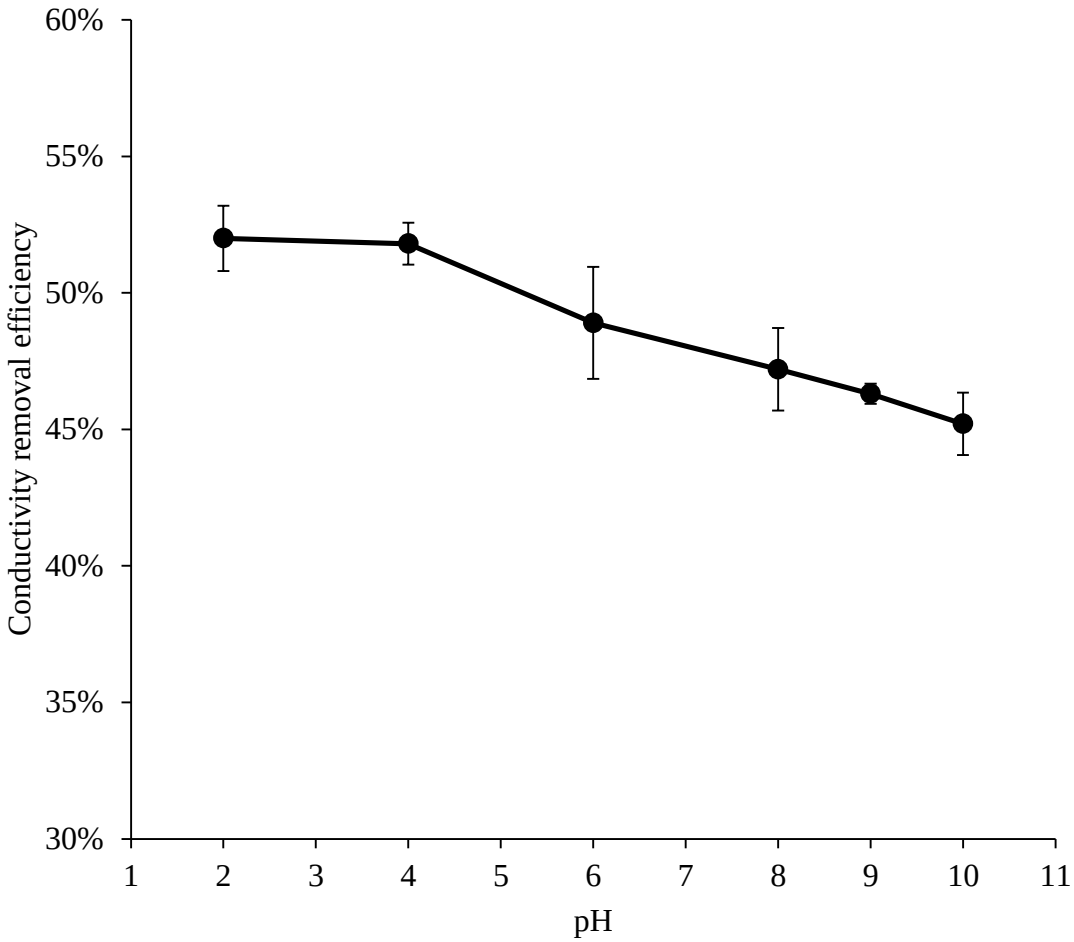
60%
55%
50%
45%
40%
35%
30%
Conductivity removal efficiency
1
2
3
4
5
6
7
8
9
10
11
pH

