

Understanding the natural organic matter removal mechanism from mine and surface water through the electrocoagulation method

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ABSTRACT

In the present study, the concept of 'Sample alteration of surface water' has been employed to improve the efficiency of the aluminum-based electrocoagulation (EC) treatment method for the removal of reactive fractions of natural organic matter (NOM) from chlorinated water.

The characteristics of surface water have been slightly modified by adding mine water in different ratios. The process has been optimized using the response surface methodology (RSM) considering pH, current density, mix ratio, and contact time as factors. At the optimized condition, the EC method has significantly reduced total organic carbon, dissolved organic carbon (DOC), and UV₂₅₄ absorbance values up to 24%, 27%, and 80%, respectively. The cumulative impact of sample alteration and EC method has exhibited outstanding coagulant activity in terms of UV₂₅₄ abs, DOC, turbidity, phenol, and absorbance slope index (ASI) as well. A decrease in ASI values indicated the reduction of trihalomethane's formation in water-containing chlorine. This was validated by reduced chlorine demand. It can be concluded that mixing mine water with surface water can be a feasible and efficient method for treating water with a high NOM content.

Key words | absorbance slope index, dissolved organic carbon, electrocoagulation, mine water, natural organic matter

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ABBREVIATIONS

ASI	absorbance slope index
DOC	dissolved organic carbon
EC	electrocoagulation
NOM	natural organic matter
RSM	response surface methodology
SUVA	specific UV absorbance
THMs	trihalomethanes
abs	absorbance

INTRODUCTION

According to the United Nations, 5 billion people might suffer from water shortages by 2050 due to climate

change, polluted supplies, and increased demand. It is reported that nearly half of the population in developing countries suffers from health problems associated with the lack of potable drinking water as well as the presence of microbial contamination in the water. During the 19th and early 20th centuries, occurrences of waterborne diseases (cholera, typhoid, dysentery, etc.) were common around the world, which led professionals to develop various water treatment methods, to minimize microbial contaminants, and to reduce the waterborne diseases. However, the treatment of surface water requires modern water treatment technologies, as it contains a high concentration of suspended particles, inorganic pollutants, and organic contaminants, mainly natural organic matter (NOM), which

doi: 10.2166/aqua.2019.167

leads to the formation of disinfection by-products (DBPs) during the chlorination process (Chu *et al.* 2011).

NOM is defined as a complex matrix of organic materials contributing >50% of total organic carbon in water (humic substances such as humic acids, fulvic acids, and phenolic compounds). The qualitative and quantitative properties of NOM vary considerably according to the origin of water (sharp *et al.* 2006). Recent studies have justified the theory that hydrophobic fractions of NOM play a crucial role in the formation of carcinogenic DBPs, primarily trihalomethanes (THMs) in chlorinated water (Wang *et al.* 2013). Hydrophilic NOM has a lower charge density than hydrophobic NOM and, therefore, is difficult to remove during coagulation (Priya *et al.* 2017). The phenolic group has been identified as an integral constituent of NOM, which leads to THMs formation in drinking water (Westerhoff *et al.* 2004). The rate of chlorine consumption has been observed to increase significantly in the presence of these groups (Gallard & Von Gunten 2002). Interaction between chlorine and the phenolic group is a pH-dependent process and, because of that chlorine consumption rate in the presence of phenol, starts increasing in the alkaline or neutral environment (Faust & Hunter 1967). Over the decades, the coagulation-based treatment approaches have been widely explored by researchers as the most feasible treatment method for NOM-enriched water.

Electrochemical technologies have emerged as a prominent alternative to conventional coagulants owing to the recent technological developments in this field. During electrocoagulation (EC), the formation of dissolved hydroxyl complexes and insoluble hydroxide precipitate takes place when current is passed through the anode. The benefits of using electrolytic technologies can be accredited to less sludge formation, minimum use of chemicals, increased efficiency of pollutant removal, and the ability to be operated using solar energy that often reduces the cost of operation (Mamelkina *et al.* 2019). In most of the studies, Al- and Fe-based electrodes are used due to their trivalent forms and the low solubility of their hydroxides (Attour *et al.* 2014). Previous studies on the EC process have elaborated its capability as a superior process to remove a wide range of pollutants such as heavy metals, turbidity, NOM, and phenol. Aluminum-based EC for NOM fraction removal

