

Electrocoagulation and nanofiltration integrated process application in purification of bilge water using response surface methodology

Ceyhun Akarsu, Yasin Ozay, Nadir Dizge, H. Elif Gulsen, Hasan Ates, Belgin Gozmen and Meral Turabik

ABSTRACT

Marine pollution has been considered an increasing problem because of the increase in sea transportation day by day. Therefore, a large volume of bilge water which contains petroleum, oil and hydrocarbons in high concentrations is generated from all types of ships. In this study, treatment of bilge water by electrocoagulation/electroflotation and nanofiltration integrated process is investigated as a function of voltage, time, and initial pH with aluminum electrode as both anode and cathode. Moreover, a commercial NF270 flat-sheet membrane was also used for further purification. Box–Behnken design combined with response surface methodology was used to study the response pattern and determine the optimum conditions for maximum chemical oxygen demand (COD) removal and minimum metal ion contents of bilge water. Three independent variables, namely voltage (5–15 V), initial pH (4.5–8.0) and time (30–90 min) were transformed to coded values. The COD removal percent, UV absorbance at 254 nm, pH value (after treatment), and concentration of metal ions (Ti, As, Cu, Cr, Zn, Sr, Mo) were obtained as responses. Analysis of variance results showed that all the models were significant except for Zn ($P > 0.05$), because the calculated F values for these models were less than the critical F value for the considered probability ($P = 0.05$). The obtained R^2 and R^2_{adj} values signified the correlation between the experimental data and predicted responses: except for the model of Zn concentration after treatment, the high R^2 values showed the goodness of fit of the model. While the increase in the applied voltage showed negative effects, the increases in time and pH showed a positive effect on COD removal efficiency; also the most effective linear term was found as time. A positive sign of the interactive coefficients of the voltage–time and pH–time systems indicated synergistic effect on COD removal efficiency, whereas interaction between voltage and pH showed an antagonistic effect.

Key words | bilge water, electrochemical treatment, integrated system, membrane processes, response surface methodology (RSM)

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INTRODUCTION

Marine pollution from ships can be caused by oil spills as a result of accidents, ship paints and ballast water but mostly arises from discharge of solid and liquid waste into the sea. Ships have to store their waste, which is forbidden from being discharged into the sea, and must use the waste reception facilities in ports. Therefore, ports must keep these waste reception facilities to avoid environmental problems (Wilhelmsson *et al.* 2013). As is known, the International Maritime Organization

prohibited the direct discharge of bilge water according to the regulations of the International Convention for the Prevention of Pollution from Ships (MARPOL 73/78) which was introduced in 1973.

Bilge water is a complex and corrosive shipboard wastewater produce from machinery leakage and fresh water wash downs that contains lubricating oils, hydrocarbons, fuel, hydraulic oils, and cleaning agents (Peng *et al.* 2005; Sun *et al.* 2010; Körbahti & Artut 2010).

Bilge water is a two-phase dispersive system and water is the continuous phase while oil is the dispersed phase. Oil droplets, also namely emulsions, are known as stable oil-in-water (o = w) solutions which disperse in water phase. The water phase contains hydrocarbon traces as well as metallic impurities such as zinc, lead, and vanadium and therefore it requires additional purification treatment (Carlesi *et al.* 2015). So far, various methods such as wet air oxidation (Bernal *et al.* 1999), ultrafiltration (UF) (Tremblay *et al.* 2002), UF/photocatalytic oxidation (Karakulski *et al.* 1998), UF/membrane distillation (MD) (Gryta *et al.* 2001), biotechnological (Caplan *et al.* 2000), electrocoagulation (EC) (Woytowich *et al.* 1993; Asselin *et al.* 2008), and electrochemical oxidation/degradation (Körbahti & Artut 2010) methods have been applied for bilge water treatment. However, an effective universal method for oily bilge water treatment was not reported until the beginning of this century (Caplan *et al.* 2000; Gryta *et al.* 2001).

The EC process can be used for treatment of different kinds of wastewater such as domestic, textile, slaughterhouse, leachate, tannery, dairy, pulp and paper, and mining wastewater. Heavy metal, grease, organic matter, color, suspended solids, nitrate, phenol, arsenic, etc. can be removed by using EC process (Kuokkanen *et al.* 2013). EC/electroflotation method is the most commonly used for bilge water treatment in the literature. The restrictive effect for electrochemical process is the type of electrode. The sacrificial electrode reacts with water and is converted to their metal hydroxide forms during the process which absorbs contaminants (Canizares *et al.* 2005). During this process, very small gas bubbles also rise throughout the water surface as a result of electrochemical reactions on electrodes. Thus, electroflotation is occurred at the same time with EC process (Dimitrijević *et al.* 2013).

Among the available physicochemical treatment methods, membrane processes have been found to be effective for the treatment of wastewater. Membranes are capable of achieving strict discharge criteria, while providing high efficiency, easy operation and a low site 'footprint' (Fu & Wang 2011; Mullett *et al.* 2014). Membrane treatment by reverse osmosis (RO) and nanofiltration (NF) is also a promising strategy for heavy metal removal. NF, in common with most other membrane processes, can be used to further increase the quality of the wastewater.

Chemical or physical classical processes such as flotation, separation by centrifuge, filtration, and coagulation are widely used for the aim of the purification of bilge water. On the other hand, the physical methods may fail to satisfy the desired treatment levels because of emulsified

oil in bilge water. Therefore, it is important to improve advanced wastewater treatment technologies.

Körbahti and Artut studied the feasibility of treating bilge water using an upflow electrochemical reactor in order to design a compact onboard wastewater treatment system. The authors stated that the highest removal efficiencies were obtained at optimum 390 min retention time and 480 min reaction time with the synthetic bilge water. Under response surface optimized conditions, the responses were estimated as: 90% chemical oxygen demand (COD) removal, 97% turbidity removal, and outlet pH value of 8.1 (Körbahti & Artut 2010).

Ulucan & Kurt (2015) investigated treatability of bilge water by EC/electroflotation process using aluminum and iron electrodes in accordance with pH, time, temperature and current density. The authors reported that the aluminum electrodes were more efficient than iron electrodes when compared with the EC/electroflotation process in a short period of time of 10 min. COD and oil-grease removal values were obtained as 64.8% and 57% for Al electrode and 36.2% and 12.5% for Fe electrode, respectively.

Peng *et al.* (2005) and Tremblay *et al.* (2002) indicated that the microfiltration of bilge water in a pre-treatment stage is a desirable application because used oils and coarse particles can block the feed channels of UF spiral and hollow fiber modules. Furthermore, Caplan *et al.* (2000) reported that membranes must be replaced when fouled so seriously, and fouling causes rise of the price in addition to high capital and maintenance costs.

Karakulski *et al.* (1998) investigated the purification of bilge water by a combination of UF and photocatalytic integrated processes. They performed further treatment of UF permeate by heterogeneous photocatalytic oxidation using TiO₂-based catalyst in order to remove the residual oil.

Woytowich *et al.* (1993) studied the treatment of ship bilge water contaminated with high concentrations of oil, suspended solids, and heavy metals in a continuous EC system using two different electrodes of iron and aluminum. They reported that the EC treatment was effective in removing heavy metals and in destabilizing oil emulsions.

Another research study was presented by Rincon and La Motta (Rincón & La Motta 2014). They used EC method to treat bilge water, with a focus on oily emulsions and heavy metal (copper, nickel and zinc) removal. Aluminum and stainless steel were used as anode and cathode, respectively. Bilge water contained 5,000 mg/L of oil and grease, 5 mg/L of copper, 1.5 mg/L of nickel, and 2.5 mg/L of zinc. The experimental results show that EC is very efficient for removing of oil-grease and heavy metal. Oil and grease

concentration were less than 10 mg/L and 99% zinc, 70% copper, and 70% nickel removal efficiency were also achieved.

