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# Electrosoption of Aromatic Organic Acids From Aqueous Solutions Onto Granular Activated Carbon Electrodes for Water Purification

## Aromatik Organik Asitlerin Sulu Çözeltilerden Granüllü Aktiflenmiş Karbon Elektrotlar Üzerine Elektrosorpsiyonu

Research Article

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## ABSTRACT

Waste water treatment systems have great importance as a result of the increasing population and environmental pollution. In this study, electrosorptive removal of benzoic acid (BA) and nicotinic acid (NA) from aqueous solutions onto activated carbon electrodes (ACEs) were studied. ACEs were fabricated from the industrially available granular activated carbon and polyethylene as binder. During the electrosorption process, the change in concentration of organic molecules was followed by using an online UV-Vis spectrophotometric system. Effects of operational parameters such as applied potential and volumetric flow rate on electrosorption of BA were examined. Optimum parameters for the process were found to be 60 mL.min$^{-1}$ for volumetric flow rate and 1.5 V for polarization of ACEs. Electrosorption of binary mixtures of BA and NA was also studied. it can be concluded that BA and NA can be effectively removed by electrosorption from aqueous solutions using activated carbon electrodes.

**Key Words**
Activated carbon electrode, electrosorption, aromatic organic acids, water treatment.

## ÖZET

Su arıtma sistemleri, artan insan nüfusu ve çevre kirliliği sonucunda oldukça önemli hale gelmiştir. Bu çalışmada, benzoik asit (BA) ve nikotinik asitin (NA) sulu çözeltilerinden, aktiflenmiş karbon elektrotlar (ACEs) üzerine elektrosorpsiyon yolu ile uzaklaştırılmaları incelenmiştir. ACEs, endüstriyel olarak elde edilebilen granüllü aktiflenmiş karbon ve polietilen bağlayıcı kullanılarak üretilmiştir. Elektrosorpsiyon sırasında organik moleküllerin derişimlerinde oluşan değişimler, online UV-Vis spektrofotometrik sistem kullanılarak takip edilmiştir. BA nın elektrosorsiyonu üzerine uygulanan potansiyel ve çözelti akış hızı gibi sistem parametrelerinin etkileri incelenmiştir. Optimum proses parametrelerinin, çözelti akış hızı için 60 mL.dk$^{-1}$ ve ACEs polarizasyonu için 1.5 V olduğu bulunmuştur. BA ve NA içeren ikili karışımların elektrosorpsiyon davranışları da incelenmiştir. BA ve NA nın aktiflenmiş karbon elektrotlar kullanılarak sulu çözeltilerinden elektrosorpsiyon ile etkili bir şekilde uzaklaştırılabileceği sonucuna varılmıştır.

**Anahtar Kelimeler**
Aktiflenmiş karbon elektrot, elektrosorpsiyon, aromatik organik asitler, su arıtma.

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## INTRODUCTION

Throughout the past several decades, an increasing trend in the extensive emission of various organic and inorganic pollutants into the ecosystems has been witnessed [1], underlying the exponential growth rate of population and social civilization, and development of industry and technology as its key drivers [2]. Charged and/or ionizable aromatic compounds including dyes, acids and pesticides constitute an important group of substances responsible from water pollution. Some of the techniques used in purification treatment of waste waters containing these pollutants are flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques and ozonation [3]. Chemical degradation by oxidative agents such as chlorine constitutes one of the most relevant and effective methods, but it may produce some toxic secondary products, such as organochlorine compounds [4]. Although, biodegradation process is cheaper than other methods, the recalcitrant nature of aromatic organic molecules, together with their toxicity to microorganisms, makes aerobic treatment difficult [5]. Adsorption onto activated carbons is among the most utilized techniques. Its major drawbacks are short lifetime of activated carbons due to low regeneration capacities and slow speed of adsorption process originating from the diffusion limitations [6,7].