has depicted 96% and 89% removal of humic substances and TOC, respectively (Särkkä *et al.* 2015). Aromatic fraction removal is more prominent during the treatment of NOM-containing water, which can be inferred from the observation that UV₂₅₄ abs reduction is more as compared to dissolved organic carbon (DOC) removal (Uyak *et al.* 2007), but the removal efficiency varies depending on the qualitative characteristics of NOM. In the present study, two water sources have been selected, i.e. river water and mine water. The characteristic properties of surface water include highly hydrophobic and reactive fractions of NOM, low hardness, and low conductivity as compared to mine water. Recent research has shown that mixing of different water sources can be a viable option for surface water treatment (Lu *et al.* 2018). Mine water, which is present in abundance, can be used to increase the efficiency of surface water treatment owing to its specific properties, such as high hardness, which increases the concentration of multivalent cations in the mix, thus helping in NOM removal (Zhao *et al.* 2014). The removal rate of the reactive part of NOM was measured using the absorbance slope index (ASI) in the present study. It has shown a linear (positive) correlation with a chloroform formation rate (correlation factor ~0.9) in chlorinated water (Korshin *et al.* 2009).

In the present study, the effects of mixing mine water and surface water on NOM removal have been accessed by observing a reduction in levels of DOC, UV₂₅₄ abs, phenol, and turbidity. The concept of the ASI was used to investigate the effects of EC on the mechanism of chlorine–NOM reactivity. The optimization of the EC process has been done using the RSM software to elucidate the correlation between various factors chosen.

MATERIALS AND METHODS

Collection of water samples

The water samples were collected from the Damodar River near the Jamadoba Water Treatment Plant (WTP), and mine water was collected from the 'Pit No. 2' sampling location near the Jamadoba WTP situated in the Jharia region of Dhanbad during the October month, i.e. post-monsoon

season. The water samples were collected from mid-stream into HDPE (high-density polyethylene) sampling bottles and stored in a refrigerator at 4°C after preserving samples for the TOC/DOC test with the addition of phosphoric acid. Mixing of mine and surface water was done in various proportions as 1:1, 1:2, 1:3, and 1:4 based on the volume and effects of mixing were studied on various parameters that explain the NOM nature.

Electrochemical treatment

A Plexiglas chamber with a dimension of 160 mm × 130 mm × 120 mm was constructed for the EC treatment process. A single anode and cathode made up of aluminum were used in a monopolar connection mode during the treatment process. The dimension of electrodes was 150 mm × 100 mm × 2 mm each. The reactor was designed for 1 L working volume, and the electrodes were 2 cm above the bottom of the reactor to facilitate in stirring of the solution. The gap between electrodes was maintained as 1 cm in parallel and placed 4 cm from the wall of the reactor, and they were connected to a digital power supply (bio-rad power pac HC). The sample was tested under various operating conditions, such as pH, current density, and contact time, and mix proportion at a constant stirring speed of 120 rpm using a magnetic stirrer with a magnetic bar of 8 × 20 mm dimension, for each experimental run. Samples were drained using an outlet pipe fitted to the reactor at 4 cm from the bottom level of the reactor. A 0.45 μm pore size filter paper was used for filtration before UV₂₅₄ abs and DOC analysis. The electrodes were rinsed with 0.5 N H₂SO₄ before starting the treatment. The total active surface area (A_{total}) of the electrodes was 80 cm². Current densities were calculated for each applied current by dividing the applied current by A_{total} . To observe the impacts on the removal efficiencies of parameters chosen, different current densities (0.50, 1.50, 2.50, 3.50, and 4.50 mA/cm²) were applied. Experiments were carried out over a specific range of pH (2.5, 4, 5.5, 7, and 8.5), for a contact time of 10–30 min.

Analytical methods

A river water sample and mine water sample were tested for pH, TOC, DOC, UV absorbance (at 254 nm), specific UV

absorbance (SUVA), alkalinity, turbidity, and phenol content as per APHA protocols. The pH of the water samples was measured using a pH meter (Hanna Instrument, Germany). After filtering the samples by a 0.45 μm filter membrane, DOC was measured using the TOC analyzer (Shimadzu, Japan). Turbidity was recorded using a turbidity meter (E.I, India), and UV absorbance was recorded using a lambda 45 UV/VIS spectrophotometer at a wavelength of 254 nm (LabTech, China). The ASI can be represented as follows:

$$ASI = 0.56 \left(\frac{Ab_{254} - Ab_{272}}{Ab_{220} - Ab_{230}} \right)$$

In this formula, Ab_{254} , Ab_{272} , Ab_{220} , and Ab_{230} nm denote UV absorbance at the wavelength of 254, 272, 220, and 230 nm, respectively (Korshin *et al.* 2009).