Purification of oily wastewater from wastewater, e.g. bilge water originating from an engine-room, with the EC or membrane techniques was investigated individually in the relevant researches. However, there are a limited number of studies regarding the purification of bilge water used integrated processes. Therefore, there is an urgent need to develop an effective process to treat oily bilge water. Until now, use of integrated processes such as UF/MD (Gryta *et al.* 2001), UF/RO (Tomaszewska *et al.* 2005), biofilm/membrane bioreactor (Sun *et al.* 2010), and photo-reactor/ultrafiltration systems has been reported in the literature. Especially, 'oily and sticky' substances in the bilge water can cause serious membrane blocking and fouling when the membrane is used alone. Therefore, it is necessary to apply a preliminary treatment to prevent membrane fouling and increase flux. The novelty of this study is the usage of EC system as a pre-treatment method for eliminating 'oily and sticky' substances from the wastewater. The response surface methodology was used to determine optimum operation conditions of EC process such as voltage, time, and initial pH with aluminum electrode as both anode and cathode. Then the EC reactor was run once again under these optimum conditions and effluent was passed from the nanofiltration membrane (NF270). COD and heavy metal (Ti, Cr, Cu, As, Sr, Mo, Pb, Zn) removal efficiencies were measured. However, pH and UV₂₅₄ were also analyzed.

MATERIALS AND METHOD

Bilge water

Bilge water used for this study was supplied by Mersin Waste Receiving Facilities. Samples were collected in polypropylene bottles, and kept at 4 °C, until further use. Characteristics of the bilge water can be seen in Table 1.

Bilge water purification with electro-reactor and operation

EC experiments were carried out in a cylindrical reactor made of glass material (10.5 cm (radius) × 14.5 cm (deep)). Aluminum electrodes (anode and cathode) were used (6 cm wide × 9 cm high) and both electrodes have the same dimensions with 1 mm as thickness. For each

Table 1 | The composition of bilge water

Parameters	Value
pH	8.0
Conductivity (μS/cm)	1,370
Absorbance at UV ₂₅₄	0.428
COD (mg/L)	423
Cr (ppb)	26.19
Cu (ppb)	12.76
As (ppb)	4.644
Sr (ppb)	640.8
Mo (ppb)	13.07
Pb (ppb)	4.938
Ti (ppb)	209.3
Zn (ppb)	67.99

electrode, the immersed (active) surface was 54 cm² and the distance between the electrodes was fixed at 8 cm. Mixing in the reactor was achieved by a Teflon-covered stirring bar installed at the bottom of the reactor. The volume of the electrochemical reactor was 1,000 mL, and the net reaction volume was 800 mL. New electrodes were used for each experiment. The anode and cathode sets were connected to the positive and negative outlets of a DC power source (AATech ADC-3303D) with a maximum current rating of 30 A. However, several experiments were performed in order to obtain the best COD removal efficiency at the lowest energy consumption as well as operation costs. Table 2 shows a list of the experiments.

Before EC tests and in order to avoid any interference, aluminum electrodes were prepared as follows: (1) rinse with distilled water, (2) clean in sodium hydroxide solution (10%), (3) rinse with distilled water, (4) dry with absorptive paper. After the introduction of bilge water solution to the reactor, the pH was adjusted at its selected initial value (4, 6.25 or 8) using HCl or NaOH (1 N) solutions.

The analyses were done by the procedures outlined in *Standard Methods for the Examination of Water and Wastewater* (APHA 1992). A pH-meter (Thermo Scientific Orion 3-star) equipped with a Cole-Micrometer electrode was utilized for pH measurements. The conductivity and temperature were measured using a conductivity meter (inoLab Cond Level 1). The samples, vacuum-filtered through a Whatman 934AH membrane (pore diameter = 0.45 μm) filter, were immediately acidified with 0.2% sulfuric acid and preserved at 4 °C until COD analysis. The metal analysis was carried out using inductively coupled plasma mass

Table 2 | Box–Behnken design for purification of bilge water and observed responses

Run	Actual (coded) levels			Y ₁ R _{cod} (%)	Y ₂ UV ₂₅₄	Y ₃ pH	Y ₄ Ti (ppb)	Y ₅ Cr (ppb)	Y ₆ Cu (ppb)	Y ₇ As (ppb)	Y ₈ Sr (ppb)	Y ₉ Mo (ppb)	Y ₁₀ Pb (ppb)	Y ₁₁ Zn (ppb)
	X ₁ V	X ₂ pH	X ₃ t											
0	–	–	–	–	0.428	8.0	209.3	26.2	12.8	4.6	640.8	13.1	4.9	68
1	5 (–1)	6.25 (0)	90 (+1)	31	0.241	4.46	161.0	16.4	9.3	3.2	557.3	9.2	4.7	60
2	5 (–1)	8.00 (+1)	60 (0)	31	0.296	6.42	157.1	17.7	9.5	3.4	535.8	9.2	4.4	12
3	5 (–1)	6.25 (0)	30 (–1)	33	0.256	5.36	170.3	20.9	10.8	4.0	590.5	9.4	4.7	52
4	5 (–1)	4.50 (–1)	60 (0)	29	0.254	4.42	198.5	24.1	10.9	4.3	635.2	10.1	4.6	66
5	10 (0)	6.25 (0)	60 (0)	40	0.289	5.08	184.7	15.3	11.8	3.5	640.6	8.9	4.9	39
6	10 (0)	8.00 (+1)	30 (–1)	35	0.286	6.44	173.0	19.4	11.5	3.4	612.2	12.0	4.7	46
7	10 (0)	6.25 (0)	60 (0)	31	0.263	5.57	193.6	15.8	11.2	3.5	603.2	9.1	5.8	53
8	10 (0)	6.25 (0)	60 (0)	37	0.228	4.64	183.3	17.6	10.6	4.1	601.2	8.9	4.8	51
9	10 (0)	8.00 (+1)	90 (+1)	52	0.221	5.19	147.5	16.5	8.0	3.3	528.7	9.7	4.9	48
10	10 (0)	6.25 (0)	60 (0)	36	0.262	5.10	181.2	15.2	11.5	3.7	628.3	9.0	4.9	46
11	10 (0)	4.50 (–1)	30 (–1)	37	0.263	4.64	204.3	11.2	9.9	3.6	640.1	9.1	4.1	29
12	10 (0)	4.50 (–1)	90 (+1)	39	0.225	4.73	182.1	16.2	9.2	3.7	640.0	10.9	4.8	49
13	10 (0)	6.25 (0)	60 (0)	36	0.244	4.87	191.4	16.3	11.1	3.2	598.7	8.8	4.5	50
14	15 (+1)	4.50 (–1)	60 (0)	31	0.288	4.58	178.4	15.7	11.2	4.1	631.1	9.4	4.9	45
15	15 (+1)	6.25 (0)	90 (+1)	33	0.161	4.97	161.6	22.2	9.0	3.5	636.7	9.0	4.2	64
16	15 (+1)	6.25 (0)	30 (–1)	21	0.258	5.04	184.9	15.7	8.1	3.9	630.1	9.5	4.2	59
17	15 (+1)	8.00 (+1)	60 (0)	31	0.316	7.11	156.7	26.3	10.4	3.0	604.2	9.4	4.8	46

spectrometry (Agilent, 7500ce Octopole Reaction System model). The dissolved metals were filtered using Whatman 934AH membrane, followed by acidification with nitric acid (5%, w/v), and preserved at 4 °C, until further analysis (APHA 1992).

Samples were taken for analysis after the end of experiment. After 30 min of sedimentation, a 50 mL sample was taken from the settled solution by pipetting. Conductivity and pH were immediately measured. All the experiments were conducted at ambient room temperature (25 ± 1 °C).

Bilge water purification with NF

Commercial NF270 flat-sheet membrane was used for further purification. Its principal characteristics supplied by the manufacturer DowChemical are summarized as follows: molecular weight cutoff ≈ 200–400 Daltons; charge: negative; max. operating temperature: 45 °C; pH range: 2–11.

The attenuated total reflection–Fourier transform infrared (ATR-FTIR) (Perkin Elmer) analyses were obtained in order to verify the functional groups on NF270 membrane surfaces before and after EC pre-treatment.

