

Cite this: *J. Environ. Monit.*, 2011, **13**, 605www.rsc.org/jem**PAPER**

Evaluation of electrochemical processes for the removal of several target aromatic hydrocarbons from petroleum contaminated water†

Yamen AlSalka,* François Karabet and Shahir Hashem

Received 23rd August 2010, Accepted 16th December 2010

DOI: 10.1039/c0em00450b

Ground and surface water contamination resulting from the leakage of crude oil and refined petroleum products is a serious and growing environmental problem throughout the world. Consequently, a study of the use of electrochemical treatment in the clean-up was undertaken with the aim of reducing the water contamination by aromatic pollutants to more acceptable levels. In the experiments described, water contamination by refined petroleum products was simulated under laboratory conditions. Electrochemical treatment, using aluminium electrodes, has been optimised by full factorial design and surface response analysis in term of BTEX and PAHs removal and energy consumption. The optimal conditions of pH, current density, electrolysis time, electrolyte type, and electrolyte concentration have then been applied in the treatment of real water samples which were monitored as petroleum contaminated samples. Treatment results have shown that electrochemical methods could achieve the concentration of these pollutants to undetectable levels in particular groundwater and surface water, hence, they can be highly effective in the remediation of water contaminated by aromatic hydrocarbons, and the use of these processes is therefore recommended.

1. Introduction

The contamination of the environment by petroleum hydrocarbons is widespread because modern society uses many petroleum-based products such as gasoline, kerosene, fuel oil. Common sources of this contamination are petrol stations, underground storage tanks, home and commercial heating oil storage tanks, and fuel distribution centres, in addition to refineries, crude oil production sites, and accidental spills of the transportation pipes. About 250 million barrels of oil produced

water are generated every day, in the rate of about 3 barrels of produced water for every barrel of oil produced.¹

Petroleum products are complex mixtures of hydrocarbons which vary not only among the types of fuel, but also in the same type of fuel itself. Aromatic hydrocarbons are more soluble in water than aliphatic hydrocarbons; in addition, aromatics have more toxicological and carcinogenic effects. Increased attention has been paid to aromatic compounds in environmental chemistry because of mutagenic, teratogenic and carcinogenic properties of some of these pollutants.² Therefore, they were included in the European Union (EU) and the Environmental Protection Agency (EPA) list of priority pollutants.

With the ever increasing standards and the stringent environmental regulations concerning water and wastewater, the electrochemical technologies have enjoyed their importance worldwide during the last two decades.³ Nowadays, these technologies have reached such a state that they are not only

Department of Chemistry, Faculty of Sciences, University of Damascus, Damascus, Syria. E-mail: yamensalka@yahoo.com; Fax: +96311 44684141; Tel: +96393 3306459

† Electronic supplementary information (ESI) available: HPLC analysis conditions, full factorial and central composite designs, results and plots. See DOI: 10.1039/c0em00450b

Environmental impact

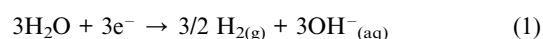
BTEX and PAHs, parts of petroleum aromatic hydrocarbons, are widespread contaminants in the environment water bodies, and they have been included in (EU) and (EPA) priority pollutant lists because of their carcinogenic properties; therefore, their monitoring and remediation is very important. We optimise an electrochemical treatment method for the removal of aromatic pollutants from petroleum contaminated water by a number of physicochemical processes which contribute in the removal procedure. While other works have focused merely on a few pure aromatic compounds or on COD values, this paper improves the knowledge on the fate of each pollutant during the treatment as a prelude to removing them from the water, besides the monitoring of the contributing of other petroleum components in the treatment method.

comparable with other technologies in terms of cost, but are also more efficient and compact.³

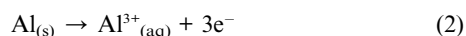
Electrochemical treatment is actually a combination of many processes involving electrocoagulation, EC, electroflocculation, electrofloatation, EF, and electrooxidation, EO. The electrochemical technique consists of the generation of coagulants *in situ* by electrolytic oxidation of an appropriate sacrificial anode.^{4,5} The metal ion generation takes place at the anode. The nascent aluminium ions are very efficient coagulants for particulates flocculating, where the hydrolysed aluminium ions can form large networks of Al–O–Al–OH which could sweep pollutants from water.^{3,6} The electrofloatation process involves the floatation of pollutants and flocculated particles to the surface of water by tiny bubbles of hydrogen gas, which are released at the cathode, and oxygen which is generated by water electrolysis.³ The released gases may also improve the process of flocculation by the turbulence generated by themselves which produces a sweet mix, helping the destabilised particles to produce larger particles.^{4,7}

The reactions occurring in an electrochemical cell using aluminium electrodes are as follows.^{4,8}

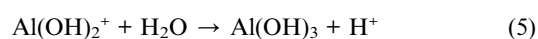
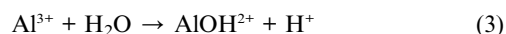
At the cathode:



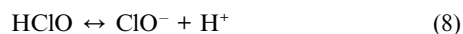
At the anode:



In the solution:



Electrooxidation of pollutants can be fulfilled through both, direct and indirect methods. At high chloride concentrations, an effective indirect oxidation occurred to destroy pollutants by the generation of chlorine and hypochlorite due to the electrolysis of chloride at the anode, as in the following reactions,⁹ leading to the oxidation of many inorganic and organic pollutants.^{3,10}



The design of experiments (DoE) is the methodology of how to conduct and plan experiments in order to obtain the maximum amount of information in the fewest number of runs. Usually, most experiments are done by modifying the levels of one factor at a time (COST), and this is performed in a random way to try and find the optimal conditions, but, as shown by Fisher, COST does not give much information about the position of the optimal parameters, especially when there are interactions among the factors. The most important aspect of DoE is that it provides a strict mathematical framework for changing all

pertinent factors simultaneously, showing the interactions between factors.¹¹ With DoE it is possible to optimise critical factors and identify the best combination of values.¹²

The present study provides an evaluation and optimisation of the removal of several petroleum aromatic hydrocarbons involving BTEX and the 16 PAHs from water using aluminium electrodes at different operating conditions. A number of experimental parameters including pH, current density, electrolysis time, and electrolyte concentration have been analysed, controlled, and optimised using full factorial model of design of experiments to investigate their effects on the removal efficiency and energy consumption. The optimal parameters were then applied to treat water samples suspected to be contaminated by petroleum hydrocarbons.

