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Flow-through electrosorption process for removal of 2,4-D pesticide from aqueous solutions onto activated carbon cloth fixed-bed electrodes

Edip Bayram, Çağdaş Kızıl and Erol Ayrancı

ABSTRACT

Wastewater treatment systems have great importance in dealing with increasing environmental pollution. In this study, a specially designed and constructed flow-through electrochemical cell was used to enhance the electrosorptive removal capacity of 2,4-Dichlorofenoxyacetic acid (2,4-D) pesticide from aqueous solutions onto high area activated carbon cloth (ACC) fixed-bed electrodes. The change in concentration of 2,4-D during the electrosorption process was followed by an online UV–Vis spectrophotometric system. Effects of operational parameters such as volumetric flow rate, applied potential and existence of Na_2SO_4 salt on electrosorption of 2,4-D were examined. Optimum values were found to be 10 mL·min^{-1} for volumetric flow rate and +900 mV for the applied potential to polarize ACC. Maximum capacity of 729 mg·gACC^{-1} has been achieved for removal of 2,4-D pesticides.

Key words | 2, 4-D pesticide, activated carbon cloth, electrosorption, flow-through, water treatment

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INTRODUCTION

Releasing various organic and inorganic pollutants into the ecosystems has been exponentially increased during the past several decades due to growing social civilization, industrialization and technology (Ghodbane *et al.* 2008; Michalski & Ficek 2016). Dyes, pesticides and acids containing charged or ionizable groups in their molecules are considered as important water pollutants. Separation techniques such as precipitation, adsorption and filtration or destructive techniques including ozonation and electrochemical reactions are extensively used in removal of pollutants from wastewaters (Sun *et al.* 2016). Adsorption is probably the most widely used one among these. However, the adsorption process has major drawbacks, such as slow removal rate originating from the diffusion limitations and short lifetime of most adsorbents due to low regeneration capacities (Niu & Conway 2003; Bayram & Ayranci 2010). On the other hand, limitations of adsorption can be eliminated by applying certain potential or current to high surface area electrodes. This potential-induced adsorption is generally termed as electrosorption which appears to be a promising technique for the removal of pollutants more effectively, especially by utilizing high specific surface area carbon electrodes (Ania & Béguin 2007). The basic principle in electrosorption is that the electrical double layer at the electrode surface is charged and/or discharged. No Faradaic process takes place in electrosorption. Another important advantage of electrosorption over usual adsorption process is the possibility of in-situ regeneration of the adsorbent without consuming much energy (Duan *et al.* 2015). Besides, performance of electrosorption process can also be affected by the characteristics and forms of electroadsorbent used in electrosorption. The diffusion limitation can be minimized with the use of electrosorbents having quasi-three-dimensional structure such as cloth, foam, felt and some other porous materials (Peng *et al.* 2013). This increases the overall rate of adsorption/electrosorption process. Activated carbon cloth (ACC), one of such quasi-three-dimensional adsorbent materials, has the additional advantage of mechanical integrity so that it can be designed as a stable electrode to carry out electrosorption processes for the removal of pollutants from wastewaters (Ania & Béguin 2007; Bayram & Ayranci 2012; Gineys *et al.* 2017).

The type of reactor used for treatment of wastewaters is another important factor that affects the removal efficiency. Batch type reactors are often used for laboratory studies but are less convenient for practical applications. Flow-through

doi: 10.2166/wst.2017.598

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fixed-bed reactor systems improve the mass transport of pollutants which are usually present at low concentrations in water streams. Additionally, fixed-bed columns are commonly used in industry due to their simple operation. Ban *et al.* (1998) studied the treatment of industrial wastewaters with the application of electrosorption/electrodesorption process using granular activated carbon pack-bed electrodes. In their study, electrosorption isotherms of aromatic organic compounds were derived under various conditions and compared with the ones derived from flow-through column systems. Two flow-through electrochemical cell designs were proposed by Ban *et al.* (1998). They found carbon fibers to be more effective than granular activated carbons as fixed-bed electrodes in removal of aromatic organic molecules. Woodard *et al.* (1986) reported a study about the use of flow-through system with carbon fiber electrodes for electrosorption of low molecular weight organic molecules, amino acids, a peptide and a protein.