Dead-end filtration experimental procedure

The NF270 membrane performance was tested by a stainless steel dead-end flat-sheet membrane module (Sterlitech HP4750) which has an operating volume of 300 mL with a filtration area of 14.6 cm² and an operating pressure of 8 bar. The module has a circular flat-sheet cell with the two halves fastened together using bolts, and it has a porous support to allow permeation. Nitrogen gas (N₂) was used to apply pressure throughout all experiments, with a maximum working pressure of 69 bar. Additionally, the wastewater was stirred at a constant rate of 500 rpm to homogenize the feed samples. A schematic diagram of the experimental setup is shown in Figure 1.

The permeation flux was measured by collecting the filtered water in the determined intervals and calculated using the following Equation (1):

$$J = \frac{V}{A \times \Delta t} \quad (1)$$

where J is permeate flux (L/m²h); V the volume of permeate pure water (L), A the effective area of the membrane (m²), and Δt the permeation time (h).

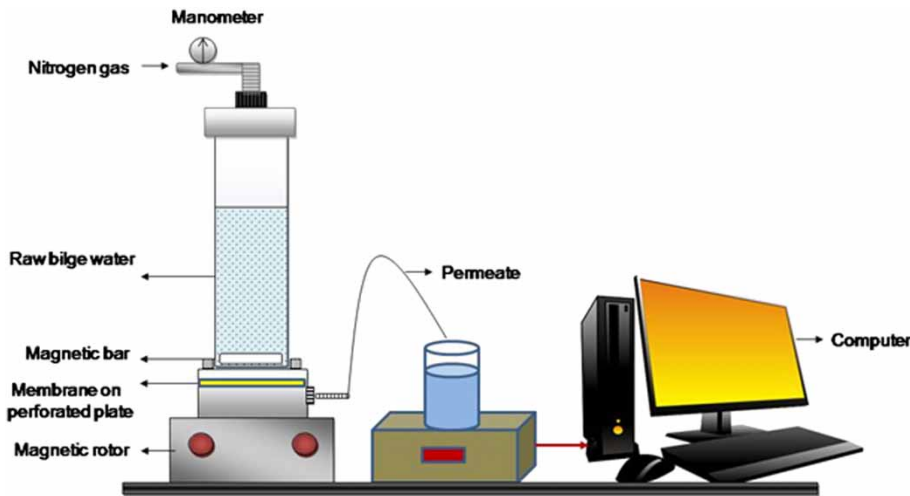


Figure 1 | Schematic diagram of the dead-end NF experimental setup.

Experimental design

The statistical software Design Expert v.8.0.4 (Stat-Ease Inc., Germany) was used for the experimental design, analysis and optimization. The Box–Behnken design (BBD) was chosen because it is more efficient and economical than the other 3^k designs, especially for a large number of variables (Bezerra et al. 2008). In total 17 runs were performed in duplicate according to the BBD matrix with three independent variables at three levels ($-1, 0, +1$), shown in Table 2, and average values were used in data analysis. The number of runs was calculated by using the following formula as Equation (2):

$$N = k^2 + k + cp \quad (2)$$

where k is the factor number and cp is the replicate number of the central point. This design was used to study the response pattern and determine the optimum conditions for maximum COD removal and minimum metal ion contents of bilge water. While voltage (X_1), initial pH (X_2) and time (X_3) were the three independent variables, the COD removal efficiency, UV absorbance at 254 nm, pH value (after treatment), and the concentration of metal ions (Ti, As, Cu, Cr, Zn, Sr, Mo) were obtained from responses. The regression model was obtained using Design Expert v.8.0.4. In the optimization process, the responses can be simply related to the chosen factors by linear or quadratic models. A quadratic model, which also includes the linear model, is given below as Equation (3):

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (3)$$

where Y is the predicted response, X_i indicate the independent variables, and β_0 , β_i , β_{ii} and β_{ij} are the constant coefficient, the linear coefficient, the quadratic coefficient and the interaction coefficient, respectively.

RESULTS AND DISCUSSION

Bilge water purification with electro-reactor

In order to ensure the statistical significance of the models employed for fitting the experimental data at a 95% confidence level, the models were tested by analysis of variance (ANOVA). On the basis of the experimental values, statistical testing was carried out using Fisher's test (F -test). The ANOVA results for suggested models in Table 3 showed the F values with a low probability value ($P < 0.05$). The F value is used to test the significance of adding new model terms to the existing ones. The P values were also used to check the significance of each coefficient and display the interaction pattern between the variables can be clearly seen from Table 3 that ANOVA results suggest that all the models were significant except for Zn ($P > 0.05$), because the calculated F values for these models were less than the critical F value ($F_{\text{table}} = F_{0.05, \text{df}, (n - (\text{df} + 1))}$ for the considered probability ($P = 0.05$).

The goodness of fit of the model was also tested by the correlation coefficient (R^2) and adjusted correlation coefficient (R_{adj}^2), chi-square (χ^2), the root mean square error of prediction (RMSEP) and the relative standard error of prediction (RSEP). The correlation coefficients indicate the reliability of the model. The obtained R^2 and R_{adj}^2 values signifying the correlation between the experimental data and predicted

Table 3 | ANOVA tables of the model equations

Source	Sum of squares	Df	Mean square	F value	F _{table}	Prob > F	R ² , R ² _{adj}	Adeq. Prec.	CV %	χ^2_{table} χ^2	RMSEP	RSEP%
R _{COD} % Model	554.91	9	61.66	5.48	3.68	0.0177	0.8757, 0.7158	10.8	9.8	16.92, 2.24	2.15	6.19
X _v	8.82	1		0.78		0.4054						
X _{pH}	21.13	1		1.88		0.2130						
X _t	105.13	1		9.34		0.0184						
X _v ²	291.11	1		25.87		0.0014						
X _{pH} ²	29.23	1		2.60		0.1511						
X _t ²	15.73	1		1.40		0.2752						
Residual	78.78	7	11.25									
Lack of fit	31.43	3	10.48	0.89		0.5208						
Pure error	47.35	4	11.84									
Cor total	633.68	16										
UV ₂₅₄ Model	0.016	6	2.6 × 10 ⁻³	5.27	3.22	0.0108	0.7597, 0.6154	8.7	8.7	12.59, 0.020	0.017	6.63
X _v	7.2 × 10 ⁻⁵	1		0.14		0.7117						
X _{pH}	9.9 × 10 ⁻⁴	1		1.99		0.1889						
X _t	5.8 × 10 ⁻³	1		11.60		0.0067						
X _{pH} ²	2.8 × 10 ⁻³	1		5.66		0.0387						
X _t ²	4.8 × 10 ⁻³	1		9.61		0.0112						
Residual	4.98 × 10 ⁻³	10	4.98 × 10 ⁻⁴									
Lack of fit	2.89 × 10 ⁻³	6	4.81 × 10 ⁻⁴	0.92		0.5602						
Pure error	2.10 × 10 ⁻³	4	5.24 × 10 ⁻⁴									
Cor total	0.021	16										
pH Model	6.47	3	2.16	9.44	3.41	0.0014	0.6853, 0.6127	9.6	9.2	7.82, 0.55	0.42	7.94
X _v	0.14	1		0.59		0.4554						
X _{pH}	5.76	1		25.24		0.0002						
X _t	0.57	1		2.48		0.1391						
Residual	2.97	13	0.23									
Lack of fit	2.49	9	0.28	2.34		0.2146						
Pure error	0.47	4	0.12									
Cor total	9.43	16										
Ti Model	3,825.63	9	425.07	9.78	3.68	0.0033	0.9263, 0.8316	10.3	3.7	16.92, 1.74	4.23	2.38
X _v	3.51	1		0.081		0.7844						
X _{pH}	2,080.13	1		47.87		0.0002						
X _t	806.01	1		18.55		0.0035						
X _v ²	483.87	1		11.13		0.0125						
X _{pH} ²	49.97	1		1.15		0.3191						
X _t ²	187.32	1		4.31		0.0765						
Residual	304.20	7	43.46									
Lack of fit	188.79	3	62.93	2.18								