On the other hand electrosorption, which is generally defined as potential-induced adsorption of molecules on the surface of charged electrodes, is a promising technology for faster and more effective removal of pollutants from waste waters especially with the use of high specific-area carbon electrodes [8,9]. The essence of electrosorption is charging and discharging the electrical double layer at the surface of electrodes by applying potential or current. In this respect, electrosorption is distinguished from conventional electrochemical or Faradaic processes and offers some advantages such as water purification with high removal efficiency and enhanced adsorption rates of pollutants, and in-situ regeneration of adsorbent with less energy consumption compared with the thermal processes [7]. Besides, the reversibility of electrosorption plays a promising role in its practical industrial applications such as solvent recycle and the enrichment of valuable substances. Due to such advantages electrosorptive removal of organic impurities is effective, simple, and economic as compared with more commonly used direct electrolysis and other methods.

Flow-through fixed-bed reactor systems have been described which provide improved mass-transport of pollutant impurities that are often present at low concentrations which would otherwise lead to low current-density, diffusion-control of the electrochemical decontamination processes [10]. Although batch laboratory electrosorption studies are known to provide useful information toward the application of the removal of specific waste constituents, continuous column studies of electrosorption provide more practical applications in wastewater treatment. Batch reactors are easy to use in the laboratory study, but less convenient for industrial applications. However, fixed-bed systems are widely used in various chemical industries because of their simple operation.

In the present study a specially designed and constructed flow-through electrochemical cell was used to improve the efficiency of electrosorptive removal of organic molecules from aqueous solutions onto activated carbon electrodes (ACEs). Benzoic acid (BA) and nicotinic acid (NA) were used as model pollutants. The change in concentration of organic molecules with time was followed by using an online UV–Vis spectrophotometric method. The effect of operational parameters such as applied potential and volumetric flow rate on performance of electrosorption process was investigated. Competitive electrosorption of binary mixtures of organic molecules was also examined.

## MATERIALS AND METHOD

### Materials

Granular activated carbons, produced from coconut shells and polyethylene powders obtained from Sel corp. Turkey. Granular activated carbons was first washed with high purity water until reaching constant pH and ionic conductivity. Fabrication of ACEs was achieved using hot press method. Polyethylene powders was used as a binder in order to fabrication of activated carbon electrodes from granular activated carbon particles.

BA and NA were purchased from Aldrich. Their mass fraction purity was at least 0.99 and they were used after drying under vacuum without further purification. High purity water, used in all experiments, was from 18.2 MΩ Milli-Q UV (Millipore) water system.

### Resistivity and Iodine Number Measurements

The electronic resistance of the ACE were measured by placing the ACE (5 cm length x 5 cm width x 2 cm height) between two gold coated copper plates under 1.0 MPa pressure. The electrical current was measured in series with the power supply with a multimeter (Gamry, PCI4). Voltage was simultaneously measured with a second multimeter that was connected to the electrodes (Newport, HHM290/N). The measured current and voltage values were used to calculate resistance (Ω) based on Ohm's law and then resistivity of the ACE is determined by following equation of $r= RA/L$ , where r, R, A and L are the resistivity, resistance, area and thickness of the sample, respectively.

Iodine numbers of both granular activated carbon particles and ACEs was determined according to the ASTM-D4607-94 method. Briefly, a certain amount of grinded ACE boiled with 5% HCl for 30 s. Then, iodine solution was poured into mixture and treated for 5 min. After filtration, the filtrate was titrated with $Na_2SO_4$ and iodine number was calculated accordingly.

### Description of the System and the Procedure for the On-line Spectrophotometric Analysis

Flow-through electrolytic cell was constructed accordingly; ACEs were used both cathode and anode electrodes and located into a rectangular carved teflon mold. A perforated thin teflon plate was located between cathode and anode in order to avoid any short circuit. Carved teflon and electrodes were placed between Plexiglas covers and threaded. Solution inlet and outlet were placed on Plexiglas covers. Any leakage of solution was prevented by O-rings. Set-up of on-line spectrophotometric analysis system is illustrated in Figure 1.

The system consists of a UV–Vis spectro photometer (Varian Carry 100, UV–Vis spectrophotometer) equipped with a quartz flow cell (Hellma), a peristaltic pump, a solution vessel containing adsorbate solution on a magnetic stirrer, a potentiostat/galvanostat (Gamry Instruments Inc.) and the flow-through electrolytic cell specially designed for this work. The flow of the adsorbate solution from the beaker, first to the spectrophotometer cuvette, then to the electrosorption cell and then back to the beaker was achieved with the aid of a peristaltic pump through silicon tubing (0.2 cm i.d.). The beaker is equipped with a magnetic bar to assure good mixing. Flow-through electrolytic cell was positioned vertically and operated in up flow plug mode. Potentiostatic polarization of ACC pack bed electrode was achieved by the potentiostat/galvanostat connected to the electrolytic cell.