In the present study, a specially designed flow-through electrochemical cell was used to enhance removal efficiency of organic molecules from aqueous solutions onto high specific surface area ACC fixed-bed electrodes by electrosorption. 2,4-Dichlorofenoxyacetic acid pesticide (2,4-D) was selected as the model pollutant molecule due to its dense usage in agriculture. 2,4-D concentration was followed by on-line UV-Vis spectrophotometric method. Operational parameters such as volumetric flow rate, applied potential and the presence of Na_2SO_4 were investigated for their effects on electrosorption.

The originality of the present work arises mainly from the use of specially designed flow-through electrochemical cell, inclusion of single piece ACC as fixed-bed electrode in this cell, the overall small size of the flow-through electrochemical cell and finally monitoring the pollutant concentration by online spectrophotometric method.

EXPERIMENTAL SECTION

Materials

The ACC material used as fixed-bed electrode was purchased from Spectra Corp. (MA, USA) with a code of Spectracarb 2225. The ACC was washed repeatedly with warm deionized water before it was used in the electrosorption process. Washing procedure, physicochemical and electrochemical properties of ACC were described previously (Bayram & Ayranci 2010). 2,4-D and Na_2SO_4 were purchased from Aldrich with a mass fractional purity of at least 0.99 and used without further purification. Ultra pure water was produced from 18.2 MΩ Milli-Q UV (Millipore) water system.

Description of flow-through electrolytic cell

Electrosorption experiments were carried out by using the specially designed flow-through electrolytic cell which is schematically shown in Figure 1. The main body of the electrolytic cell was constructed from Teflon material (I). The flow channel drilled through the Teflon body has an inner diameter of 1.5 cm. There is a stainless steel mesh half-way through the channel acting as base for fixed-bed electrode and providing a homogeneous potential distribution upon establishing the electrical contact with ACC. A threaded Teflon plug (II) having a hole of 0.8 cm was screwed through the flow channel. In this way, two pieces of circular ACC are pressed between the plug and stainless steel mesh. The total mass of ACC pieces was 40 ± 0.2 mg. The pressed ACC in contact with a Pt wire acted as the fixed-bed working electrode (WE). The reference electrode (RE) was a Ag/AgCl electrode from bioanalytical systems (BAS, MF2030, USA). It was introduced into the channel through a hole in a perpendicular position. An O-ring prevented any leakage from the hole of RE. A piece of coiled Pt wire was fitted to outlet part (III) of the cell as a counter electrode (CE).

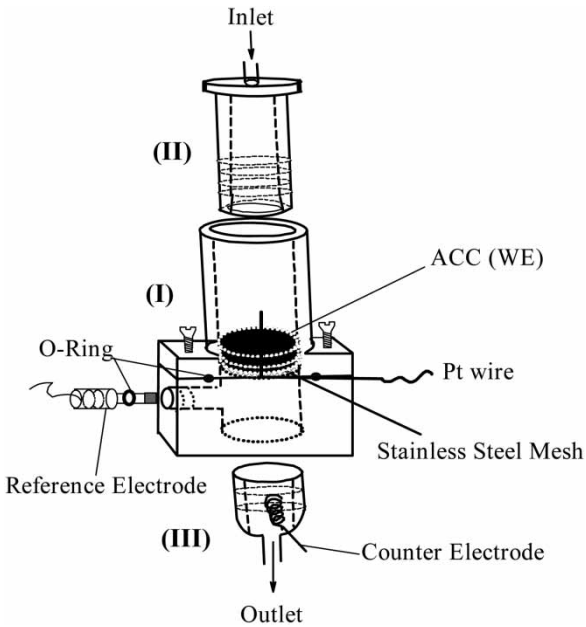


Figure 1 | Scheme of flow-through electrolytic cell. Teflon body (I), threaded Teflon plug (II) and outlet part (III).