2. Experimental

2.1. Materials and chemicals

Acetonitrile, methylene chloride and water were of HPLC grade, purchased from Acros organics (Geel, Belgium).

A certified standard mixture solution (aromatic hydrocarbons mix 11) used for calibration was purchased from Dr Ehrenstrofer reference materials (Augsburg, Germany). This solution contained 2000 mg L⁻¹ of each substance: benzene, toluene, ethylbenzene and *o*-, *m*-, *p*-xylene. A certified standard mixture solution (EPA 610 PAH Mix), used for calibration, was purchased from Supelco Analytical (Bellefonte, USA) and contained 2000 mg L⁻¹ of acenaphthylene, 1000 mg L⁻¹ of each of acenaphthene, and naphthalene, 200 mg L⁻¹ of each of Benzo(b)fluorene, Benzo(g,h,i)perylene, dibenzo(a,h)anthracene, fluorene, fluorene, and 100 mg L⁻¹ of each of anthracene, Benzo(a)anthracene, Benzo(a)pyrene, Benzo(k)fluoranthene, chrysene, indeno(1,2,3-cd)pyrene, phenanthrene, and pyrene.

Aliquots of some Syrian gasoline and diesel products were used to spike water of HPLC grade in order to prepare the samples for the experiments used in treatment evaluation and optimisation. Table 1 shows the characteristics of the gasoline and diesel used. Spiking was done by dissolving 5 mg of gasoline in 25 mL methylene chloride and 25 mg of diesel in 25 mL methylene chloride, then by adding 250 µL of gasoline solution and 500 µL of diesel solution to 200 mL water of HPLC grade to give the concentrations mentioned in Table 1.

2.2. Instruments

HPLC analysis was done using a smartline HPLC system produced by Knauer GmbH (Berlin, Germany) which consisted of a degasser, gradient pump, manual injector, column oven, photo diode array detector and fluorescence detector. Chromatographic separation of BTEX was performed on 250 × 4.6 mm, 3 µm, Eurospher C18 column (Knauer GmbH, Berlin, Germany), and of PAHs on 250 × 4.6 mm, Supelcosil LC-PAH column (Supelco Analytical, Bellefonte, USA). A PC interfaced to the HPLC using ClarityChrom software (Knauer GmbH) was used for data acquisition and processing.

Sample preparation of BTEX prior their analysis was done using a glass apparatus as mentioned in our previous study.¹³ Extraction steps for PAHs determination were done by

Table 1 The contents of the gasoline and diesel used and the final concentration of the spiked water

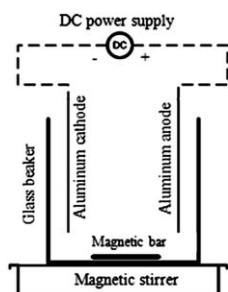
Compounds	Gasoline % (mean $n = 3$)	Diesel % (mean $n = 3$)	Spiked water concentration $\mu\text{g L}^{-1}$
Benzene	1.7220	0.0415	5.3425
Toluene	11.022	0.2535	33.8925
<i>o</i> -xylene	1.6143	0.0305	4.7983
Ethylbenzene	1.5824	0.1035	6.5435
<i>m</i> - + <i>p</i> -xylene	3.8053	0.3811	19.0408
Naphthalene	0.2846	0.4055	13.3790
Acenaphthylene		0.0135	0.4625
Acenaphthene		0.0105	0.6775
Fluorene		0.1466	3.6650
Phenanthrene		0.1343	3.3575
Anthracene		0.0096	0.3150
Fluoranthene		0.0113	0.2825
Pyrene		0.0178	0.4950
Benzo(a)anthracene		0.0007	0.0175
Chrysene		0.0003	0.0075
Benzo(b)fluoranthene		0.0002	0.0050
Benzo(k)fluoranthene		0.0001	0.0025
Benzo(a)pyrene	0.00015	0.0005	0.0279
Dibenzo(a,h)anthracene		0.00003	0.0008
Benzo(g,h,i)perylene		0.00002	0.0005
Indeno(1,2,3-cd)pyrene		0.00005	0.0023
Total BTEX	20.0301	0.7066	69.6175
Total of 16 PAHs	0.00015	0.8546	22.6979

liquid–liquid extraction which was performed using a 1 L extraction funnel, then by the concentration of the extract by means of rotary evaporator, model Rotavapor R-210 (BÜCHI Labortechnik AG, Flawil 1, Switzerland).

pH and conductivity measurements were done using a calibrated pH metre, model PH-2001 and conductivity metre, model CD-2005, respectively, produced by J.P. Selecta (Barcelona, Spain).

2.3. Electrochemical cell

Electrochemical treatment system includes an electrochemical glass beaker with a total volume of 250 mL as a reactor and a DC power supply system. A digital hot plate magnetic stirrer, model AREC (VELP Scientifica srl, Milano, Italy), was used to provide sufficient mixing inside the reactor and control its temperature. The aluminium electrodes were made of rectangular sheets with dimensions of $45 \times 60 \times 0.5$ mm and were dipped into the sample and connected to an ammeter. The current density was maintained constant by using a voltage regulator. A schematic diagram of the electrochemical reactor is shown in Scheme 1.

**Scheme 1** Schematic diagram of the electrochemical reactor.

2.4. Electrochemical experiments

All experiments were conducted in batches. In each experimental run, a spiked water sample of 200 mL was placed in the electrolytic cell. The sample was vigorously stirred by the magnetic stirrer at 150 rpm at a constant temperature of 25 °C. This temperature was chosen because all the sampling points were in warm zones, hence, the water samples had temperatures between 21 to 23 °C, and since most reference studies indicate that the effectiveness of electrochemical processes achieved when the temperature is about 25 °C because of the increase in the ion movements in solution, while higher temperatures could break the flocs from the increased movement of the ions. Also very high temperature increases the solubility of precipitates.⁴

The aluminium electrodes were dipped into the solution up to an active surface area of 45 cm² and the interelectrode distance was maintained at 40 mm according to our previous study.¹⁴ After each batch experiment, the sample was kept for flocculation by setting the stirring speed at 30 rpm for 10 min. Subsequently, the flocculated sample was kept unstirred for 30 min, in order to allow the flocs that formed during the flocculation to settle down. Then, the supernatant sample was collected to perform the analysis of remaining BTEX and PAHs. Before each run, organic impurities on electrode surface were removed by washing the electrodes with acetone and HCl solution (10 wt%) before the final washing with distilled water.