(continued)

Table 3 | continued

Source	Sum of squares	Df	Mean square	F value	F _{table}	Prob > F	R ² , R ² _{adj}	Adeq. Prec.	CV %	χ^2_{table} χ^2	RMSEP	RSEP%
Pure error	115.41	4	28.85									
Cor total	4,129.84	16										
As Model	1.03	3	0.34	3.72	3.41	0.0393	0.4623, 0.3382	6.4	8.4	7.82, 0.32	0.27	7.34
X _v	0.024	1		0.26		0.6189						
X _{pH}	0.83	1		9.03		0.0101						
X _t	0.19	1		2.04		0.1764						
Residual	1.20	13	0.093									
Lack of fit	0.74	9	0.082	0.71		0.6915						
Pure error	0.46	4	0.12									
Cor total	2.24	16										
Cr Model	216.59	9	24.07	28.22	3.68	0.0001	0.9732, 0.9387	21.4	5.2	16.92, 0.36	0.59	3.26
X _v	0.11	1		0.13		0.7523						
X _{pH}	19.88	1		23.31		0.0019						
X _t	2.14	1		2.51		0.1570						
X _v ²	65.81	1		77.18		< 0.0001						
X _{pH} ²	3.91	1		4.58		0.0695						
X _t ²	5.75	1		6.75		0.0355						
Residual	5.97	7	0.85									
Lack of fit	2.34	3	0.78	0.86		0.5300						
Pure error	3.63	4	0.91									
Cor total	222.55	16										
Cu Model	17.29	7	2.47	3.73	3.29	0.0352	0.7439, 0.5447	5.3	8.0	14.07, 0.61	0.59	5.74
X _v	0.40	1		0.61		0.4564						
X _{pH}	0.44	1		0.66		0.4372						
X _t	2.86	1		4.32		0.0675						
X _v ²	1.41	1		2.13		0.1788						
X _t ²	8.33	1		12.60		0.0062						
Residual	5.95	9	0.66									
Lack of fit	5.01	5	1.00	4.24		0.0933						
Pure error	0.94	4	0.24									
Cor total	23.24	16										
Sr Model	17,978.11	6	2,996.35	11.21	3.22	0.0006	0.8705, 0.7928	10.9	2.7	12.59, 4.40	12.54	2.06
X _v	4,199.86	1		15.71		0.0027						
X _{pH}	8,811.28	1		32.95		0.0002						
X _t	1,518.01	1		5.68		0.0384						
Residual	2,673.89	10	267.39									
Lack of fit	1,248.07	6	208.01	0.58		0.7356						
Pure error	1,425.82	4	356.45									

(continued)

Table 3 | continued

Source	Sum of squares	Df	Mean square	F value	F _{table}	Prob > F	R ² , R _{adj} ²	Adeq. Prec.	CV %	χ ² _{table} χ ²	RMSEP	RSEP%
Cor total	2,0652.00	16										
Mo Model	10.11	9	1.12	8.85	3.68	0.0045	0.9191, 0.8150	10.2	3.8	16.92, 0.09	0.23	2.40
X _v	0.080	1		0.63		0.4519						
X _{pH}	0.10	1		0.82		0.3951						
X _t	0.15	1		1.18		0.3138						
X _v ²	0.33	1		2.59		0.1516						
X _{pH} ²	3.22	1		25.50		0.0015						
X _t ²	1.61	1		12.79		0.0090						
Residual	0.89	7	0.13									
Lack of fit	0.82	3	0.27	16.51		0.0102						
Pure error	0.064	4	0.017									
Cor total	11.00	16										
Zn Model	1,737.64	6	289.61	3.11	3.22	0.0550	0.6510, 0.4416	7.3	20.2	12.59, 22.26	7.40	14.97
X _v	68.39	1		0.73		0.4121						
X _{pH}	162.99	1		1.75		0.2158						
X _t	160.74	1		1.72		0.2187						
X _{pH} ²	445.31	1		4.77		0.0539						
X _t ²	158.54	1		1.70		0.2217						
Residual	931.62	10	93.16									
Lack of fit	797.91	6	132.99	3.98		0.1012						
Pure error	133.71	4	33.43									
Cor total	2,669.26	16										

DG: degrees of freedom; Adeq. Prec.: adequate precision; CV: coefficient of variation.

responses are given for each model in Table 3. Except for the model of Zn concentration after treatment, the high R² values showed the goodness of fit of the model. The actual and predicted COD removal (%) and Zn value are given in Figure 2 to show tendency in the linear regression fit.

When chi-square test was applied to indicate the goodness of fit of the model, RMSEP and RSEP values were used to evaluate the predictive ability of the selected model (Gozmen et al. 2013). Chi-square, RMSEP and RSEP were calculated as given in previous publications (Perry & Green 1997; Singh et al. 2011; Gozmen et al. 2013; Tak et al. 2015).

It is desirable for the chi-square values obtained for the responses to be lower than the tabulated values (Table 3). This result demonstrated that there was no significant difference between the experimental data and model response except for Zn. RMSEP and RSEP values were also calculated by using Microsoft Excel 2013 for each model and are given in Table 3. In this study involving three variables, the mathematical relationship of the responses of these coded

variables (X_v, X_{pH}, X_t) is given by their corresponding model equations (Equations (4)–(13)). Some models have been modified by removing the terms with high P value.

$$\begin{aligned} \text{Removal}_{\text{COD}} \% = & +35.98 - 1.05 X_V + 1.62 X_{pH} \\ & + 3.63 X_t - 0.65 X_V X_{pH} + 3.25 X_V X_t + 3.65 X_{pH} X_t \\ & - 8.31 X_V^2 + 2.64 X_{pH}^2 + 1.93 X_t^2 \end{aligned} \quad (4)$$

$$\begin{aligned} UV_{254} = & +0.26 - 3.0 \times 10^{-3} X_V + 0.011 X_{pH} - 0.027 X_t \\ & - 0.020 X_V X_t + 0.026 X_{pH}^2 - 0.034 X_t^2 \end{aligned} \quad (5)$$

$$\begin{aligned} Ti_{ppb} = & +186.84 - 0.66 X_V - 16.13 X_{pH} - 10.04 X_t \\ & + 4.92 X_V X_{pH} - 3.50 X_V X_t - 0.82 X_{pH} X_t - 10.72 X_V^2 \\ & - 3.44 X_{pH}^2 - 6.67 X_t^2 \end{aligned} \quad (6)$$

$$\begin{aligned} Cr_{ppb} = & +16.02 + 0.12 X_V + 1.58 X_{pH} + 0.52 X_t \\ & + 4.29 X_V X_{pH} + 2.75 X_V X_t - 1.98 X_{pH} X_t + 3.95 X_V^2 \\ & + 0.96 X_{pH}^2 - 1.17 X_t^2 \end{aligned} \quad (7)$$

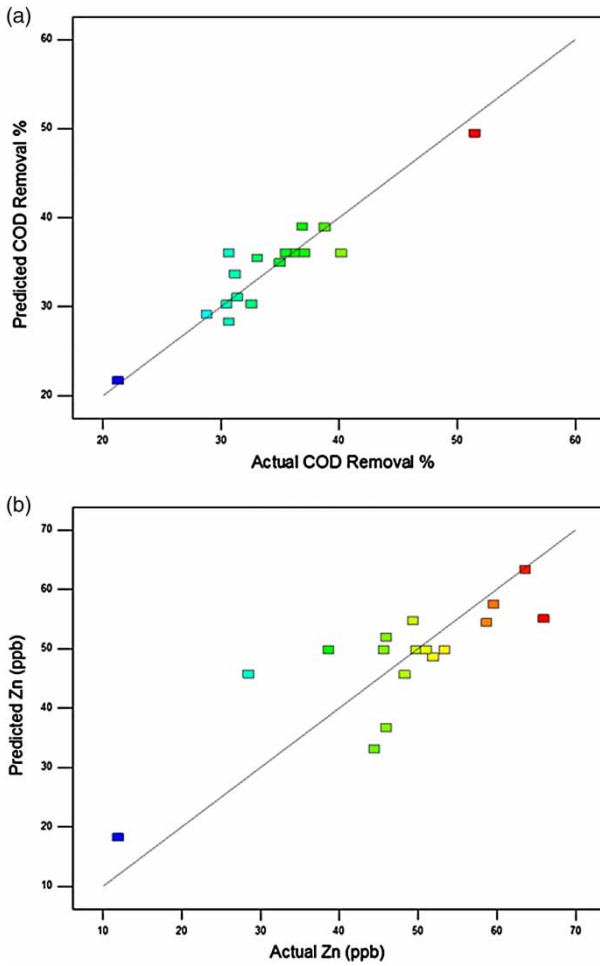


Figure 2 | Predicted vs. actual plot for (a) COD removal (%) and (b) Zn (ppb) efficiency.