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Procedure for the on-line spectrophotometric analysis of electrosorption

The diagram in Figure 2 illustrates the layout for the continuous flow electrosorption process with an on-line spectrophotometric analysis system.

Besides the specially designed flow-through electrolytic cell, the system contains a UV-Vis spectrophotometer (Varian Cary 100) with a quartz flow cell (Helma), a peristaltic pump and a potentiostat/galvanostat (Gamry Instruments Inc.). The adsorbate solution is placed in a beaker over a magnetic stirrer in this system and it flows first to the electrosorption cell then to the quartz flow cell of the spectrophotometer through a silicon tubing (0.2 cm i.d.) with the help of the peristaltic pump. Flow-through electrolytic cell was operated in up-flow plug mode. ACC fixed bed electrode was provided by the potentiostat/galvanostat through the connection of three electrodes of the electrolytic cell. A flow rate of 10 mL·min^{-1} allowed the solution to travel in 1.5 s from original beaker to the electrolytic cell and in about 3 s to the spectrophotometer cell. The total volumes were about 2 mL for tubings and 4 mL for the flow channel. The temperature for all experiments was 25 °C. On-line absorbance measurements, leading to concentration determinations, were carried out at the selected wavelength of 280 nm for 2,4-D. It is to be noted that a control experiment without any 2,4-D was also carried out and no signal was received from the spectrophotometer originating from ACC or medium.

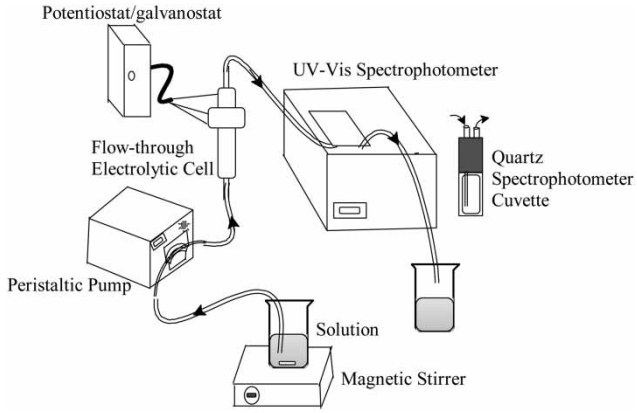


Figure 2 | Layout for continuous flow electrosorption process.

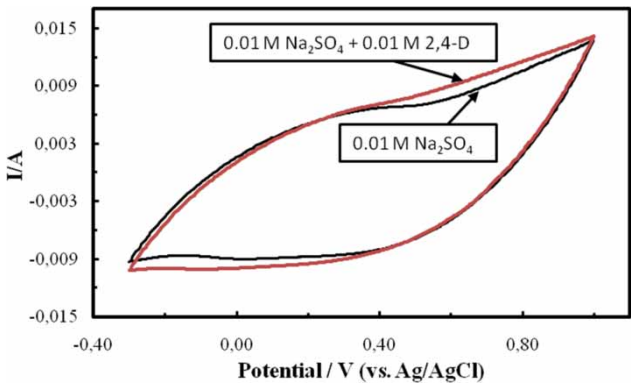


Figure 3 | Cyclic voltammograms of 0.01 M Na_2SO_4 with and without 0.01 M 2,4-D at a potential scan rate of 5 mVs^{-1}.

RESULTS AND DISCUSSION

Electrosorptive behavior of 2,4-D

Electrosorption is a non-Faradaic process. Thus, it is important to check the electrochemical stability of an adsorbate within the polarization potential range studied. In order to determine the electrochemical stability window and avoid the electrochemical by-products of 2,4-D, cyclic voltammetric studies were carried out in aqueous solutions of 0.01 M Na_2SO_4 with and without 0.01 M 2,4-D at a potential scan rate of 5 mVs^{-1} using Ag/AgCl as RE, 20 ± 1 mg ACC as WE and a Pt wire as CE. Voltammograms are shown in Figure 3.