Design of experiments and response surface method

Central composite design (CCD) has been used to explore the correlation of factors and to optimize the independent factors to ensure the maximum efficiency of the EC process during the research. Four significant factors were pH, current density (mA/cm²), mix ratio, and contact time (min) (Kasiri *et al.* 2008). During the process, 30 experiments were conducted with three replicates to ensure accuracy. The design of experiments and further modeling was done using the design expert software. Experimental responses were evaluated using the polynomial as given in the following equation (Pang *et al.* 2011):

$$y = \alpha_0 + \sum_{i=1}^k \alpha_i X_i + \sum_{i=1}^k \alpha_{ii} X_i^2 + \sum_{i < j \leq k} \alpha_{ij}^2 X_i X_j + \varepsilon \quad (1)$$

where y is the predicted response for the removal of UV₂₅₄ abs, DOC, turbidity, and phenol. α_0 is the constant coefficient, α_i is the linear coefficient, α_{ii} is the coefficient of the second-order parameter, α_{ij} is the coefficient of interaction, X_i and X_j are the coded values of the variables, and ε is the random error. Interaction between independent variables and responses was analyzed using analysis of variance (ANOVA). The accuracy of the fit model was

reflected by the determination coefficient (R^2), while the Fischer exact test (F -test) examined the statistical significance. Statistical model terms were evaluated by the P -value (probability) with a confidence level of 95%. Table 1 shows the range and levels of the factors.

RESULTS AND DISCUSSION

Physicochemical characteristics of water samples

Physicochemical properties of the untreated samples have been presented in Table 2.

Effects of mixing on various properties

Various experiments performed on mine and surface water indicated the different nature of NOM in the samples.

Table 1 | Factors level of CCD design

Parameters	Units	Levels			
		-1	+1	- α	+ α
pH	–	4	7	2.5	8.5
Mix ratio	–	0.5	1	0.25	1.25
Current density	mA/cm ²	1.5	3.5	0.5	4.5
Contact time	min	15	25	10	30

Table 2 | Physicochemical properties of water samples

Parameters	Surface water (SW)	Mine water (MW)
pH	8.0 ± 0.2	8.40 ± 0.2
Total dissolved solids (TDS) (mg/L)	220 ± 45	447 ± 56
Conductivity (µs/cm)	461.50 ± 85	893 ± 105
Turbidity (NTU)	15 ± 3.1	2.2 ± 1.2
Total hardness (mg/L)	148 ± 16.2	352 ± 22.1
Alkalinity (mg/L)	172 ± 21.3	480 ± 28.7
TOC (mg/L)	5.45 ± 1.8	3.87 ± 1.1
DOC (mg/L)	5.16 ± 1.5	3.31 ± 0.8
UV ₂₅₄ abs (cm ⁻¹)	0.34 ± 0.1	0.04 ± 0.01
Chloride (mg/L)	29.9 ± 3.2	59.9 ± 4.5
Phenol (mg/L)	0.15 ± 0.02	0.07 ± 0.01

DOC is higher in surface water than mine water, which can be attributed to the presence of multivalent cations in the mine water. These divalent ions restrict the availability of NOM in mine water (Priya et al. 2017). A high SUVA value for surface water (Figure 1(c)) indicated a more reactive and hydrophobic fraction of NOM in surface water, whereas mine water readings indicated a less reactive and hydrophilic fraction of NOM. The UV₂₅₄ absorbance value of surface water indicated the presence of highly aromatic fractions, whereas the mine water value indicated low aromatic fractions (Ulu et al. 2014). A high conductivity value showed high ionic mobility in mine water, which would help in the EC process upon mixing.