## RESULTS AND DISCUSSION

### Fabrication and Characterization of Activated Carbon Electrodes (ACEs)

Granular activated carbons was first washed with high purity water until reaching constant pH and dried in an vacuum oven for 24 h. Washed and dried granular activated carbon particles mixed with polyethylene powders, which was used as a binder, and heated to 150°C for 30 min. Fabrication of ACEs was achieved using hot press method under 15 Mpa pressure. Images, taken from different magnitudes of ACEs, are shown in Figure 2.

The monolith structure of ACE can clearly been seen from Figure 2. The activated carbon granules have successfully been adhered by using polyethylene powders as binder (x5 and x10 images of Figure 2). The electronic conductivity of a given electrode has crucial importance in electrochemical processes. The strong adhesion of activated carbon granules is resulted as a sufficient conductivity of ACE. The resistivity of ACEs were calculated as 0.8±0.23 Ω cm. This value is comparable with activated carbon fibers given in literature [11] and permits homogeneous

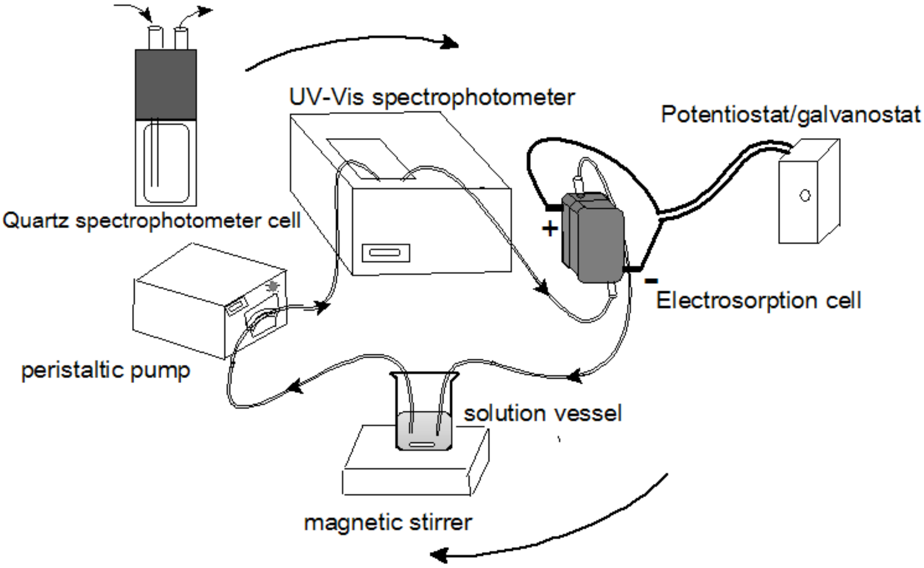

**Figure 1.** Experimental set-up of continuous flow electrosorption process.

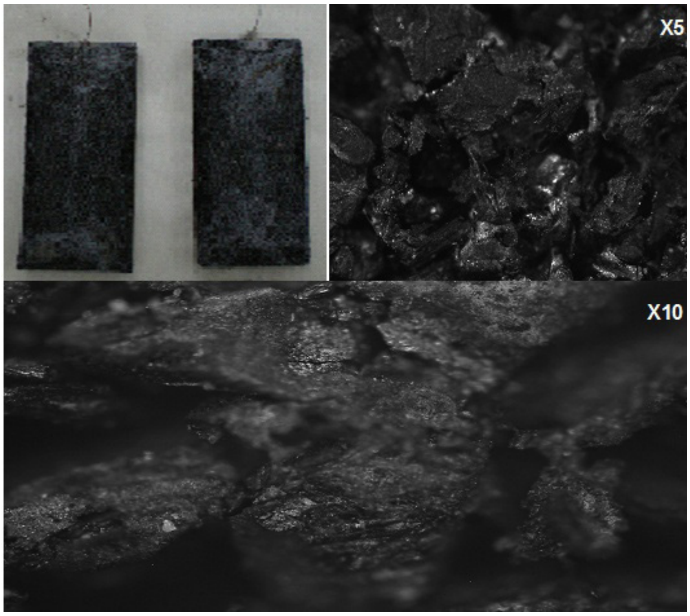

**Figure 2.** Images of activated carbon electrodes (ACEs).

distribution of applied potential or current on the ACEs for electrosorption process. Performance of electrosorption is also depends on the surface area of electrodes used. It is to be noted that, due to the grinding difficulties of polyethylene binders, homogenous