The absence of any noticeable change in the voltammograms upon inclusion of 0.01 M 2,4-D into the solution indicates the electrochemical stability of the 2,4-D in the potential range from −0.35 V to 0.90 V. Enlargement in voltammogram upon inclusion of 0.01 M 2,4-D shows the capacitative behavior of ACC originating from the electrosorption/desorption of 2,4-D.

Batch operation mode is more convenient for observing the adsorption/electrosorption behaviors of an adsorbate. In this study, electrosorption of 20 mL 2.1×10^{-4} M 2,4-D in 0.01 M Na_2SO_4 solution onto 20 ± 1 mg ACC was carried out using a specially designed V-shaped electrolytic cell with in-situ UV-vis concentration measurements as described in our previous studies (Ayranci & Bayram 2005; Bayram & Ayranci 2010). First, adsorption data were recorded on open circuit (OC) condition until equilibrium (first 85 min), followed by electrosorption under +900 mV polarization for the next 50 min. Results are shown in Figure 4.

It is seen that positive polarization of ACC by applying +900 mV potential causes an increase in adsorption, deduced from the further decrease in concentration of 2,4-D after OC adsorption. In the case of OC adsorption, solution is acidic (pH 4.28) due to the partial ionization of

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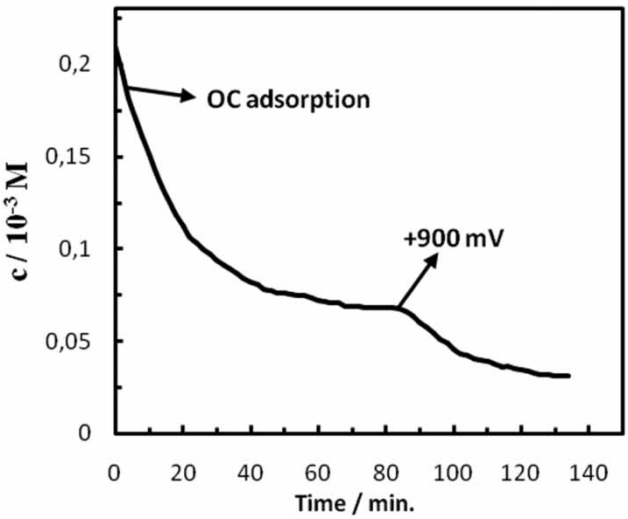


Figure 4 | OC adsorption and electrosorption behavior of 2,4-D at +900 mV polarization in 0,01 M Na_2SO_4 solution onto 20 ± 1 mg ACC.

2,4-D. This pH is smaller than pH_{PZC} of ACC and causes the carbon surface to be positively charged (Bayram & Ayranci 2010). On the other hand, analytical calculations based on pKa (2.77) of 2,4-D showed that at an initial concentration of 2.0×10^{-4} M and natural pH of 4.65 in 0.01 M Na_2SO_4 solution, 2,4-D is found predominantly in anionic form (98% anionic, 2% neutral). So, the electrostatic attractions between these anionic 2,4-D species and positively charged surface as well as the dispersion interactions between 2,4-D molecules and ACC surface are possibly responsible from the observed OC adsorption behavior. After polarization, positive charge density of ACC surface is further increased, resulting in rearrangement of water dipoles and strength of their electrostatic adsorption (Niu & Conway 2003). So, electrostatic interaction between anionic form of 2,4-D and ACC surface is mainly responsible from the electrosorptive, as well as OC adsorptive behavior.

Potential dependence of electrosorption

Investigation of the influence of applied potential on the electrosorption rate and capacity is crucial for the accurate design and modeling of electrosorption processes. For this purpose, a series of experiments on electrosorption kinetics were carried out until equilibrium by applying varying potentials at room temperature. The initial 2,4-D concentration of about 2.0×10^{-4} M in 0.01 M Na_2SO_4 solution, ACC electrode mass of 40.0 ± 0.2 mg and volumetric flow rate of 10 mL·min^{-1} were kept constant in this series in order to see the effect of mainly the applied potential. The effect of applied potential on the rate and extent of adsorption can be seen from Figure 5. OC adsorption data was also included in this figure for comparison.