2.5. Optimisation of electrochemical treatment using DoE

As the literature identified the significant factors which affect the electrochemical treatment methods, the next step is to quantitatively evaluate their influences on the responses of interest, as well as any possible interactions between them. To do this with a minimum number of experiments, we can employ full factorial designs.²⁵ When the goal is to optimise the method, that is, maximise or minimise some responses. In this case, an adequate technique is response surface methodology (RSM), based on least-squares fitting.²⁵

In general full factorial design, FFD, multiple factors are investigated simultaneously to identify the factors that have a significant effect on the response, as well as to investigate the effect of interactions. Each factor could have a different number of levels and the experiments performed at all possible combinations of the factor levels. The central composite design CCD, a part of response surface methodology, is two level full factorial design augmented by a number of centre points and uses a second order model to approximate the response once it is realised that the experiment is close to the optimum response region.²⁶

A general full factorial design contained 162 runs and consisted of four factors in three levels [current density CD (20, 25 30 mA cm⁻²), electrolyte concentration EC (0.5, 1, 2 g L⁻¹), electrolysis time ET (80, 100, 120 min), and pH (5, 8, 10)], was carried out with an aim to investigate the effects of variable factors on the total removal of BTEX and PAHs.

After having established the significant factors from full factorial design, the optimal electrochemical treatment conditions were attained by using response surface methodology, applying central composite design CCD with 2⁴ (2levels-4factors) and face centred design (alpha = 1) contained 53 runs. Maximal

and minimal levels in CCD design are [current density CD (22, 28 mA cm⁻²), electrolyte concentration EC (1, 2 g L⁻¹), electrolysis time ET (100, 120 min), and pH (7, 9)]. The statistical and optimisation calculations were made using DOE++ software V.1.0.5, ReliaSoft Corp. (USA).

Quadratic models were validated by several techniques that could be used to check the appropriateness of the second order models including the coefficient of multiple determinations R^2 , the prediction error sum of squares, PRESS, the numerical and graphical residual analysis, and the lack of fit test. The variance for polynomial could be calculated from the replicas in FFD and from the central point in CCD.

2.6. Sample preparation procedures

2.6.1. Sample preparation of BTEX. The procedure was based on the purge of BTEX and all other volatile compounds from water samples to a specific volume of acetonitrile using a pure nitrogen gas and a glass apparatus to reach a final volume of 1 mL according to our previous work.¹³

2.6.2. Sample preparation of PAHs. A liquid–liquid extraction procedure based on the extraction steps mentioned in the US-EPA method 550.1 to reach a final volume of 1 mL.¹⁵

2.7. Analysis procedures

2.7.1. The analysis of BTEX. According to our previous work,¹³ an aliquot of 50 μ L of the sample after preparation was injected into the HPLC system using a flow rate of 1.8 mL min⁻¹ and an isocratic elution with acetonitrile : water (50 : 50) as mobile phase. The separation was accomplished using the mentioned HPLC column at 30 °C for 12 min. The detection was carried out at 201 nm using the diode array detector with scanning from 200 to 350 nm.

2.7.2. The analysis of PAHs. Some modifications on the analysis procedure mentioned in Dionex application note 213 were done.¹⁶ An aliquot of 20 μ L of the extract was injected into the HPLC system using a flow rate of 1.0 mL min⁻¹, and a gradient elution of water and acetonitrile was used as mobile phases. The separation was accomplished using the mentioned column at 30 °C for 60 min. The detection was carried out using diode array and fluorescence detectors.

2.8. Collection of samples

Two sampling points were chosen in the Deir Azzor area (North East Syria), one of them was petroleum produced water (Jourzi location, 34°55'26" N, 40°35'57" E) and the second was surface water next to this petroleum well. Another sampling location was well Ein Taban in Al Hasakeh area (36°19'00" N, 40°46'55" E) where a petroleum contamination was expected. Water samples were collected in 1000 mL glass containers which were completely filled to the top and stoppered with no headspace. Drops of HCl (1 : 1) were added to each sample at the time of collection to adjust the pH to below 2. All samples were maintained at 4 °C, treated and analysed within 72 h of sampling.

3. Results and discussion

3.1. Effect of initial pH

To know the approximate values of the ideal pH for later use in the optimisation process, the effect of the initial pH on the removal of BTEX and the 16 PAHs from water was evaluated, based on electrochemical conditions tested in a previous study,¹⁴ which are a current density of 20 mA cm⁻², using NaCl at 1 g L⁻¹ for 100 min, and by varying the initial pH from 5 to 10 using H₂SO₄ or NaOH (0.1 M). The results presented in Fig. 1 show that the optimal pH for the reduction of these contaminants was found to be about 8 since the solid aluminium hydroxide Al(OH)₃, which formed during the process, contributes to the removal of pollutants through co-precipitation of these organic compounds, and considering that the solubility of aluminium hydroxide has been reported to be minimal at the pH range of 6–8.^{4,17} The decrease in the removal rate at both, low and high pH values could be explained by the amphoteric character of aluminium hydroxide which does not precipitate at very low pH,^{18,19} while high pH leads to the formation of soluble Al(OH)₄⁻.^{18,20}

3.2. Influence of electrolysis time and current density

Based on the electrochemical conditions tested in a previous study,¹⁴ the approximate values of the ideal current density and electrolysis time were evaluated for later use in the optimisation method. As demonstrated in Fig. 2, the removal efficiency increases with increasing time at all current densities as a result of the augmentation in aluminium ions generated in solution during time. After 120 min using 1 g L⁻¹ NaCl, the maximum removal efficiency of BTEX and PAHs were about 73, 86, 92, 99 and 100% for current densities of 20, 22, 25, 28 and 30 mA cm⁻² respectively.