sample could not be obtained to perform reliable $N_2$ adsorption measurements which requires samples in mg scale. Thus, Iodine number which can be roughly used to estimate the surface area of activated carbons at room temperature conditions [12], were determined for pristine granular activated carbon and ACE electrodes. Iodine numbers of pristine granular activated carbon particles and ACEs were found as 1062 mg/g and 862 mg/g, respectively. The decrease observed in iodine numbers is probably due to the blockage the entrance of pores by polyethylene particles. Although the decrease observed in iodine number, ACEs are still have acceptable surface area for electrosorption process [12].

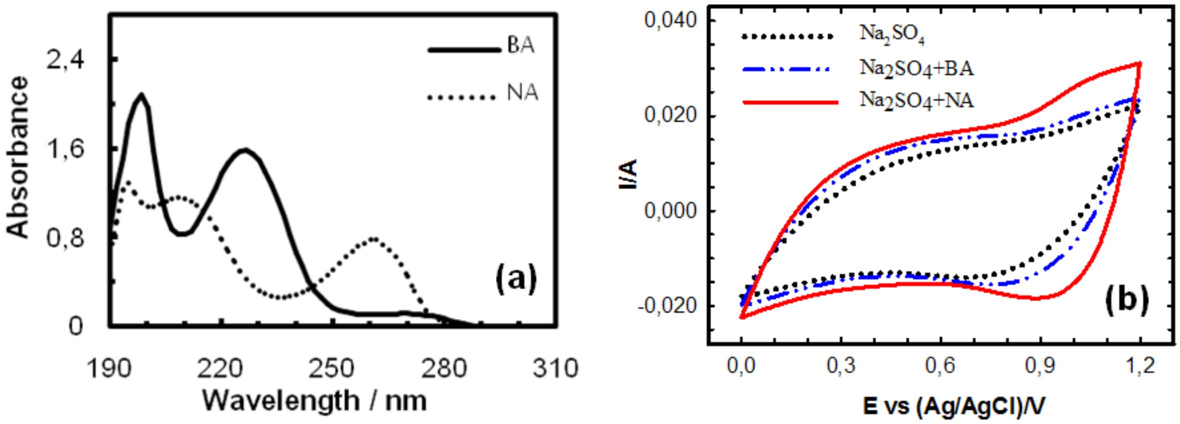

**Figure 3.** (a) UV spectra of benzoic acid (BA) and nicotinic acid (NA). (b) Cyclic voltammograms of 0.1 M $Na_2SO_4$, 0.01 M BA in 0.1 M $Na_2SO_4$ and 0.01 M NA in 0.1 M $Na_2SO_4$ at a potential sweep rate of 5 mV.s$^{-1}$.

### Optical absorption characteristics and eletrochemical properties of benzoic acid and nicotinic acid

UV spectra of the studied organic molecules are shown in Figure 3. Separate calibration experiments were run at the 226 nm for BA and 261 nm for NA required for concentration calculations. Absorbance vs. concentration data for each single compound was treated according to the Lambert–Beer law by linear regression analysis to determine $\varepsilon$ and the correlation coefficient, r. Correlation coefficients of all molecules were greater than 0.999 in the studied concentration range and wavelength.