$$As_{ppb} = +3.61 - 0.054 X_V - 0.32 X_{pH} - 0.15 X_t \quad (8)$$

$$Cu_{ppb} = +11.16 - 0.22 X_V - 0.23 X_{pH} - 0.60 X_t + 0.61 X_V X_t - 0.70 X_{pH} X_t - 0.58 X_V^2 - 1.40 X_t^2 \quad (9)$$

$$Sr_{ppb} = +606.70 + 22.91 X_V - 33.19 X_{pH} - 13.78 X_t + 18.12 X_V X_{pH} + 9.95 X_V X_t - 20.85 X_{pH} X_t \quad (10)$$

$$Mo_{ppb} = +8.92 - 0.10 X_V + 0.11 X_{pH} - 0.14 X_t + 0.21 X_V X_{pH} - 0.088 X_V X_t - 1.04 X_{pH} X_t - 0.28 X_V^2 + 0.87 X_{pH}^2 + 0.62 X_t^2 \quad (11)$$

$$Zn_{ppb} = +49.78 + 2.92 X_V - 4.51 X_{pH} + 4.48 X_t + 13.89 X_V X_{pH} - 10.27 X_{pH}^2 + 6.10 X_t^2 \quad (12)$$

$$pH = +5.21 + 0.13 X_V + 0.85 X_{pH} - 0.27 X_t \quad (13)$$

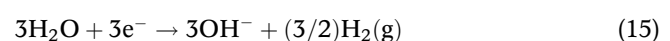
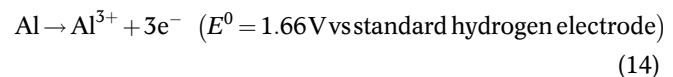
According to both magnitude and sign of the model coefficients (β_i), the linear, quadratic or interactive impact of each of the terms (voltage, pH and time) on the responses was estimated. Increasing of applied voltage showed negative effects; however, increasing of time and pH showed a positive effect on COD removal efficiency. The most effective linear term was found as time (X_t), which was more significant than its respective quadratic effect (X_t^2). A positive sign of the interactive coefficients of $X_V X_t$ and $X_{pH} X_t$ indicated synergistic effect on COD removal efficiency, when interaction between voltage and pH showed an antagonistic effect.

Three dimensional (3D) response surfaces provide a detailed view of the influences of the parameters and their interactions on the responses based on the model equations.

The effect of pH and potential on COD removal and absorbance at 254 nm

The interactive effect of applied potential and initial pH on the COD removal efficiency for bilge water while holding electrolysis time at 90 min is shown in Figure 3(a). It can clearly be observed that a rise in the initial pH was significantly effective for the removal of COD in bilge water. The high COD removal results were obtained when the initial pH of bilge water was held above 7.5. The optimum COD removal efficiency of 49.5% was achieved at 10.45 V potential and pH 8 after 90 min treatment. When other parameters were kept the same, the COD removal results were obtained at pH 4.5, 6.25 and 8 (original pH) as 39.1%, 40.9% and 48.9%, respectively. Ulucan & Kurt (2015) also showed that the best coagulation was obtained at pH 8, but they preferred to study at 6.8 (the original pH of sample).

The critical applied potential effect can be also observed in Figure 3(a). Even at the lowest pH of 4.5, raising the potential from 5 to 10.45 V resulted in a predicted COD removal efficiency increase of 11.4 percentage points (from 27.7 to 39.1%). At the optimum pH of 8, increasing the potential from 5 to 10.45 V resulted in increasing COD removal efficiency from 39.6% to 49.5%. However, with a further increase of the potential up to 15 V, COD removal efficiency reduced (42.7%). The soluble Al^{3+} ions were produced by anodic reaction in EC with Al electrode. At the same time the cathodic reaction produced hydroxide ions (Can et al. 2003; Daneshvar et al. 2007).



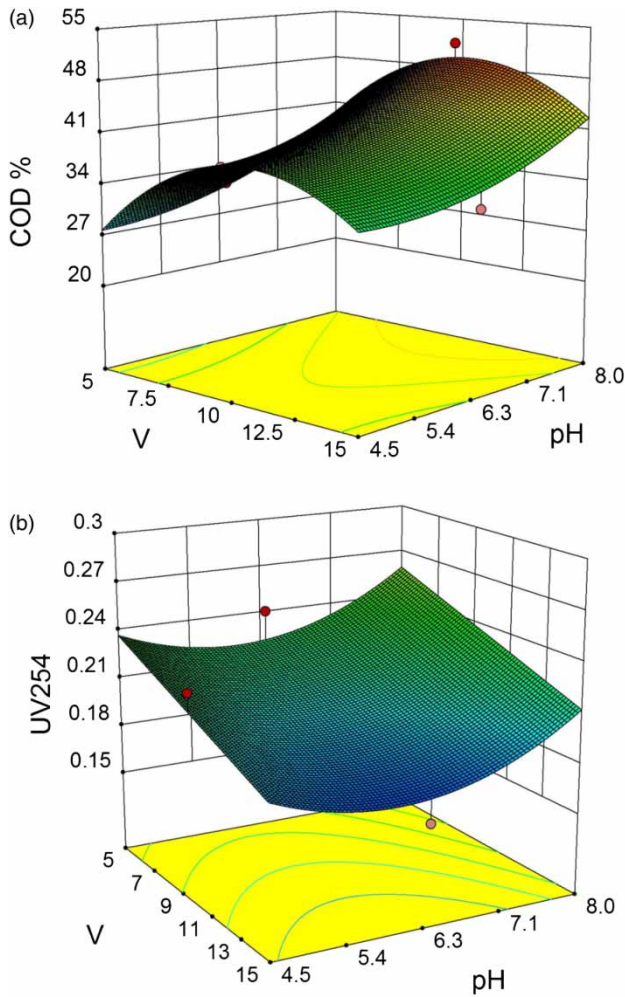


Figure 3 | Effect of voltage and pH on (a) COD removal efficiency and (b) UV_{254} ($t = 90$ min).

Al^{3+} ions were transformed into soluble monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$ and $Al(OH)_4^-$ depending on the pH range in the medium; $Al(OH)_4^-$ monomeric anion is predominant in alkaline medium (Martínez-Huitle & Brillas 2009). Although the concentration of $Al(OH)_3$ is independent from pH, the concentration of the remaining species decrease with increasing pH. However, the soluble monomeric and polymeric cations in solution are also converted into insoluble $Al(OH)_3$ flocs. The organic compounds in wastewater can be adsorbed on $Al(OH)_3$ flocs, because of large surface area, and separated from wastewater at $pH > 6.5$ (Can et al. 2003). Increase in applied potential resulted in the increase of Al^{3+} and, correspondingly, $Al(OH)_4^-$ production. Because of the negatively charged $Al(OH)_3$ with excess $Al(OH)_4^-$, the adsorption mechanism of the organic compounds was inhibited. Absorbance value at 254 nm may be an indicator of organic pollutant content of bilge water.