Fig. 3 shows the variation of formation of sludge as a function of current densities at a fixed electrolysis time of 120 min, as well the dissolution of the aluminium anode calculated from the following relation, where I is the applied current (A), M is the molecular weight of aluminium (26.98 g mol⁻¹), t is the time (s), z is the number of electrons transferred ($z_{\text{Al}} = 3$), F is the Faraday's constant (96500 C mol⁻¹), and V is the volume of treated water (m³):

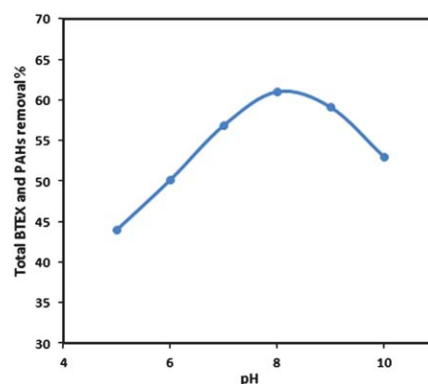


Fig. 1 Effect of pH on the total BTEX and PAHs removal efficiency (Current density: 20 mA cm⁻², NaCl: 1 g L⁻¹, temp: 25 °C, time: 100 min).

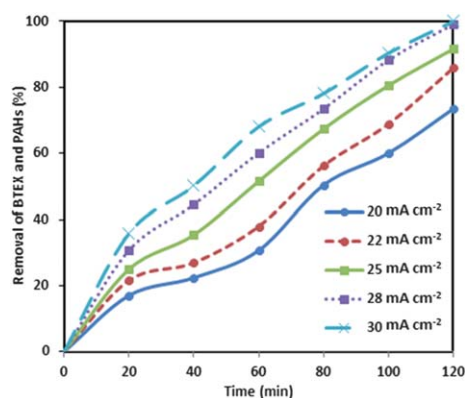


Fig. 2 Influence of electrolysis time and current density on the removal efficiency (NaCl: 1 g L⁻¹, pH: 8 and temp: 25 °C).

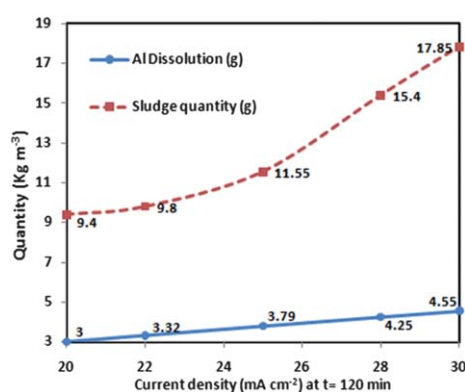


Fig. 3 Production of sludge and dissolution of aluminium at different current densities (NaCl: 1 g L⁻¹, pH: 8, time: 120 min and temp: 25 °C).

$$\text{Aluminium dissolution} = (I.t.M)/(z F V) \quad (9)$$

As the current density increased the anodic dissolution is favoured according to Faraday's law, enhancing the formation of aluminium hydroxides which produce more sludge with a consequent removal of pollutants due to sweep coagulation.^{18,21} Moreover, the removal efficiency at higher current density could be due to the increased amount of formation of chlorine, which may enhance the electrooxidation in the presence of NaCl as an electrolyte.

In addition, more bubbles will be generated at higher current density, improving the degree of mixing of Al(OH)₃ and pollutants, enhancing floatation ability and increasing the removal efficiency.^{18,22} Moreover, these bubbles could permit the purging of BTEX compounds from water, especially at higher current densities, due to their volatile properties and their low vapour pressures.

3.3. Statistical analysis using FFD

The experiments of full factorial design were performed following the above mentioned design at a temperature of 25 °C, and the total removal of the BTEX and the 16 PAHs compounds were calculated. Experimental runs were performed in duplicate and in random order according to the developed design to reduce

error. The analysis results (analysis of variance ANOVA using partial sum squares and 5% level of significance) were performed.

The analysis of variance results are provided in Table 2. Statistical analysis of the removal rates revealed that all four studied factors and their interactions were each statistically significant and could therefore be affecting the removal efficiency, which can be seen from a *P* value below 0.05. The rank ordering of statistically significant factors is discovered from the Pareto chart which showed that current density is the predominant factor affecting removal rate. *R*² and adjusted *R*² values of the model were above 0.999, showing excellent variability by the regression model. The graphical residual analyses were randomly and normally distributed about a mean of zero and did not have any trends or patterns in their plots, confirming the adequacy in the regression model.

3.4. Optimisation of the treatment method using CCD

In order to optimise the electrochemical treatment method in terms of maximum removal efficiency and minimum energy consumption, the four significant independent factors established by FFD results were further explored by a second order model based on face centred 2⁴ plus central point design. CCD experiments were performed in a random order and in duplicate at a temperature of 25 °C to ensure reproducibility and reduce error.

The following relation was used to calculate the consumption of energy (kWh g⁻¹), where *I* is the applied current (A), *V* is the applied voltage (V), *t* is the time (h), *m* is the weight of the treated pollutants (g):

$$\text{Energy consumption} = (I.V.t)/m \quad (10)$$

ANOVA results of CCD (using partial sum squares and 5% level of significance) were used to establish a quadratic polynomial (second order) model. As obtained in full factorial design, all the four studied factors and their interactions were each statistically significant.

The validation of the quadratic model was based on several techniques. The ANOVA results revealed that the values of the correlation of multiple determinations *R*² and adjusted *R*² were 0.9969 and 0.9943 for the removal model, and 0.9922 and 0.9902 for the energy consumption model, showing excellent variability and indicating that the regression models fit the data well. The small values of PRESS indicate that the regression models could predict new observations well. The residuals appear to behave randomly, suggesting that the models fit the data well. The scatter plots of residuals *versus* each factor showed that residuals were scattered both above and below the reference line at all values of factors, confirming the sufficiency of the functional part of the model. The residuals *versus* fitted values plots showed that there was a random tendency, thus, the normality, independence and randomness of the residuals were satisfied. The run orders scatter plots of the residuals demonstrated random scatter without any systematic relationship assuming no drift in the measurement process. The plotted points of the normal probability plots lied close to straight line, suggesting that the random errors were distributed normally. ANOVA tests showed that the lack of fit of the two models had significant effects. We used