Electrosorption is non-Faradaic process and it is important to avoid the Faradaic reactions originating from both ACE and adsorbate solution during electrosorption. In order to make sure that BA and NA are electroinactive in this potential range, cyclic voltammetric studies were carried out in a conventional three electrode electrochemical cell in 0.01 M $Na_2SO_4$ solution with and without BA and NA at a potential sweep rate of 5 mV.s$^{-1}$ using Ag/AgCl as RE, pelletized 1 g of ACE as WE and Pt plate as RE. Voltammograms given in Figure 2b show that there is no Faradaic reactions taking place with BA or NA within a wide potential range. Comparing with the voltammogram of $Na_2SO_4$ solution, the observed increases in voltammetric response starting from the 0.7 V to the 1.2 V in the voltammograms of BA and NA solutions are arise from the electrosorption of adsorbates as indicated previously [13].

### Potential Dependence of Electrosorption

In order to investigate the effect of electrochemical polarization on the adsorption rate, which is necessary for the accurate design and modeling of adsorption processes, a series of experiments on adsorption/electrosorption kinetics were carried out starting with the same initial BA concentration of about 1.0x10$^{-3}$ M, ACEs electrode mass of 32.0 ± 0.2 g and volumetric flow rate of 60 mL min$^{-1}$, but applying varying potentials at room temperature. The effect of applied potential on the rate and extent of adsorption can be seen from Figure 4.

A possible way for quantitative comparison of the extent of electrosorption can be made by calculating the percentage of removed BA at equilibrium, %$R_{eq}$, through the following equation;

$$\%R_{eq} = [(c_0 - c_e)/c_0]x100 \qquad (1)$$

where $C_0$ and $C_e$ are initial and equilibrium concentrations of BA in solution, respectively. Calculated %$R_{eq}$ values are 50.1% for 0.5 V, 87.0% for 1.5 V and 90.6% for 2.0 V polarization. It can be seen from Figure 4 and %$R_{eq}$ that

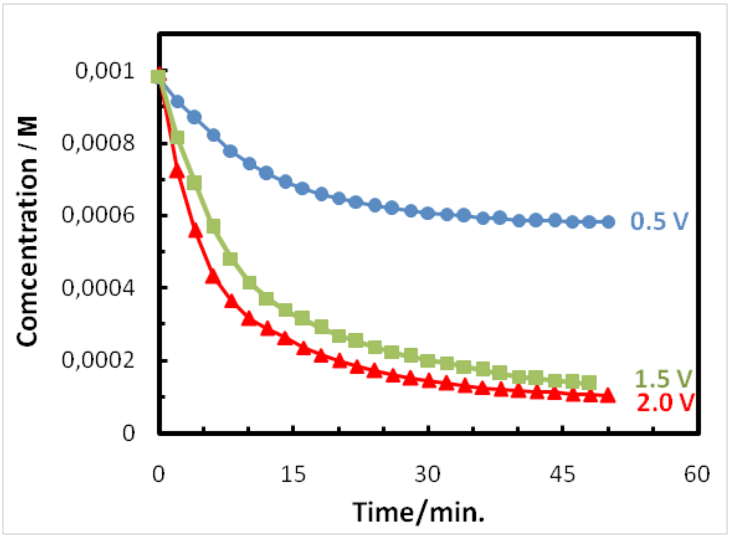

**Figure 4.** Effect of applied potential on electrosorption benzoic of acid (BA). $C_0$=1.0x10$^{-3}$ M, mass of ACEs electrode: 32.0 ± 0.2 g and volumetric flow rate: 60 mL.min$^{-1}$.

polarization causes a dramatic increase in the rate and extent of adsorption. Aromatic organic acids are weak acids and usually exits as a mixture of ionized species in aqueous solutions due to the dissociation. Electrostatic attraction between positively charged ACE and negatively charged benzoate ions and also dispersion forces are responsible from the observed enhancement in both rate and capacity. The fact that the electrosorptive removal rate depends on applied potential shows that the overall electrosorption process is not controlled by the diffusion of BA species from bulk solution onto ACE surface [7] as observed in batch mode electrosorption of basic dyes [6]. On the other hand, it is reported that positive polarization above ~1.3 V causes oxidation of activated carbons [14,15] thus decrease the conductivity and specific surface area of electrodes. Although a relatively slight enhancement was observed by applying 2.0 V compared to the 1.5 V applied potential, 1.5 V was chosen as an optimum polarization potential for other experiments in order to avoid the further oxidation of ACEs.