Mixing of both the waters led to dilution, which resulted in the following trends in various properties. TOC and DOC values of the mix were found to decrease in the range of 13–26% for TOC and 16–27% for DOC from the initial level of NOM in surface water (Figure 1(a)). Mine water, which had high hardness values, tended to increase the hardness of various mix proportions (Figure 1(d)). Phenol content in the mix proportions was also reduced (Figure 1(e)). The turbidity of the mix was observed to be less than the initial turbidity value of surface water, but it showed an increasing trend upon increasing the surface water in the mix proportion, which can be attributed to the dilution effect. UV₂₅₄ absorbance values showed about 78–80% reductions in absorbance values upon mixing (Figure 1(b)), which suggests that highly aromatic NOM of surface water reacts with less aromatic NOM of mine water and aromatic content of mix decreases, thus reducing the spectroscopic readings. On increasing the quantity of surface water in the mix, UV₂₅₄ abs values showed an increasing trend, indicating that an increase in surface water increases the aromatic content of mix as aromatic fractions are prominent in surface water. SUVA is a useful indicator of the characteristics of the dissolved organic matter concerning its susceptibility to coagulation and its reactivity with chlorine. Upon mixing, SUVA values reduced considerably indicating the reaction between the NOM fractions (Figure 1(c)). The higher reduction of UV₂₅₄ abs and SUVA in the mixed proportion was achieved because of ionic support gained from mine water. Highly reactive, hydrophobic and aromatic NOM of surface water reacts with less

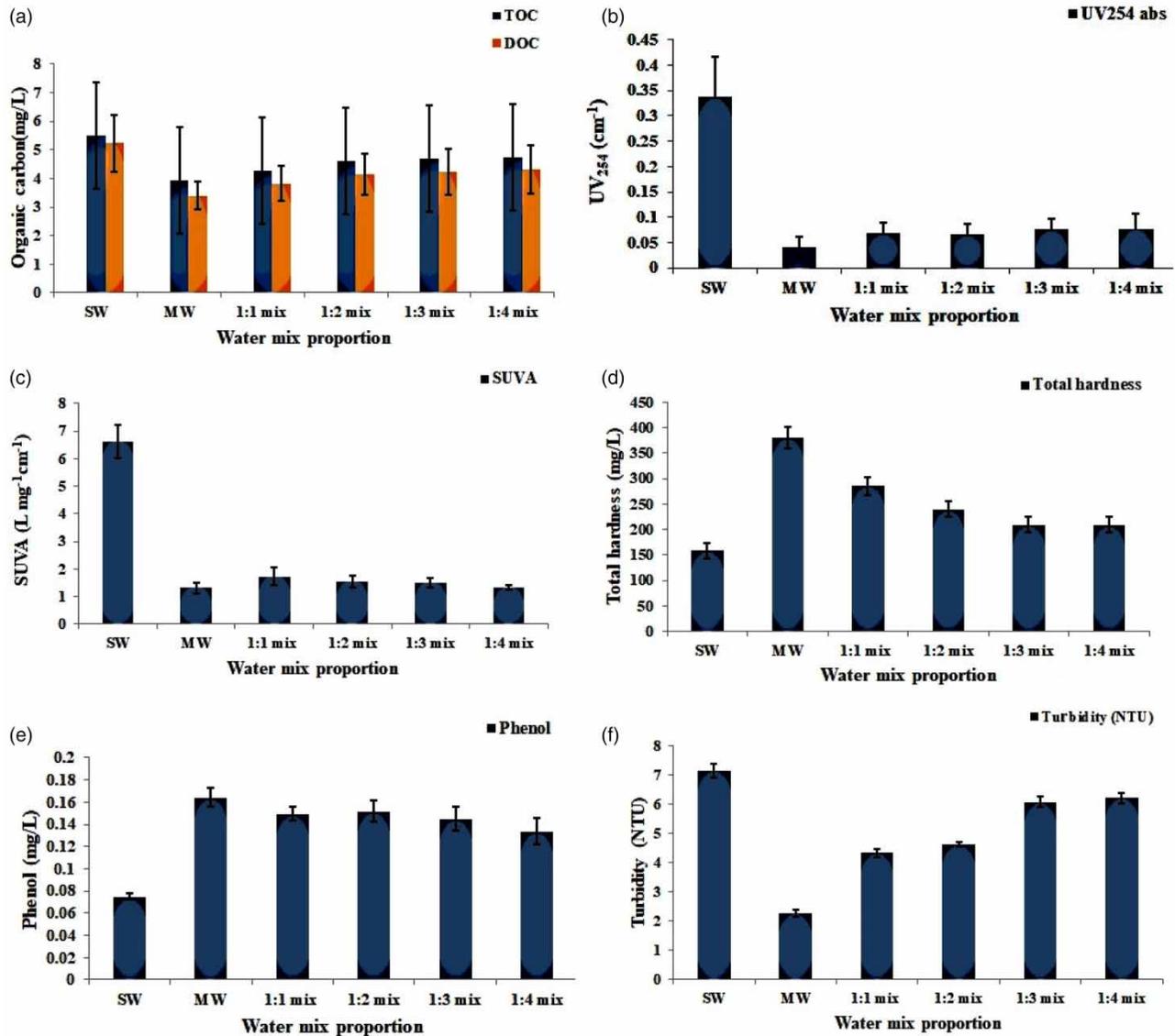


Figure 1 | Effect of mixing of water on various properties: (a) organic carbon; (b) UV₂₅₄ abs; (c) SUVA; (d) total hardness; (e) phenol; and (f) turbidity.

reactive, hydrophilic and less aromatic NOM of mine water, thus reducing the UV₂₅₄ abs and SUVA values in the mix.