It can be clearly seen that polarization causes dramatic changes in the rate and extent of adsorption. In electrosorption process, the charge of ACC is determined by the direction and magnitude of applied potential. The positive charge loaded onto ACC is expected to be the highest at +900 mV and the influence of applied potential on electrosorption is observed to be the highest at this potential from the *breakthrough* curves in Figure 5.

In some cases, electrochemical by-products may be more toxic than the original molecule. Since electrosorption is a non-Faradaic process, it is important to confirm the structural integrity of 2,4-D electrosorbed onto ACC fixed bed electrodes. For this purpose, an electrodesorption experiment, described in our previous study (Bayram & Ayranci 2012), has been performed in cyclic mode using the ACC saturated with 2,4-D at +900 mV polarization as fixed-bed electrode. During electrodesorption process, −900 mV potential was applied to the saturated ACC electrodes while fresh 0.01 M Na_2SO_4 solution was cycling with volumetric flow rate of 10 mL·min^{-1} in the system and scanning-kinetic spectra were recorded in 2 min intervals. Results are shown in Figure 6. The inset in this figure represents the concentration-time profile by converting the absorbance data to concentration using the calibration relation at 230 nm.

Absence of observable shift in absorbance bands clearly confirms the structural integrity of 2,4-D and absence of undesired electrochemical reactions.

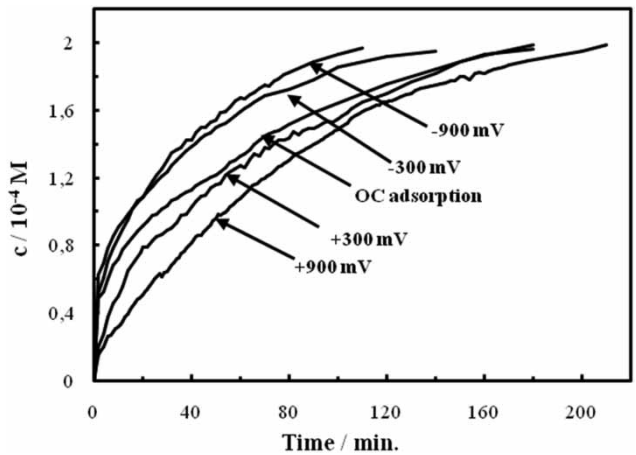


Figure 5 | *Breakthrough* curves of 2.0×10^{-4} M 2,4-D in 0.01 M Na_2SO_4 supporting electrolyte at different applied potentials obtained by 40.0 ± 0.2 mg ACC packed bed electrodes. Volumetric flow rate =10 mL·min^{-1}.

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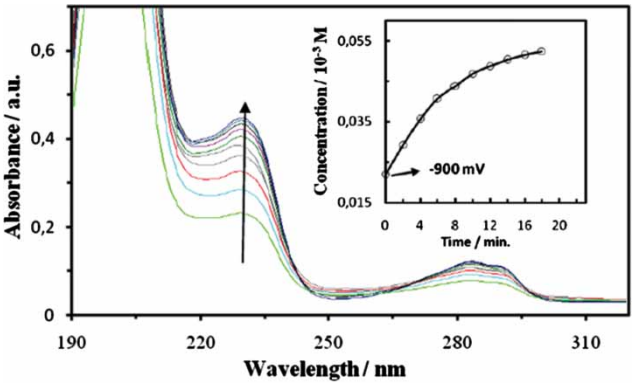


Figure 6 | Scanning-kinetic spectra for electrodesorption process of 2,4-D at −900 mV polarization. Inset is the concentration-time plot at 230 nm (see text for details).