Table 2 Factors and their interaction effects (ANOVA results) in FFD

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F ratio	P value ^a
Model	64	5.01E+04	783.5671	2924.886	4.83E–138
A:CD	2	1.83E+04	9145.506	3.41E+04	7.35E–139
B:EC	2	9166.566	4583.283	1.71E+04	2.44E–124
C:ET	2	8555.747	4277.874	1.60E+04	6.86E–123
D:pH	2	1.22E+04	6077.164	2.27E+04	2.89E–130
AB	4	645.7601	161.44	602.6206	1.49E–67
AC	4	315.8369	78.9592	294.7376	2.43E–53
AD	4	167.6263	41.9066	156.4281	2.15E–41
BC	4	53.9998	13.5	50.3924	7.03E–23
BD	4	118.7647	29.6912	110.8307	2.72E–35
CD	4	61.7023	15.4256	57.5803	8.47E–25
ABC	8	463.9654	57.9957	216.4853	2.54E–58
ABD	8	83.4407	10.4301	38.9332	5.06E–27
ACD	8	34.0676	4.2585	15.8959	9.31E–15
BCD	8	35.4756	4.4345	16.5528	3.18E–15
Residual	97	25.986	0.2679		
Lack of Fit	16	23.0839	1.4427	40.2681	8.42E–32
Pure Error	81	2.9021	0.0358		
Total	161	5.02E+04			

^a Alpha = 0.05, S = 0.5176, $R^2 = 99.95\%$, $R^2(\text{adj}) = 99.91\%$.

Table 3 Optimisation solutions

Name	A: CD ^a (mA cm ⁻²)	B: EC ^b (g L ⁻¹)	C: ET ^c (min)	pH	Removal (%)	Energy (kwh g ⁻¹) × 10 ⁻³
Solution 1	28	2	111.57	8.20	103.460	27.933
Solution 2	28	2	112.34	8.23	103.565	28.031
Solution 3	28	2	118.38	8.59	103.892	30.651
Selection	28	2	110.00	8.00	103.151	29.709

^a CD: Current density. ^b EC: NaCl concentration. ^c ET: Electrolysis time.

standard response surface methodology, which is based on a quadratic model. We recognise that these models may have some lack of fit; indeed our full factorial ANOVA indicated that higher order interactions are statistically significant. However, both of our quadratic models have a correlation of multiple determination which exceeds 0.992. Therefore, although there is still some small lack of fit, our quadratic models capture all but 0.8% of the variability. This is generally regarded as being sufficient for any practical application, in line with generally accepted usage of response surface methodology.

The removal and energy consumption equations of the quadratic actual value model were the following:

Removal% = $-729.7065 + 30.0209 (\text{CD}) + 57.8220 (\text{EC}) - 0.4520 (\text{ET}) + 88.8946 (\text{pH}) - 0.2758 (\text{CD})(\text{EC}) - 0.0272 (\text{CD})(\text{ET}) - 0.0115 (\text{CD})(\text{pH}) - 0.2367 (\text{EC})(\text{ET}) - 0.4750 (\text{EC})(\text{pH}) - 0.0398 (\text{ET})(\text{pH}) - 0.4640 (\text{CD}^2) - 3.8429 (\text{EC}^2) + 0.0098 (\text{ET}^2) - 5.1157 (\text{pH}^2)$.

Energy Consumption = $+1101.9861 + 37.7962 (\text{CD}) - 266.1867 (\text{EC}) - 6.9942 (\text{ET}) - 217.0988 (\text{pH}) - 5.1069 (\text{CD})(\text{EC}) + 0.0602 (\text{CD})(\text{ET}) - 1.5941 (\text{CD})(\text{pH}) - 0.1694 (\text{EC})(\text{ET}) + 23.3906 (\text{EC})(\text{pH}) - 0.0648 (\text{ET})(\text{pH}) - 0.3829 (\text{CD}^2) + 48.8548 (\text{EC}^2) + 0.0299 (\text{ET}^2) + 12.9462 (\text{pH}^2)$.

From the response surfaces plots, it can be noticed that the maximum removal efficiency was obtained at about the higher levels of the studied factors, except at the middle for pH. High conductivity is an added advantage to the process, which reduces the electrical resistance of the solution,²³ minimising the energy

consumption. The software calculates three solutions in terms of the maximum removal with the minimum energy consumption as mentioned in Table 3. We chose the solution 1 with reducing electrolysis time and rounding the pH down as the maximal application values for the next experiments as revealed in Table 3.

3.5. Effect of electrolyte type

Three types of electrolytes (NaCl, NaNO₃, Na₂SO₄) were evaluated at a constant electrolyte concentration of 2 g L⁻¹,

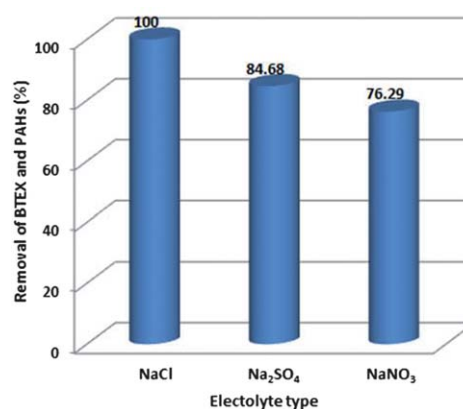


Fig. 4 Effect of electrolyte type (current density: 28 mA cm⁻², electrolyte concentration: 2 g L⁻¹, time: 110 min, pH: 8 and temp: 25 °C).