Interactive effects of potential and pH on the absorbance of bilge water at 254 nm is shown in Figure 3(b). The lowest absorbance was found as 0.174 at 15 V and pH 6 after 90 min treatments. It seems that the absorbance values at 254 nm increases above and below pH 6. However, the absorbance value measured at conditions which give maximum COD removal efficiency (10.45 V, pH 8 and 90 min) was obtained as 0.234. Besides coagulation of colloidal particles, the reduction/oxidation of organic impurities occurred at the cathode or anode. The fulfillment of this electrochemical reaction can be more effective around pH 6.

The effect of initial time and potential on COD removal and absorbance at 254 nm

The contour plots and the 3D views for the potential versus time, while holding pH at 8, are shown in Figure 4(a) and 4(b). At 10.45 V, with increasing the electrolysis time from

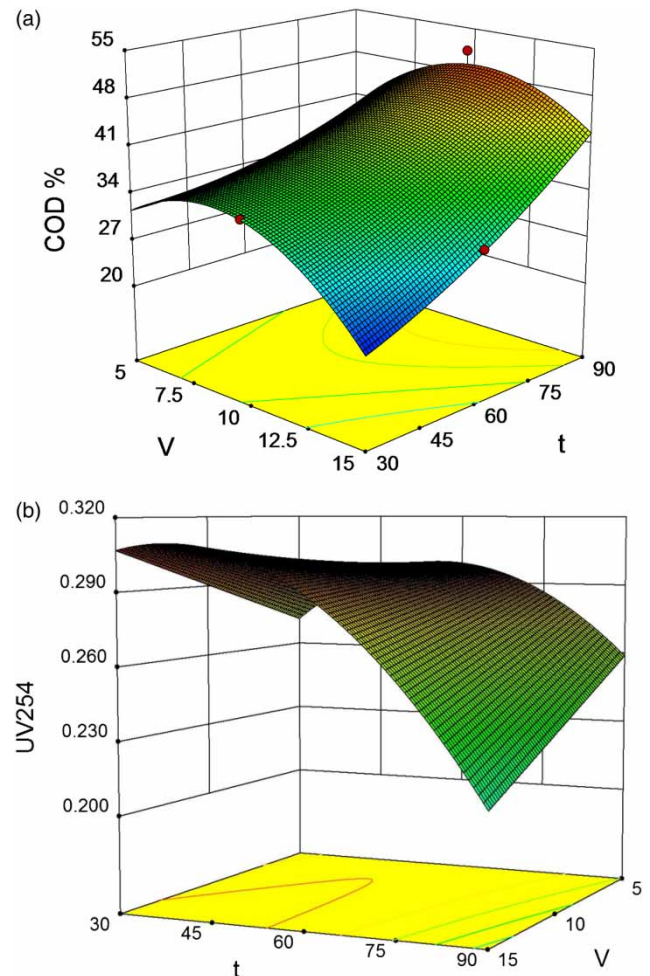


Figure 4 | Effect of voltage and time on (a) COD removal efficiency and (b) UV_{254} ($pH = 8$).

30 to 90 min, the COD removal increased from 34.4% to 49.5% (1.4-fold) in Figure 4(a). When the same increase in electrolysis time was examined at 15 V, COD removal efficiency increased from 21.6% to 42.7% (2-fold). The effect of time on the absorbance at 254 nm of bilge water is shown in Figure 4(b). When the electrolysis times were kept as 75 and 90 min at 15 V and pH 8, the absorbance of bilge water at 254 nm reduced from 0.428 (initial value) to 0.261 and 0.213, respectively. Even though 15 V potential caused absorbance decreases, COD removal efficiency at 15 V was lower than that of 10.45 V. The results clearly showed that application time needs to be increased for effective treatment.

The effect of initial pH and potential on effluent pH and conductivity

In order to determine the pH effect, a set of different experiments with varying initial pH value were carried out (pH 4.5, 6.25 and 8). The pH values of the sample were also measured after treatment and the interaction effects of initial pH and potential on pH (after treatment) are given in Figure 5(a). The pH of the solution reduced for all applied potentials after EC. For example, the pH values decreased from 8.00 to 5.81; from 6.25 to 4.96; and from 4.50 to 4.11 when applied potential was 10.45 V.

The conductivity value of bilge water before and after treatment at optimum conditions for COD removal was measured as 1,370 and 1,126 $\mu\text{S}/\text{cm}$, respectively. While the conductivity was unchanged with initial pH, it decreased to 1,068 and 1,174 $\mu\text{S}/\text{cm}$ at 5 and 15 V, respectively (Figure 5(b)).

The effect of potential and pH on removal of metal contents

In optimum conditions established for the highest COD removal, the removal efficiencies obtained for metal ions in bilge water after EC process are given Table 4.

When the removal of metal ions are examined individually, it will be seen that the maximum removal efficiency for each metal ions can be obtained under different conditions. However, the obtained removal efficiencies for metal ions were evaluated at optimum conditions for maximum COD removal efficiency.

After 90 min treatment of bilge water, the lowest Cr content was obtained at low potential (5 V) and high pH (8.0) as 12.73 ppb (Figure 6). For titanium, similar optimum conditions were observed with the optimum COD removal. It was seen that low potential applied for Cu removal was more effective. When 5, 9 and 10.45 V potential was

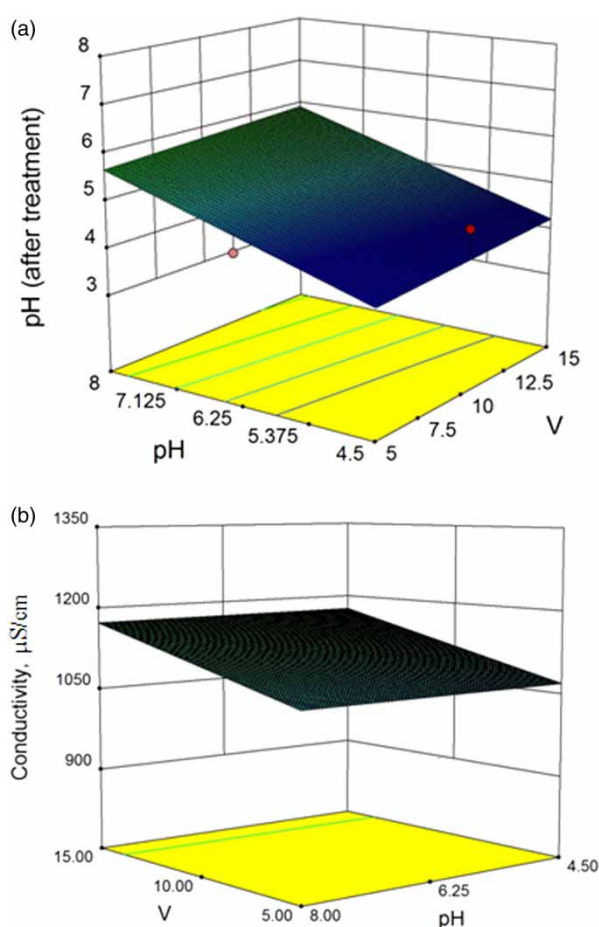


Figure 5 | Effect of initial pH and potential on (a) pH (after treatment) and (b) conductivity ($t = 90$ min).