In a dynamic system, concentration-time profiles are generally known as *breakthrough* curves and are used for determining the capacity of the adsorbent and adsorbate concentrations in a water stream at any time. For industrial applications, adsorption columns are used in the process up to its saturation time, t_s, at which the effluent concentration reaches the feed concentration. Parameter t_s is linked by a linear relationship to the saturation volume (V_s), which is the volume treated during the process up to t_s. The interpretation of the operation and performance of the fixed-bed may be evaluated by characteristic parameters determined from the breakthrough curves and graphical integration of Equation (1)

$$X_s = \frac{\int_0^{Vs} (C_0 - C)dv}{m} \quad (1)$$

where c_0 is the initial concentration of solute and c is the concentration at any time, m is the mass of the ACC fixed bed electrode. Thus, the adsorption/electrosorption capacities at the saturation point (X_s) can be used for interpretation of the performance of the electrosorption process and ACC fixed-bed electrodes. X_s may also be defined as the ratio of the quantity of the solute adsorbed at the saturation point to the mass of ACC and can be used in quantifying the results. The calculated parameters for OC adsorption and electrosorption of 2,4-D onto ACC fixed-bed electrodes are given in Table 1.

Based on the X_S values, removal capacity of ACC fixed bed electrode is increased from 409 mg·gACC^{-1} under OC conditions to 729 mg·gACC^{-1} under polarization conditions at +900 mV, corresponding to almost 78% enhancement in capacity for 2,4-D. Conversely, negative polarization at −900 mV caused a dramatic decrease in capacity of ACC, compared to that under OC, proving the existence of lesser electrostatic attractions between charged ACC and ionized form of the 2,4-D pesticide.

Table 1 | Parameters calculated for OC adsorption and electrosorption of 2,4-D onto ACC fix-bed electrodes

Polarization/ mV	X_S / mg·gACC^{-1}	V_S / L	t_S / min.
−900	291	1,1	110
−300	331	1,4	140
OC adsorption	409	1,8	180
+300	587	1,8	180
+900	729	2,1	210

Capacity for OC adsorption conducted in batch mode (Figure 4) can be calculated from the initial and equilibrium concentrations, molecular weight of 221.04 g·mol^{-1} for 2,4-D and mass of ACC used in batch mode. It can then be used as a rough base for comparing the batch and flow-through modes. The calculated capacity for batch mode is 32 mg·gACC^{-1} which is much smaller than that of the OC adsorption value of flow-through mode (Table 1). The huge difference between the two modes can be attributed to the improved mass transfer of 2,4-D in flow-through mode and to the quasi-three-dimensional structure of ACC electrode. Comparing the results with the literature studies performed on the removal of 2,4-D from aqueous solutions shows the improvements brought out with the present study. In the study of Deng *et al.* (2009) capacity for 2,4-D was calculated as 320 mg·g^{-1} using biomass. In another study, capacity of 238 mg·g^{-1} was obtained using activated carbons in a batch type reactor (Hameed *et al.* 2008). Recently, maximum removal capacity of 296 mg·g^{-1} was reported for adsorption of 2,4-D onto few layer graphene adsorbent in a batch type reactor (Kamaraj *et al.* 2017). The maximum capacity achieved in the present study is quite high compared to those reported in literature for removal of 2,4-D from aqueous solutions. This achievement can be attributed to the enhanced attraction of 2,4-D by the polarized ACC fixed-bed electrodes and improved mass transfer rate by the flow regime.

Influence of volumetric flow rate

Change in concentration of 2,4-D with time during the course of electrosorption at +900 mV polarization and at different volumetric flow rates is shown in Figure 7.

A huge decrease in removal (increase in residual concentration) is observed as volumetric flow rate is increased

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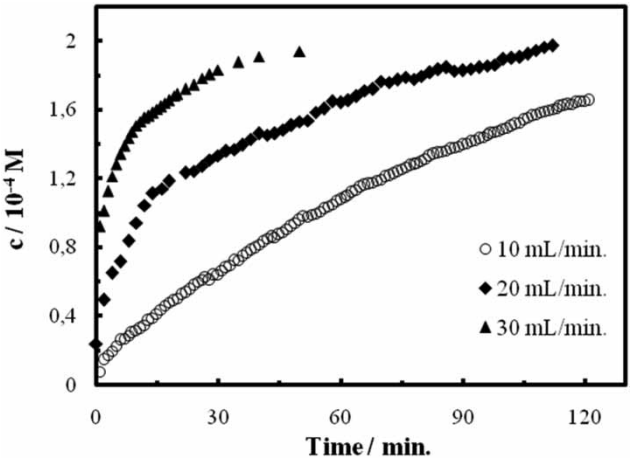


Figure 7 | Influence of volumetric flow rate on electrosorption of 2,4-D. $c_o = 2.0 \times 10^{-4}$ M, mass of ACC fixed-bed electrode: 40.0 ± 0.2 mg, applied potential: +900 mV.