Table 4 Spiked water samples used to identify the influence of initial concentration on the treatment efficiency

Samples	Volume of gasoline solution (μL)	Volume of diesel solution (μL)	Spiked water concentration ($\mu\text{g L}^{-1}$)	
			Total BTEX	Total PAHs
Sample 1	50.00	100.00	13.924	4.540
Sample 2	250.00	500.00	69.618	22.698
Sample 3	1000.00	2000.00	278.470	90.792

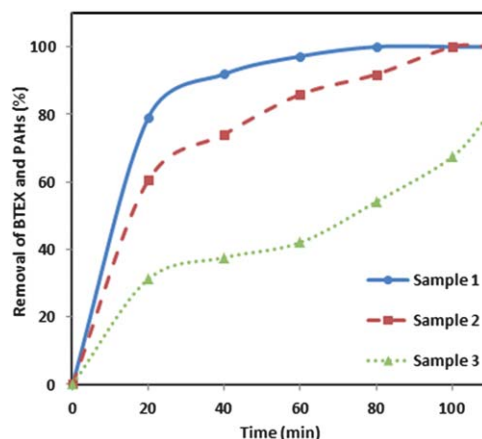
temperature of $25\text{ }^{\circ}\text{C}$, current density of 28 mA cm^{-2} , and electrolysis time of 110 min, in order to compare the performance of these electrolytes and to select the best electrolyte for the treatment of such water. The percentage removal of BTEX and PAHs was strongly affected by the electrolyte composition as shown in Fig. 4. In inert electrolyte solutions of Na_2SO_4 and NaNO_3 , the pollutants were removed by electrocoagulation,⁹ electroflocculation, and electrofloatation. The removal efficiency was significantly increased by using NaCl as an electrolyte, where indirect oxidation by hypochlorite is involved, as well the above mentioned mechanisms, showing a clear positive effect.⁹ Fear that the presence of chloride ions could lead to the formation of chlorinated intermediate organic compounds, the treated water samples were tested in term of TOC values which were closed to zero after the treatment confirming the absence of any type of organic pollutants in treated water, however, this does not prevent that these intermediates could be accumulated in the produced sludge.

The conductivity of solution in the presence of NaCl , Na_2SO_4 , and NaNO_3 were $3340\text{ }\mu\text{S cm}^{-2}$, $2706\text{ }\mu\text{S cm}^{-2}$ and $2335\text{ }\mu\text{S cm}^{-2}$ respectively. High conductivity is an added advantage to the process, which reduces the electrical resistance of the solution,²³ contributing to transfer the electric charge.³ Also, high conductivity could remove the passive oxide layer form on electrode surface, hence it increases the availability of aluminium hydroxide in the solution, improving the efficiency of aromatic removal.^{18,22}

3.6. Effect of the initial concentration of pollutants

The influence of water composition on the treatment performance was investigated by treating spiked water samples which differed in the initial pollutant concentration. Batch electrochemical experiments were conducted by changing the quantities of gasoline and diesel respectively while fixing the other factors (NaCl : 2 g L^{-1} , pH: 8, current density: 28 mA cm^{-2} at $25\text{ }^{\circ}\text{C}$).

Table 4 indicates the concentrations of spiked water used in these experiments. Fig. 5 represents the relation between the percentage removal of BTEX and PAHs and initial solution concentration. After 110 min of treatment, the removal decreases from 100% to about 79% as the concentration of pollutants increased from 92.3 to $369.3\text{ }\mu\text{g L}^{-1}$. These observations could be explained by the fact that at a constant current density, the same amount of aluminium ions passes to the solution, hence, the formed amount of complex aluminium hydroxide was insufficient to coagulate the greater amount of pollutant molecules at higher BTEX and PAH concentrations.^{18,24} Furthermore, beating this augmentation of pollutants involves generation of more aluminium ions, hypochlorite ions, and gas bubbles; hence,

**Fig. 5** Influence of initial concentrations of pollutants (Current density: 28 mA cm^{-2} , NaCl : 2 g L^{-1} , pH: 8 and temp: $25\text{ }^{\circ}\text{C}$).

higher current density or more electrolysis time should be applied.

3.7. The treatment according to the type of pollutants

A closer approach of the mechanism of the electrochemical treatment was attained by examining the changes in concentration of each type, BTEX and PAHs, at the maximal treatment conditions. During the first 40 min, there was a remarkable decrease in the concentration of PAHs, while a slight degradation of BTEX occurred, as shown in Fig. 6 and Table 5. In the less water soluble fraction of aromatic pollutants, the PAH compounds are expected to coagulate and flocculate with the

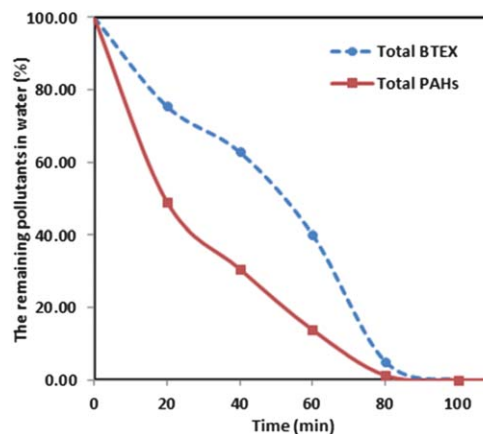
**Fig. 6** The degradation of each type of pollutant (Current density: 28 mA cm^{-2} , NaCl : 2 g L^{-1} , pH: 8 and temp: $25\text{ }^{\circ}\text{C}$).

Table 5 The results of electrochemical treatment according to the target pollutant