Fig. 6

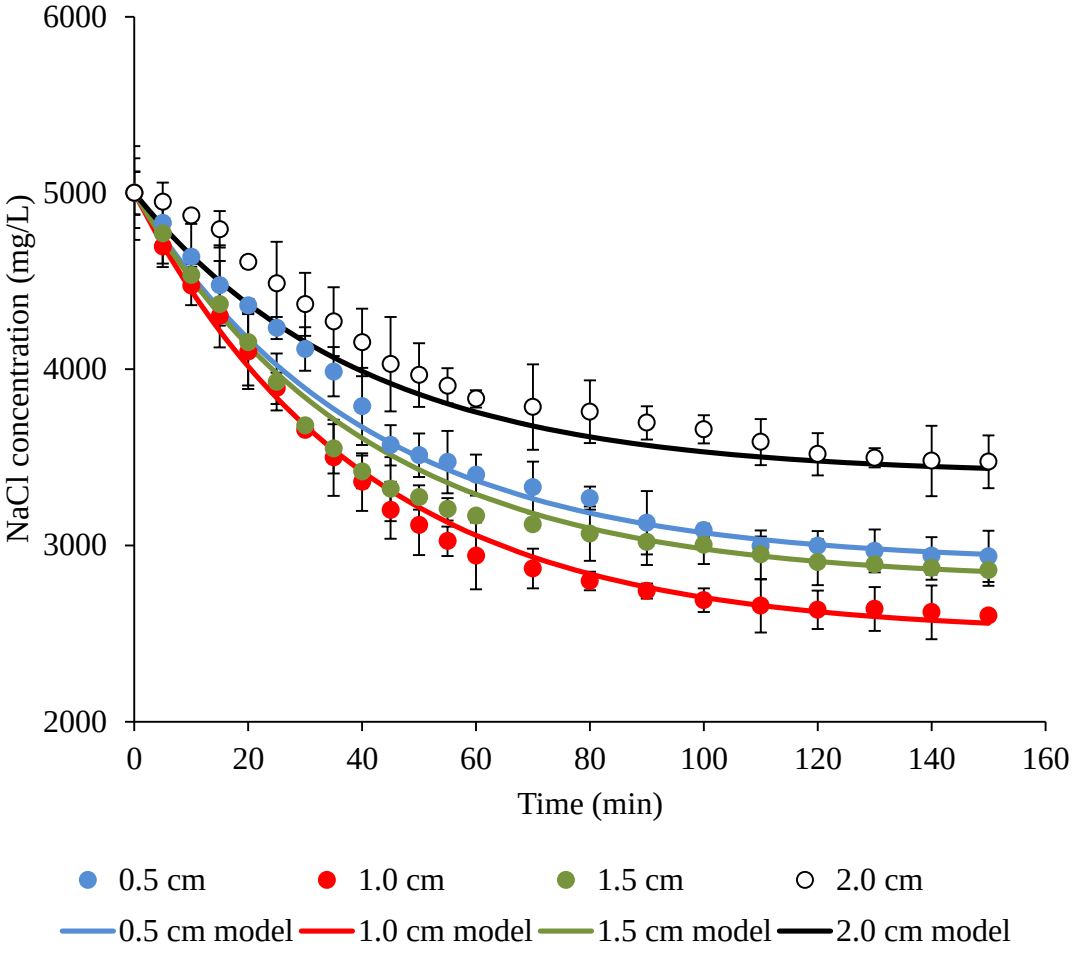
6000
5000
4000
3000
2000
NaCl concentration (mg/L)
0
20
40
60
80
100
120
140
160
Time (min)
0.5 cm
1.0 cm
1.5 cm
2.0 cm
0.5 cm model
1.0 cm model
1.5 cm model
2.0 cm model