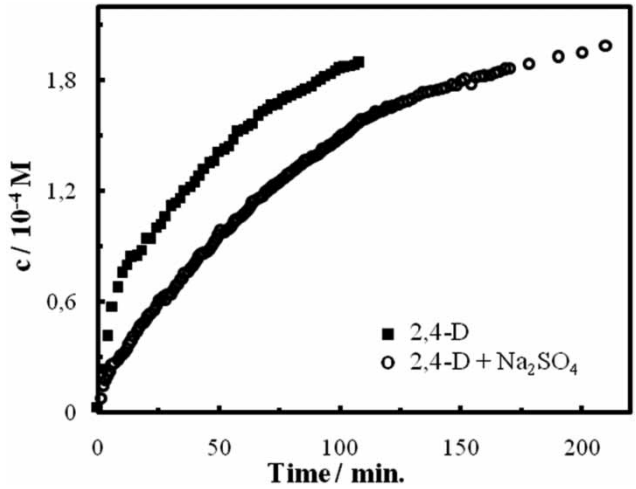


Figure 8 | Effect of presence of Na_2SO_4 on electrosorption of 2,4-D. $c_o = 2.0 \times 10^{-4}$ M, mass of ACC fixed-bed electrode: 40.0 ± 0.2 mg, applied potential: +900 mV.

from 10 to 30 mL·min^{-1}. The flow rate of 10 mL·min^{-1} seems to give the highest removal rate. At the highest studied flow rate of 30 mL·min^{-1} X_S value decreases by a factor of 8.6 (from 729 to 84 mg·gACC^{-1}) compared to the electrosorption at 10 mL·min^{-1}. It is known that the electrosorption is an electrical double layer process. In that respect, the observed decrease in removal capacity with increasing flow rate can be attributed to the to the slimming of the electrical double layer which is formed on ACC surface in solution by the increased flow regime.

Effect of Na_2SO_4 on electrosorption of 2,4-D

Industrial wastewaters usually contain different types of salts beside organic pollutants. In order to study the effect of an example electrochemically inert salt, Na_2SO_4, on electrosorption of 2,4-D, experiments have been performed at optimum conditions of +900 mV polarization and 10 mL·min^{-1} volumetric flow rate in 2.0×10^{-4} M 2,4-D solutions with and without 0.01 M Na_2SO_4. Results are shown in Figure 8.

It can visually be seen that the existence of Na_2SO_4 in aqueous solution of 2,4-D strongly affects the electrosorption of 2,4-D onto ACC fixed-bed electrodes. The increased capacity observed with Na_2SO_4 can be ascribed to a salting-out effect (Conway 1981). The salting-out effect originates from association of water molecules with the ions of Na_2SO_4 leaving less free water available for dissolution of organic species. The contribution of Na_2SO_4 to the formation of electrical double layer formed on ACC also enhances the electrosorption through lengthening the charge field effect.

CONCLUSIONS

A flow-through electrosorption process was successfully applied for the removal of 2,4-D from aqueous solutions using a specially designed electrolytic cell in which an ACC fixed-bed electrode was polarized. Electrosorptive behavior of 2,4-D was correlated with the electrostatic interactions and dispersion forces between polarized ACC and 2,4-D species in solution. Improvements in electrosorption capacity were succeeded by adjusting volumetric flow rate and applied potentials. Maximum removal capacity of 729 mg·gACC^{-1} for 2,4-D was achieved. Similar high removal capacities are expected for other ionizable, preferably aromatic, pesticide molecules which will lead the application of the present flow-through electrosorption process to real wastewaters.

ACKNOWLEDGEMENTS

Author thanks to the Scientific Research Projects Unit of Akdeniz University for support of this work with project number of 2012.01.0115.009.