Table 4 | The contents of bilge water after EC at optimum conditions ($V = 10.45$ V, $\text{pH} = 8$, $t = 90$ min, desirability = 0.981)

Parameters	Predicted value	Removal (%)
COD (mg/L)	213.45 ± 14.20	49.54
UV_{254}	0.234 ± 0.022	45.33
Ti (ppb)	149.71 ± 6.59	28.47
As (ppb)	3.13 ± 0.30	32.60
Cr (ppb)	16.60 ± 0.92	36.62
Cu (ppb)	8.26 ± 0.81	35.27
Sr (ppb)	544.00 ± 16.35	15.12
Mo (ppb)	9.36 ± 0.36	28.39
Zn (ppb)	47.14 ± 9.65	30.67
Pb (ppb)	4.64 ± 0.26	6.03

applied, Cu content were measured as 7.26, 8.13 and 8.26 ppb, respectively. The low Mo content was obtained as 8.79 ppb at 15 V and neutral pH, whereas the low As

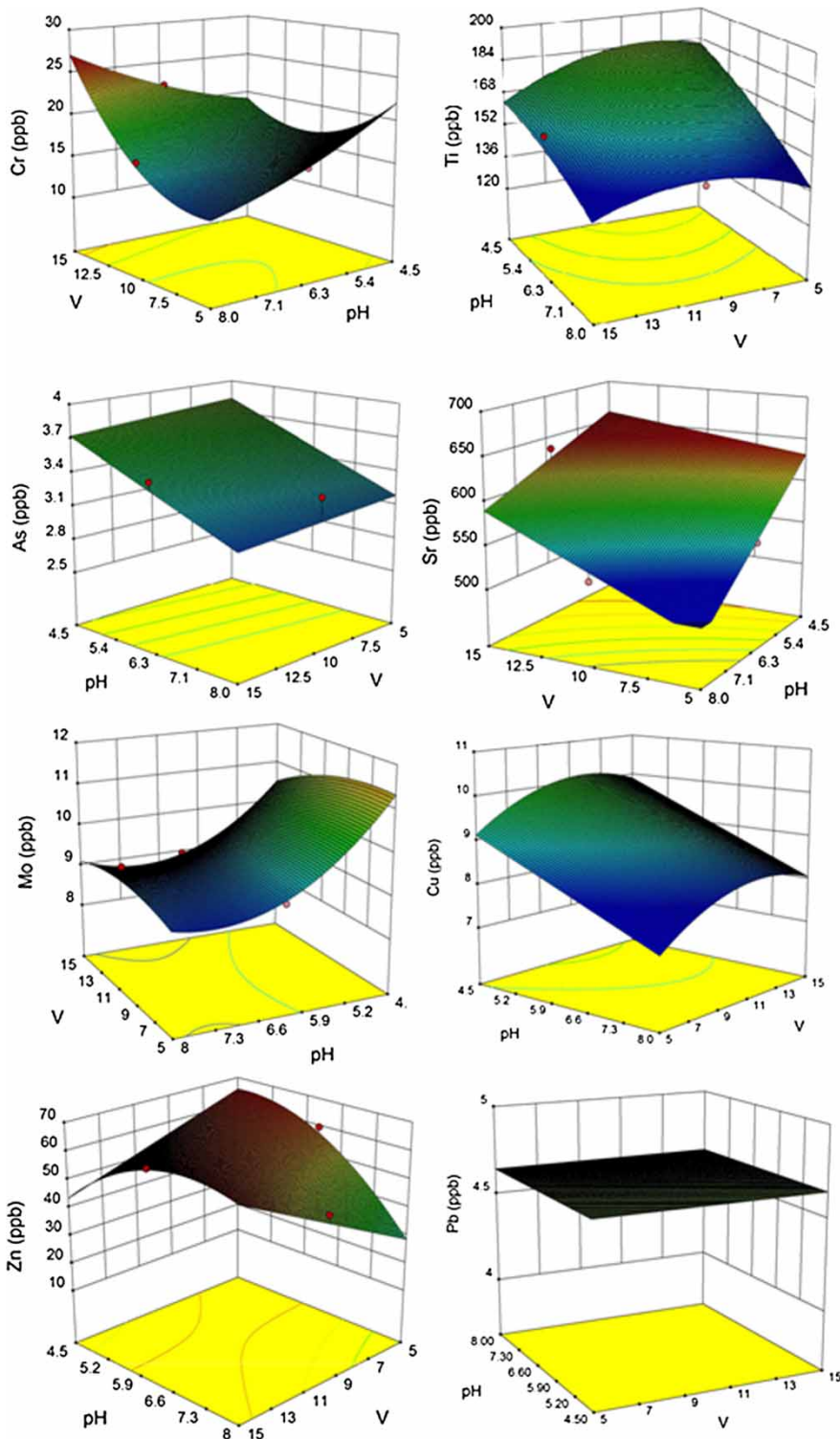


Figure 6 | Effect of voltage and pH on removal of metal contents of bilge water.

content was measured as 3.10 ppb at 15 V and pH 8. It was found that the Pb content was not influenced by potential and pH. For Sr and Zn, the lowest contents were measured

as 487.9 and 28.8 ppb at pH 8 and low potential (5 V), respectively. Hydroxide precipitation that is based on the low solubility of metal hydroxide at a specific pH value is

Table 5 | Model validation

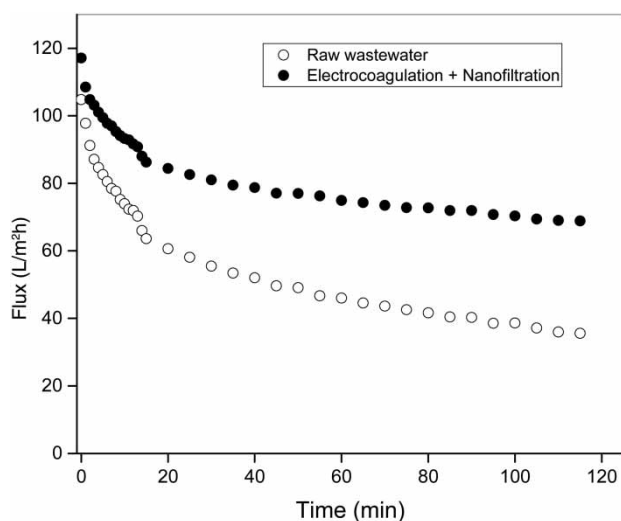
Parameters			COD removal (%)		UV ₂₅₄		pH	
X _v	X _{pH}	X _t	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.
8	6.0	80	36	37 (± 3.35)	0.277	0.232 (± 0.022)	4.86	4.86 (± 0.48)
12	8.0	75	40	43 (± 3.35)	0.330	0.269 (± 0.022)	6.35	5.89 (± 0.48)
9	5.5	45	33	35 (± 3.35)	0.257	0.257 (± 0.022)	5.79	4.96 (± 0.48)

the main process playing a key role in metal removal in EC (Martínez-Huitle & Brillas 2009; Kabdaşlı *et al.* 2012).

In the last step three additional experiments were carried out to test the validity of the model (Table 5). The obtained experimental results were very close to the theoretically predicted values. Additionally, the concentration of metal ions (Ti, As, Cu, Cr, Zn, Sr, Mo) was measured within the estimated limits (Table 5).

Bilge water purification with EC and NF integrated processes

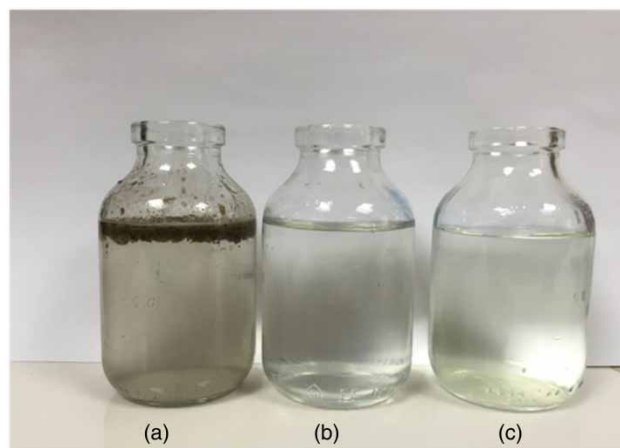
The results showed that EC process alone was not effective for COD removal and an integrated process was applied for further purification. Thus, purification of bilge water was performed in two stages using an integrated EC/NF system. Wastewater was treated by EC process and the resulting effluent was further purified by means of NF membrane. The changes of the permeate flux during 120 min of running the NF process with raw bilge water and pre-treated bilge water by EC containing 423 and 213 mg/L COD, respectively, are shown in Figure 7. A significant decrease

**Figure 7** | Flux decline versus time during NF purification of bilge water.

of the permeate flux was observed during the operation of the NF membrane without pre-treatment by EC. The initial value of the flux for wastewater with 423 mg/L COD content was 105 L/m²h and a decrease to 35 L/m²h after 120 min was observed. In the case of wastewater with a lower content of COD (213 mg/L) obtained after pre-treatment by EC, a decrease of the flux from 117 to 69 L.m².h⁻¹ was found. This variation of permeate flux during the treatment of wastewater was caused by membrane fouling. The permeate COD value of NF membrane was 300 and 110 mg/L for without and with pre-treatment with EC.