Fig. 7a

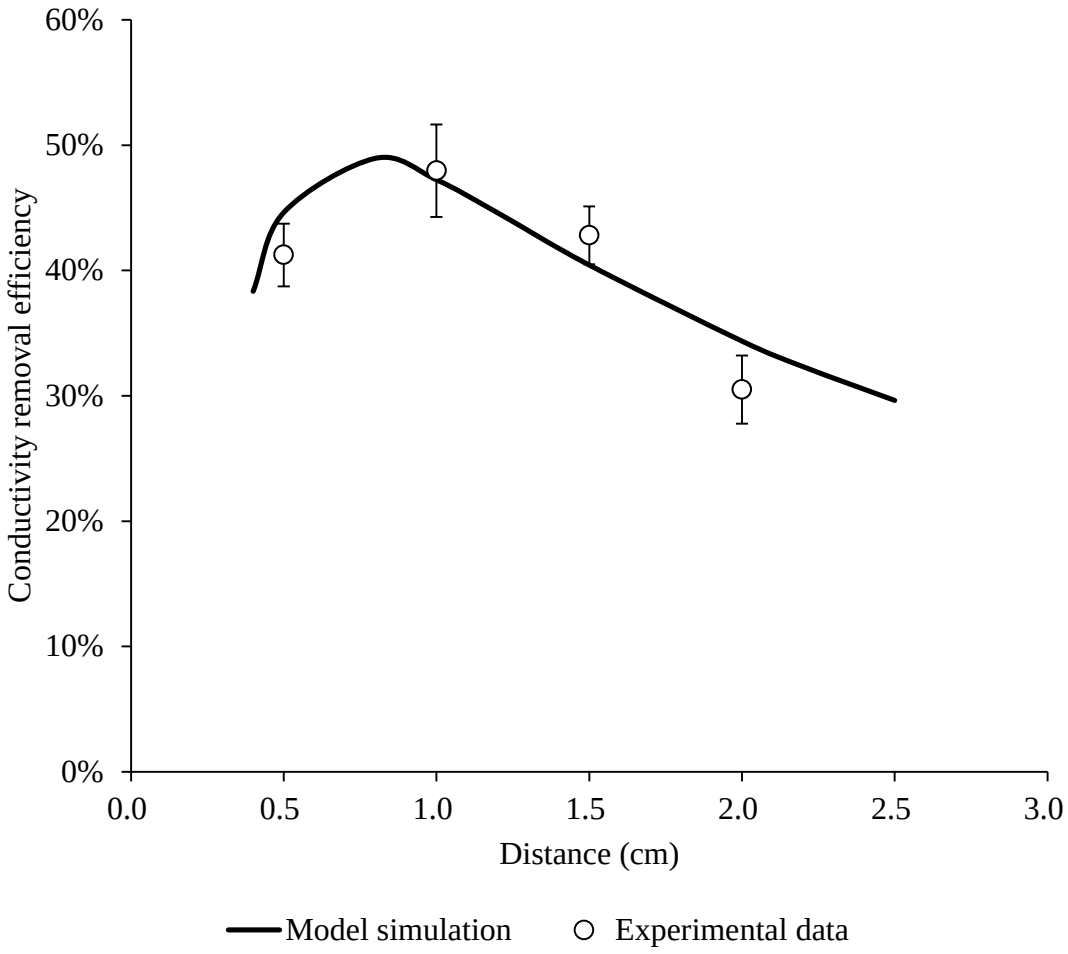
60%
50%
40%
30%
20%
10%
0%
Conductivity removal efficiency
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Distance (cm)
Model simulation
Experimental data

Fig. 7b

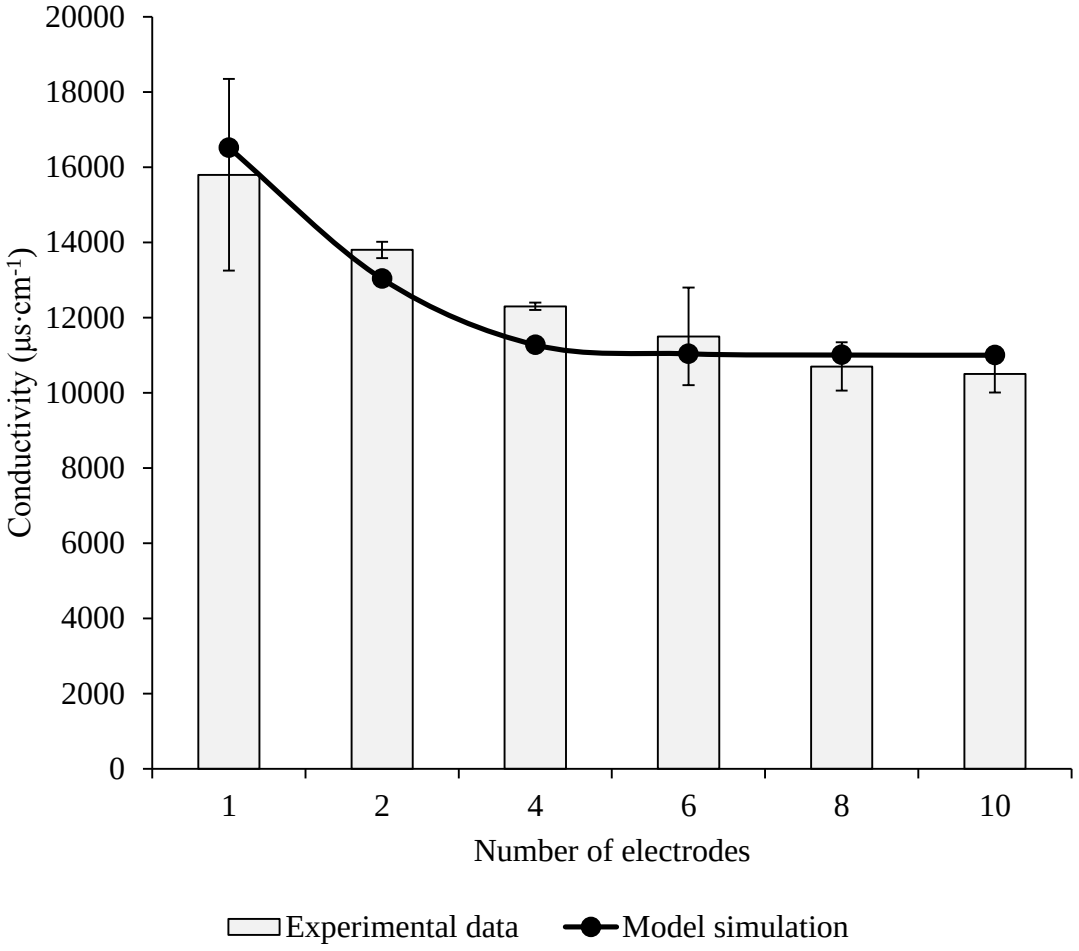
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
Conductivity (μs·cm-1)
1
2
4
6
8
10
Number of electrodes
Experimental data
Model simulation