## Influence of Volumetric Flow Rate

Change in concentration of BA recorded during the course of electrosorption at 1.5 V polarization and at different flow-rates are shown in Figure 5.

Dramatic increase is obtained as volumetric flow-rate is increased from 20 to 60 mL min$^{-1}$. The flow-rate of 60 mL min$^{-1}$ seems to give the highest removal rate. At this flow rate, %R values changes by a factor of 1.25, compared to the electrosorption at 20 mL.min$^{-1}$. It is known that the adsorption rate is a combination of external and internal mass transfer rates [16]. In that respect, the obtained enhancements in removal efficiency can be attributed to the elimination of the limitation of external mass transfer rate by increased flow rate. On the other hand, electrical double layer which is formed on ACEs surface in solution, is responsible from the electrosorption. The decrease observed in the extent of adsorption by increasing the flow rate from 60 to 80 mL.min$^{-1}$ can be attributed to the slimming of the electrical double layer by the flow regime. It is to be noted that the optimized conditions for applied potential and flow rate are valid for the present system. Similar optimum conditions should be determined for other systems as they may change depending on the type of adsorbent and configuration of the electrolytic cell.

## Competitive Electrosorption

Aromatic organic acids are usually present in waste waters as a mixture of various organic pollutants. Thus, information to be obtained from the competitive electrosorption would be useful in environmental applications for organic pollutants. For this purpose, an electrosorption study on an equimolar mixture of BA and NA was carried out. The process was followed by in

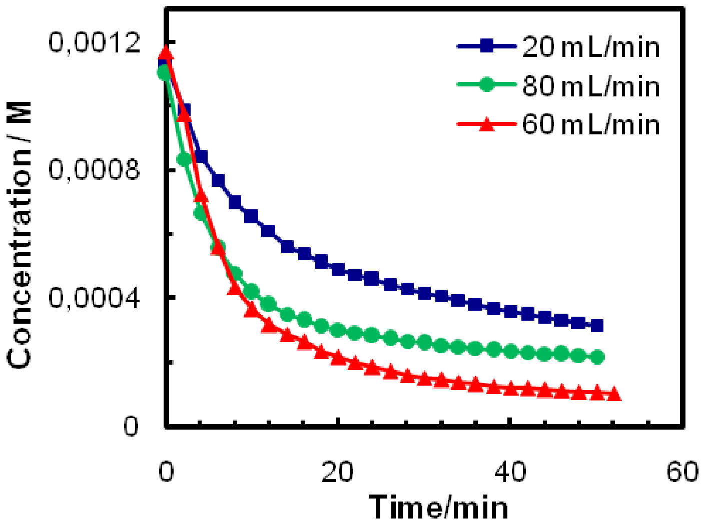

**Figure 5.** Effect of volumetric flow rate on electrosorption of benzoic acid (BA). $C_0$=1.0x10$^{-3}$ M, mass of ACEs electrode: 32.0 ± 0.2 g, applied potential: 1.5 V.

situ UV spectroscopy at scanning kinetic mode. Adsorption data were extracted at 226 nm for BA and 261 nm for NA from the scans. They were converted into concentrations from simultaneous solution of Equations (3) and (4) using 226 nm for $\lambda_1$ and 261 nm for $\lambda_2$ and the respective calibration relations (Section 3.2). The total absorbance at $\lambda_1$, $A_{total}^{\lambda 1}$ can be given by

$$A_{total}^{\lambda 1} = \varepsilon_1^{\lambda 1} c_1 + \varepsilon_2^{\lambda 1} c_2 \qquad (2)$$

and that $\lambda_{2,}$ $A_{total}^{\lambda 2}$, can be given by

$$A_{total}^{\lambda 2} = \varepsilon_1^{\lambda 1} c_1 + \varepsilon_2^{\lambda 1} c_2 \qquad (3)$$

where $\varepsilon$ is the molar absorptivity of the species at the wavelength indicated as a superscript, $c_1$ and $c_2$ are concentrations of NA and BA molecules, respectively. The light path does not appear in the above equations, since 1 cm cuvette was used in all measurements. Results are presented in Figure 6.