REFERENCES

Ania, C. O. & Béguin, F. 2007 Mechanism of adsorption and electrosorption of bentazone on activated carbon cloth in aqueous solutions. *Water Research* **41**, 3372–3380.

Ayranci, E. & Bayram, E. 2005 Adsorption of phthalic acid and its esters onto high-area activated carbon-cloth studied by in situ

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UV-spectroscopy. *Journal of Hazardous Materials B* **122**, 147–153.

Ban, A., Schaefer, A. & Wendt, H. 1998 Fundamentals of electrosorption on activated carbon for wastewater treatment of industrial effluents. *Journal of Applied Electrochemistry* **28**, 227–236.

Bayram, E. & Ayranci, E. 2010 Investigation of changes in properties of activated carbon cloth upon polarization and of electrosorption of the dye basic blue-7. *Carbon* **48**, 1718–1730.

Bayram, E. & Ayranci, E. 2012 Structural effects on electrosorptive behavior of aromatic organic acids from aqueous solutions onto activated carbon cloth electrode of a flow through electrolytic cell. *Journal of Electroanalytical Chemistry* **683**, 14–20.

Conway, B. E. 1981 *Ionic Hydration in Chemistry and Biophysics*. Elsevier, Amsterdam, The Netherlands.

Deng, S., Ma, R., Yu, Q., Huang, J. & Yu, G. 2009 Enhanced removal of pentachlorophenol and 2,4-D from aqueous solution by an aminated biosorbent. *Journal of Hazardous Materials* **165**, 408–414.

Duan, F., Li, Y., Cao, H., Wang, Y., Crittenden, J. C. & Zhang, Y. 2015 Activated carbon electrodes: electrochemical oxidation coupled with desalination for wastewater treatment. *Chemosphere* **125**, 205–211.

Ghodbane, I., Nouri, L., Hamdaoui, O. & Chiha, M. 2008 Kinetic and equilibrium study for the sorption of cadmium(II) ions from aqueous phase by eucalyptus bark. *Journal of Hazardous Materials* **152**, 148–158.

Gineys, M., Benoit, R., Cohaut, N., Béguin, F. & Delpeux-Ouldriane, S. 2017 Behavior of activated carbon cloths used as electrode in electrochemical processes. *Chemical Engineering Journal* **310**, 1–12.

Hameed, B. H., Salman, J. M. & Ahmad, A. L. 2008 Adsorption isotherm and kinetic modeling of 2,4-D pesticide on activated carbon derived from date stones. *Journal of Hazardous Materials* **163**, 121–126.

Kamaraj, R., Pandiarajan, A., Gandhi, M. R., Shibayama, A. & Vasudevan, S. 2017 Eco-friendly and easily prepared graphene nanosheets for safe drinking water: removal of chlorophenoxyacetic acid herbicides. *Chemistry Select* **2**, 342–355.

Michalski, R. & Ficek, A. 2016 Environmental pollution by chemical substances used in the shale gas extraction – a review. *Desalination and Water Treatment* **57**, 1336–1343.

Niu, J. J. & Conway, B. E. 2003 Adsorption of organics onto an high-area C-cloth electrode from organic solvents and organic solvent/water mixtures. *Journal of Electroanalytical Chemistry* **546**, 59–72.

Peng, Z., Zhanga, D., Yan, T., Zhang, J. & Shi, L. 2013 Three-dimensional micro/mesoporous carbon composites with carbon nanotube networks for capacitive deionization. *Applied Surface Science* **282**, 965–973.

Sun, X. F., Guo, B. B., He, L., Xia, P. F. & Wang, S. G. 2016 Electrically accelerated removal of organic pollutants by a three-dimensional graphene aerogel. *AIChE Journal* **62**, 2154–2162.

Woodard, F. E., McMackins, D. E. & Jansson, R. E. W. 1986 Electrosorption of organics on three dimensional carbon fiber electrode. *Journal of Electroanalytical Chemistry* **214**, 303–330.

First received 1 June 2017; accepted in revised form 13 November 2017. Available online 27 November 2017

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