Fig. 8

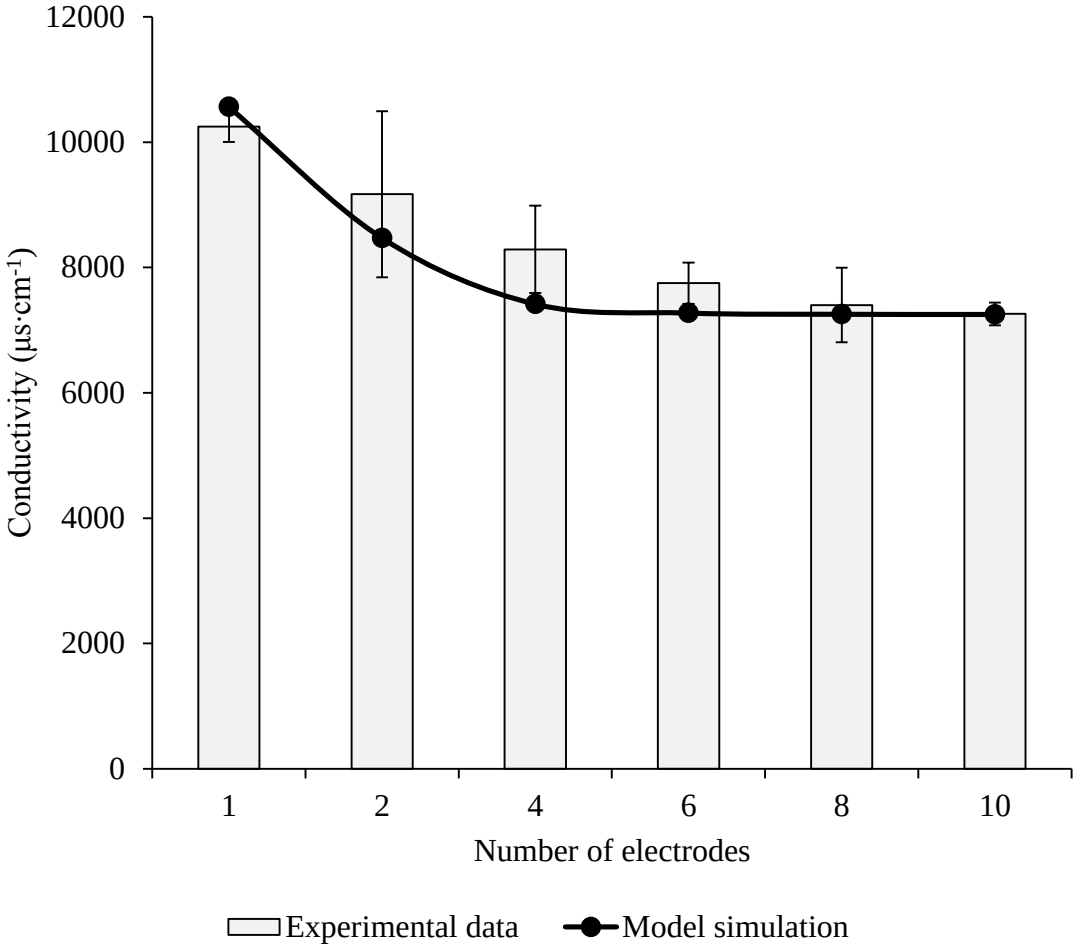
12000
10000
8000
6000
4000
2000
0
Conductivity (μs·cm-1)
1
2
4
6
8
10
Number of electrodes
Experimental data
Model simulation

Fig. 9

Supplementary Material

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