The general electrosorptive behavior of BA in the mixture resemble to behavior it show when it is alone in the solution as presented in Figure 4 for 1.5 V polarization and 60 mL.min$^{-1}$ volumetric flow rate. The removal rate of NA seems to be higher than BA in the mixture. The %Req values are 88.1% and 89.4% for BA and NA, respectively. The higher removal rate and extent of NA than BA can be linked to the percentage of ionic species that exist in solutions of NA and BA at their natural pH values of 3.62 and 4.28, respectively. These percentages can easily be calculated from the initial adsorbate concentrations and $pK_a$ values of 4.20 and 2.05 for BA and NA, respectively. These calculations yielded BA to be 54% in anionic, 46% in neutral form and NA to be 91% in zwitterionic, 7% in anionic and 2% in neutral form at their respective natural pH values. The degree of ionization suggests that electrostatic interactions between charged ACE and ionic aromatic organic acid species play an important role in adsorption under polarization. Several other factors should also be considered concerning the mechanism of electrosorption. It is expected that solute molecules are adsorbed with their aromatic rings facing the graphene layers at the surface of ACE for maximizing the dispersive $\pi$-system interactions. Such orientation seems to be favored in most organic aromatics at small coverage conditions. On the other hand, since the charge density on the electrode surface increases upon polarization, charge-dipole interactions between ACE surface and the aromatic acids with permanent dipoles continue to be operative in an enhanced manner. The dipole moments of NA and BA are 3.05 D and 1.21 D [17], respectively. All these interactions are expected to govern the observed rates and extents of adsorption/electrosorption.

## CONCLUSIONS

Flow-through application of electrosorption was successfully carried out through a specially designed electrolytic cell upon polarization of ACEs. Electrosorptive behavior of BA was linked

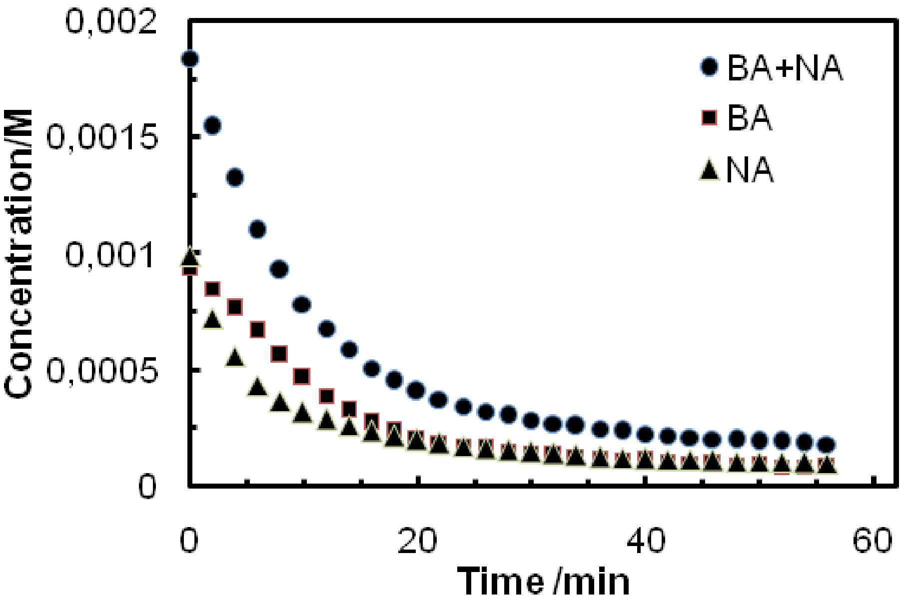

**Figure 6.** Electrosorption of NA (▲) and BA (■) from their equimolar (1x10$^{-3}$ M each) mixture onto ACEs at a volumetric flow rate of 60 mL min$^{-1}$ and 1.5 V polarization. (●) shows the sum of BA and NA concentrations.

to the electrostatic interactions and dispersion forces between polarized ACC and BA species in solution. Appreciable increases were obtained in the removal rate of BA by adjusting volumetric flow rate and applied potentials. Future studies, focused on different configurations of the electrolytic cell and operation mode, will be promising in terms of waste water treatment. Although the present study involves removal of BA and NA from its aqueous solution as a model system, the results are expected to be applicable to real waste waters probably after extending such investigations to other systems containing multiple pollutants besides BA and NA.

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