Tomaszewska *et al.* (2005) obtained the rejection of organic substances measured in total organic carbon (TOC), and oil as 23%, and 92%, respectively, in the integrated UF/RO bilge water treatment system.

Figure 8 presents the wastewater samples of raw bilge water, and NF permeates without pre-treatment and after EC pre-treatment. Clear water was obtained in both processes. Moreover, the clean membrane and filtrated bilge water membranes with and without pre-treatment by EC are shown in Figure 9. It can be clearly seen that the pre-treatment by EC prevents the membrane fouling. However,

**Figure 8** | Bilge water samples: (a) raw, (b) direct NF filtration, and (c) NF filtration after EC pre-treatment.

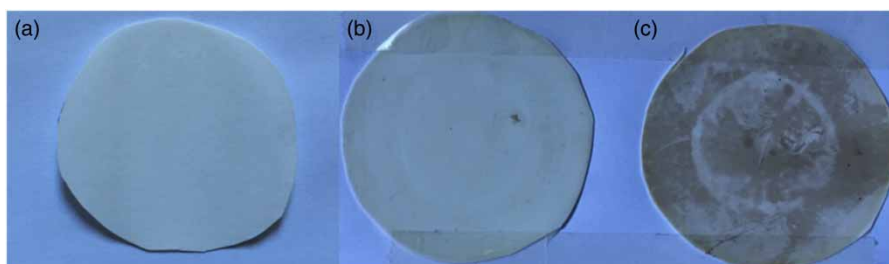


Figure 9 | Membrane (NF270) fouling: (a) neat membrane, (b) pre-treatment with EC, and (c) without pre-treatment.

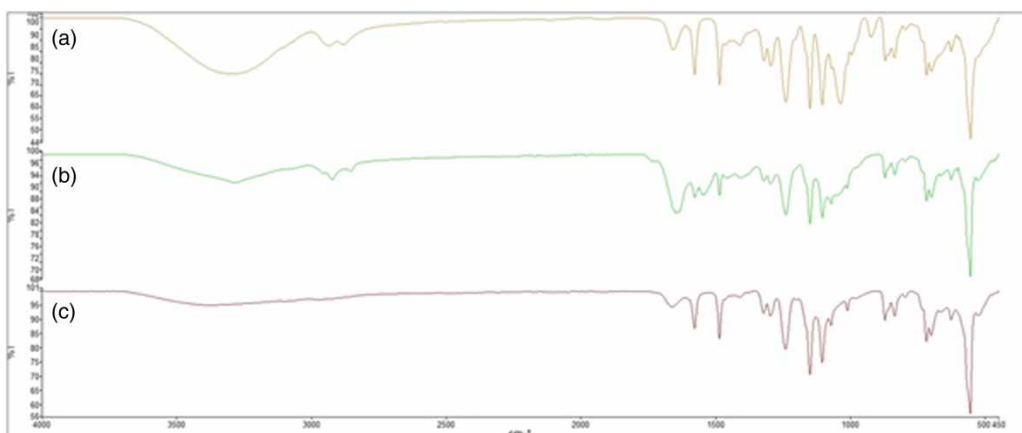


Figure 10 | The ATR-FTIR spectra of (a) neat membrane, (b) filtration before pre-treatment, and (c) filtration after pre-treatment with EC.

serious fouling of NF membrane without pre-treatment was observed.

The ATR-FTIR spectra were collected from 450 to 4,000 cm^{-1} wave numbers. The results presented in Figure 10 confirm a difference of the functional groups for the bilge water filtration using NF270 membrane before and after EC pre-treatment. The spectrum of neat NF270 membrane is shown in Figure 10(a). The small peaks between 3,000 cm^{-1} and 2,800 cm^{-1} are caused by stretching vibrations of aliphatic C-H bonds in $-\text{CH}_3$ and $-\text{CH}_2$ units (Silverstein *et al.* 2004). The region between 1,500 and 1,700 cm^{-1} can be attributed to stretching vibrations of carboxylate ions (1,580–1,660 cm^{-1}), the N-H stretching (amide I) (1,550–1,570 cm^{-1}) and C=O stretching (amide II) (1,690–1,650 cm^{-1}) of amide groups (Xue *et al.* 2009). Absorption in the band 1,660 cm^{-1} results from the C=C stretching in aromatic rings. The FTIR spectrum of the membrane fouled with bilge wastewater is shown in Figure 10(b). It can be seen that most of the sharp absorption peaks of the neat membrane are again visible: the peaks at 1,486, 1,544 and 1,578 cm^{-1} correspond to aromatic in-plane ring bend stretching vibrations of polysulfone (Tang *et al.* 2009), the two peaks

in the band 1,297–1,322 cm^{-1} are attributed to aromatic amines (Silverstein *et al.* 2004), and the peak around 1,150 cm^{-1} is attributed to symmetric SO_2 stretching vibrations of sulfone groups (Tang *et al.* 2009). This indicates that the fouling layer deposited on the membrane was thin and loose. The membrane filtered with pre-treated bilge water showed a clearer membrane surface with only minor hydrocarbon accumulation around the membrane, compared to the membrane without pre-treatment with EC.

The recommended EC/NF integrated process scheme is shown in Figure 11.

CONCLUSION

The electrochemical and membrane treatment of bilge water was investigated in an integrated reactor for designing a compact wastewater treatment system. The influence of voltage, time, and initial pH on the removal efficiencies of COD and metal ions was analyzed. COD removal efficiency was obtained as 52% in EC reactor at 90 min reaction time, pH 8, and 10 V potential. However, 62.38% UV_{254}

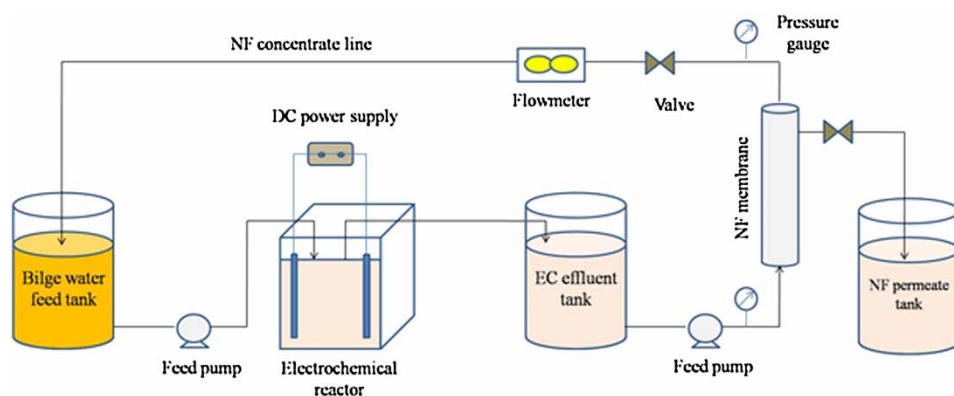


Figure 11 | A schematic plot of the EC/NF integrated system of the case study.

reduction was obtained at 90 min reaction time, pH 6.25, and 15 V potential.

The experimental data were analyzed using response surface methodology, and the highest removal efficiencies were estimated at optimum 90 min reaction time at pH 8 and 10.45 V potential. Under response surface optimized conditions, the responses were estimated as: 49.54% COD removal, 45.33% UV₂₅₄ reduction, and metal ion removal of 6.03–36.62%.

With EC treatment, a significant enhancement of NF membrane performance was achieved, and permeate quality was higher than that of the EC process. The total reduction of COD at the level of 74% results in COD content below 150 mg COD/L in the EC/NF integrated system, therefore permitting direct discharge according to the environmental regulations set in Turkey. Thus, bilge water pre-treated by EC provides a long protection for membrane fouling.

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First received 7 January 2016; accepted in revised form 24 March 2016. Available online 4 May 2016