Compounds	Electrolysis time						LOD ($\mu\text{g L}^{-1}$)
	0 min ($\mu\text{g L}^{-1}$)	20 min ($\mu\text{g L}^{-1}$)	40 min ($\mu\text{g L}^{-1}$)	60 min ($\mu\text{g L}^{-1}$)	80 min ($\mu\text{g L}^{-1}$)	100 min ($\mu\text{g L}^{-1}$)	
Benzene	5.343 \pm 0.190	3.740 \pm 0.144	2.805 \pm 0.117	1.402 \pm 0.065	N/D	N/D	0.201
Toluene	33.893 \pm 0.715	26.775 \pm 0.632	23.294 \pm 0.567	16.073 \pm 0.325	2.652 \pm 0.105	N/D	0.332
<i>o</i> -xylene	4.798 \pm 0.180	3.215 \pm 0.113	2.250 \pm 0.081	0.900 \pm 0.036	N/D	N/D	0.321
Ethylbenzene	6.544 \pm 0.260	4.580 \pm 0.188	3.435 \pm 0.145	1.477 \pm 0.068	N/D	N/D	0.423
<i>m</i> - + <i>p</i> -xylene	19.041 \pm 0.565	14.281 \pm 0.464	11.996 \pm 0.413	7.437 \pm 0.206	0.818 \pm 0.035	N/D	0.182
Naphthalene	13.379 \pm 0.269	8.027 \pm 0.177	5.338 \pm 0.124	2.776 \pm 0.076	0.300 \pm 0.012	N/D	0.290
Acenaphthylene	0.463 \pm 0.019	N/D	N/D	N/D	N/D	N/D	0.331
Acenaphthene	0.678 \pm 0.027	N/D	N/D	N/D	N/D	N/D	0.510
Fluorene	3.665 \pm 0.079	1.554 \pm 0.044	0.932 \pm 0.028	0.280 \pm 0.011	N/D	N/D	0.095
Phenanthrene	3.358 \pm 0.084	1.343 \pm 0.048	0.672 \pm 0.025	0.134 \pm 0.008	N/D	N/D	0.077
Anthracene	0.315 \pm 0.013	0.110 \pm 0.004	N/D	N/D	N/D	N/D	0.071
Fluoranthene	0.283 \pm 0.014	0.090 \pm 0.005	N/D	N/D	N/D	N/D	0.086
Pyrene	0.495 \pm 0.020	0.178 \pm 0.008	N/D	N/D	N/D	N/D	0.117
Benzo(a)anthracene	N/D	N/D	N/D	N/D	N/D	N/D	0.030
Chrysene	N/D	N/D	N/D	N/D	N/D	N/D	0.042
Benzo(b)fluoranthene	N/D	N/D	N/D	N/D	N/D	N/D	0.019
Benzo(k)fluoranthene	N/D	N/D	N/D	N/D	N/D	N/D	0.014
Benzo(a)pyrene	0.028 \pm 0.002	N/D	N/D	N/D	N/D	N/D	0.021
Dibenzo(a,h)anthracene	N/D	N/D	N/D	N/D	N/D	N/D	0.025
Benzo(g,h,i)perylene	N/D	N/D	N/D	N/D	N/D	N/D	0.065
Indeno(1,2,3-cd)Pyrene	N/D	N/D	N/D	N/D	N/D	N/D	0.033

(n = 3), N/D = not detected.

Table 6 The results of electrochemical treatment of environmental water samples

Compounds	Oil produced water (Al jourzi – Deir azzor)		Surface water (near a petroleum well – Deir azzor)		Groundwater (Ein Taban well – Al Hasakeh)	
	Before treatment ($\mu\text{g L}^{-1}$)	After treatment ($\mu\text{g L}^{-1}$)	Before treatment ($\mu\text{g L}^{-1}$)	After treatment ($\mu\text{g L}^{-1}$)	Before treatment ($\mu\text{g L}^{-1}$)	After treatment ($\mu\text{g L}^{-1}$)
Benzene	1160 \pm 6	918 \pm 4	13.2 \pm 0.4	0.21 \pm 0.01	0.91 \pm 0.03	N/D
Toluene	995 \pm 8	736 \pm 2	15.9 \pm 0.5	N/D	0.43 \pm 0.02	N/D
<i>o</i> -xylene	360 \pm 3	288 \pm 1	9.60 \pm 0.35	N/D	N/D	N/D
Ethylbenzene	131 \pm 4	94.8 \pm 0.3	6.31 \pm 0.33	N/D	N/D	N/D
<i>m</i> - + <i>p</i> -xylene	623 \pm 5	396 \pm 2	11.2 \pm 0.5	0.29 \pm 0.02	1.06 \pm 0.05	N/D
Naphthalene	208 \pm 2	129 \pm 1	9.62 \pm 0.30	N/D	6.18 \pm 0.19	N/D
Acenaphthylene	3.69 \pm 0.11	1.93 \pm 0.09	N/D	N/D	N/D	N/D
Acenaphthene	6.07 \pm 0.17	2.95 \pm 0.13	0.64 \pm 0.03	N/D	0.81 \pm 0.04	N/D
Fluorene	37.3 \pm 0.8	21.4 \pm 0.3	1.43 \pm 0.06	N/D	1.09 \pm 0.05	N/D
Phenanthrene	74.5 \pm 1.4	42.1 \pm 0.3	3.16 \pm 0.10	N/D	0.095 \pm 0.006	N/D
Anthracene	4.51 \pm 0.13	2.05 \pm 0.08	0.19 \pm 0.02	N/D	N/D	N/D
Fluoranthene	1.09 \pm 0.04	0.330 \pm 0.092	N/D	N/D	N/D	N/D
Pyrene	5.28 \pm 0.14	2.14 \pm 0.16	0.14 \pm 0.01	N/D	0.67 \pm 0.03	N/D
Benzo(a)anthracene	0.93 \pm 0.04	0.271 \pm 0.088	0.092 \pm 0.005	N/D	0.074 \pm 0.004	N/D
Chrysene	1.97 \pm 0.07	0.683 \pm 0.014	0.073 \pm 0.004	N/D	N/D	N/D
Benzo(b)fluoranthene	0.54 \pm 0.03	0.185 \pm 0.009	0.022 \pm 0.001	N/D	N/D	N/D
Benzo(k)fluoranthene	0.085 \pm 0.004	N/D	N/D	N/D	N/D	N/D
Benzo(a)pyrene	0.77 \pm 0.03	0.206 \pm 0.007	0.029 \pm 0.002	N/D	N/D	N/D
Dibenzo(a,h)anthracene	0.13 \pm 0.01	N/D	N/D	N/D	N/D	N/D
Benzo(g,h,i)perylene	0.24 \pm 0.01	N/D	N/D	N/D	N/D	N/D
Indeno(1,2,3-cd)Pyrene	0.039 \pm 0.002	N/D	N/D	N/D	N/D	N/D

(n = 3), N/D = not detected.

coagulant molecules faster and easier than the BTEX compounds which are more water soluble and their concentrations will be less influenced during the removal process.

After 60 min of treatment, a rapid decrease in the concentration of BTEX could be observed, which could be the result of the evaporation of these compounds by the electrofloatation and the releasing of floating gases. Furthermore, the heat generated by

the electrochemical processes, which raised the temperature of solution from 25 °C to 34 °C, could promote evaporation. For these reasons, suitable filters could be introduced to adsorb the pollutants which may evaporate, preventing atmospheric pollution.

The electrooxidation process may also contribute to the removal of BTEX because of their structures with a single

aromatic ring which are easier to oxidise than the other compounds consist of multiple fused aromatic rings.

3.8. Treatment of environmental contaminated water samples

Table 6 contains the results obtained from the analysis of the environmental samples before and after treatment using the maximal electrochemical conditions. As shown in this table, electrochemical treatment reduces the concentration of most of the pollutants to undetectable levels when treating the sample of surface water, but it can be seen that the efficiency of this treatment was lower than those of the synthetic samples studied because it contains other pollutants which can contribute to this treatment. On the other hand, the evaluation of this treatment in the removal of BTEX and PAHs from produced water sample was insufficient, since the initial concentration is too high, hence, only a few pollutants, which are present in lower concentrations in the sample and have less water solubility, were removed during this treatment. Consequently, to reduce other pollutants present in this sample to low levels, we need to increase the electrolysis time as well as the electrolyte concentrations and current density.

4. Conclusions

The combined electrochemical processes using aluminium as a sacrificial anode seems to be a very efficient method for the treatment of water contaminated with reasonable concentrations of BTEX and PAH pollutants, coming from the contamination of water by oil and petroleum products as revealed in the present study. The experimental results showed that the treatment is based on coagulation, co-precipitation and sweep flocculation; furthermore, it is improved by indirect oxidation by hypochlorite, especially for the reduction of BTEX compounds. Using the maximal experimental conditions in term of removal, derived from a chemometric approach based on the use of experimental design (2 g L⁻¹ of NaCl, initial pH of 8 and current density of 28 mA cm⁻² for 110 min), could help in the reduction of BTEX and PAHs pollutants to undetectable levels with minimal power consumption. It can be concluded from this study that electrochemical treatment is a promising technique for the removal of petroleum aromatic hydrocarbons from contaminated surface and groundwater.

Acknowledgments

We wish to thank Professor James H. Matis, professor of statistics in Brigham Young University, Utah, USA for his support in the statistical discussions and Eng. Murfak

Alsuliman, from the University of Damascus, for his assistance in the analytical side and in the realisation of this study.

References

- 1 A. Fakhru'l-Razi, A. Pendashteh, L. C. Abdullah, D. R. A. Biak, S. S. Madaeni and Z. Z. Abidin, *J. Hazard. Mater.*, 2009, **170**, 530.
- 2 B. Fouillet, P. Chambon, R. Chambon, M. Castegnaro and N. Weil, *Bull. Environ. Contam. Toxicol.*, 1991, **47**, 1.
- 3 L. K. Wang, Y. Hung, and N. K. Shammass, *Handbook of environmental engineering: Advanced physicochemical treatment technologies*, Humana Press, New Jersey, 2007, Vol. 5, pp 57.
- 4 M. El-Naas, S. Al-Zuhair, A. Al-Lobaney and S. Makhoulouf, *J. Environ. Manage.*, 2009, **91**, 180.
- 5 P. Cañizares, F. Martínez, C. Jiménez, J. Labato and M. A. Rodrigo, *Environ. Sci. Technol.*, 2006, **40**, 6418.
- 6 F. Shen, P. Gao, X. Chen and G. Chen, *Chem. Eng. Sci.*, 2003, **58**, 987.
- 7 P. Cañizares, F. Martínez, C. Jiménez, C. Saez and M. A. Rodrigo, *J. Hazard. Mater.*, 2008, **151**, 44.
- 8 A. E. Yilmaz, R. Boncukcuoglu and M. M. Kocakerim, *J. Hazard. Mater.*, 2007, **149**, 475.
- 9 J. Muff and E. G. Søgaard, *Water Sci. Technol.*, 2010, **61**, 2043.
- 10 N. S. Abuzaid, Z. Al-Hamouz, A. A. Bukhari and M. H. Essa, *Water, Air, Soil Pollut.*, 1999, **109**, 429.
- 11 J. Trygg and S. Wold, *Homepage of Chemometrics*, Editorials August 2002, www.acc.umu.se/~tnkjtg/Chemometrics/Editorial.
- 12 T. Adžamić, K. Sertić-Bionda and Z. Zoretić, *Nafta*, 2009, **60**, 485.
- 13 Y. AlSalka, F. Karabet and S. Hashem, *Anal. Methods*, 2010, **2**, 1026.
- 14 Y. AlSalka, F. Karabet and S. Hashem, *Damascus University Journal for the Basic Sciences*, 2010, **25**(No.2), 19.
- 15 J. W. Hodgson, W. J. Bashe, T. V. Baker, *US-EPA Method 550.1: Determination of Polycyclic Aromatic Hydrocarbons in Drinking Water by Liquid-Liquid Extraction and HPLC with Coupled Ultraviolet and Fluorescence Detection*. U.S. EPA, USA, 1990.
- 16 Application Note 213, *Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Tap Water Using On-Line Solid-Phase Extraction Followed by HPLC with UV and Fluorescence Detections*. Dionex Corporation, USA, 2008.
- 17 M. Emamjomeh and M. Sivakumar, *J. Environ. Manage.*, 2009, **90**, 1663.
- 18 O. Abdelwahab, N. K. Amin and E.-s. Z. El-Ashtoukhy, *J. Hazard. Mater.*, 2009, **163**, 711.
- 19 N. Adhoum and L. Monser, *Chem. Eng. Process.*, 2004, **43**, 1281.
- 20 J. Zhu, H. Zhao and J. Ni, *Sep. Purif. Technol.*, 2007, **56**, 184.
- 21 Z. R. Guo, G. Zhang, J. Fang and X. Dou, *J. Clean. Prod.*, 2006, **14**, 75.
- 22 A. K. Golder, A. N. Samanta and S. Ray, *Sep. Purif. Technol.*, 2007, **53**, 33.
- 23 G. Chen, *Sep. Purif. Technol.*, 2004, **38**, 11.
- 24 M. Kobya, E. Demirbas, O. T. Can and M. Bayramoglu, *J. Hazard. Mater.*, 2006, **132**, 183.
- 25 R. E. Bruns, I. S. Scarminio, and B. de Barros Neto, *Statistical design - Chemometrics (Data Handling in Science and Technology)*, Elsevier B.V, Amsterdam, 2006, Vol. 25, pp 5–8.
- 26 H. Guo, and A. Mettas, *Design of Experiments and Data Analysis*. 2010 Reliability and Maintainability Symposium, San Jose, CA, USA, 2010.