Treatment of water samples by the EC process

EC treatment was carried out for the removal of the reactive part of NOM in surface and mine water, and the performance of EC was assessed through the spectral indices approach as opposed to the conventional approach, i.e. TOC/DOC removal. The EC process was also conducted for the various

mix proportions of surface and mine water as designed using the response surface method (RSM) (i.e. Table 3), and results were compared to understand the effects of mixing on the removal efficiencies of various parameters selected.

Effect of the EC process on the removal of UV₂₅₄ abs from the proportionate mixture

The UV₂₅₄ abs removal efficiency of the Al electrode during the EC process has been estimated in the range of

Table 3 | Factors and response values of CCD

Run order	Factors				Responses			
	pH	Mix ratio	Current density (mA/cm ²)	Contact time (min)	% Removal (UV ₂₅₄)	% Removal (DOC)	% Removal (turbidity)	% Removal (phenol)
1	4	0.5	1.5	15	71.0	60.7	74.7	61.3
2	4	0.5	1.5	25	74.2	65.1	76.3	63.8
3	4	0.5	3.5	15	77.1	70.5	79.5	71.0
4	4	0.5	3.5	25	82.8	72.5	83.3	74.2
5	4	1	1.5	15	75.3	65.4	75.3	74.2
6	4	1	1.5	25	78.4	70.5	79.1	76.6
7	4	1	3.5	15	81.5	76.8	83.0	77.4
8	4	1	3.5	25	86.1	79.8	86.6	81.5
9	7	0.5	1.5	15	64.2	58.5	68.1	56.5
10	7	0.5	1.5	25	70.2	61.9	72.1	59.7
11	7	0.5	3.5	15	72.8	65.6	74.5	63.8
12	7	0.5	3.5	25	77.1	69.8	79.5	66.2
13	7	1	1.5	15	70.7	64.7	71.6	63.8
14	7	1	1.5	25	74.6	66.3	75.0	66.2
15	7	1	3.5	15	78.4	70.6	79.1	74.2
16	7	1	3.5	25	81.5	74.1	82.3	75.8
17	5.5	0.75	2.5	10	86.7	82.9	88.1	77.4
18	5.5	0.75	2.5	20	88.9	87.0	89.8	83.9
19	5.5	0.75	2.5	20	90.8	89.8	92.3	85.5
20	5.5	0.75	2.5	20	90.4	85.2	91.4	84.7
21	5.5	0.75	2.5	20	90.8	86.6	93.0	84.7
22	5.5	0.75	2.5	20	90.8	86.6	92.3	85.5
23	5.5	0.75	2.5	20	91.1	86.3	92.3	85.5
24	5.5	0.75	2.5	30	93.3	89.0	95.0	87.9
25	5.5	0.75	0.5	20	69.9	60.7	69.6	63.8
26	5.5	0.75	4.5	20	83.8	76.1	84.1	82.3
27	2.5	0.75	2.5	20	60.2	48.9	60.7	58.9
28	8.5	0.75	2.5	20	54.4	47.9	56.6	53.3
29	5.5	1.25	2.5	20	78.3	73.6	80.2	83.1
30	5.5	0.25	2.5	20	69.4	62.9	73.1	60.5

54.4–93.3% for various combinations of pH, mix ratio, current density, and contact time as shown in Figure 2(a). The process exhibited the maximum removal of UV₂₅₄ abs for 3:4 mix proportions at a current density of 2.5 mA/cm², pH 5.50, and for a contact time of 30 min. UV₂₅₄ abs primarily indicate aromatic organic fractions in solution. High current density, lower pH value, and more contact time

resulted in better UV₂₅₄ abs removal rate with Al electrodes. The mole of aluminum ions released depends on the current intensity and operating time, which enhances coagulant activity in the EC process. The synchronized impact of current density and operating time led to the formation of bubbles due to the release of H₂ gas, which facilitated the blending of organic contaminants with water leading to

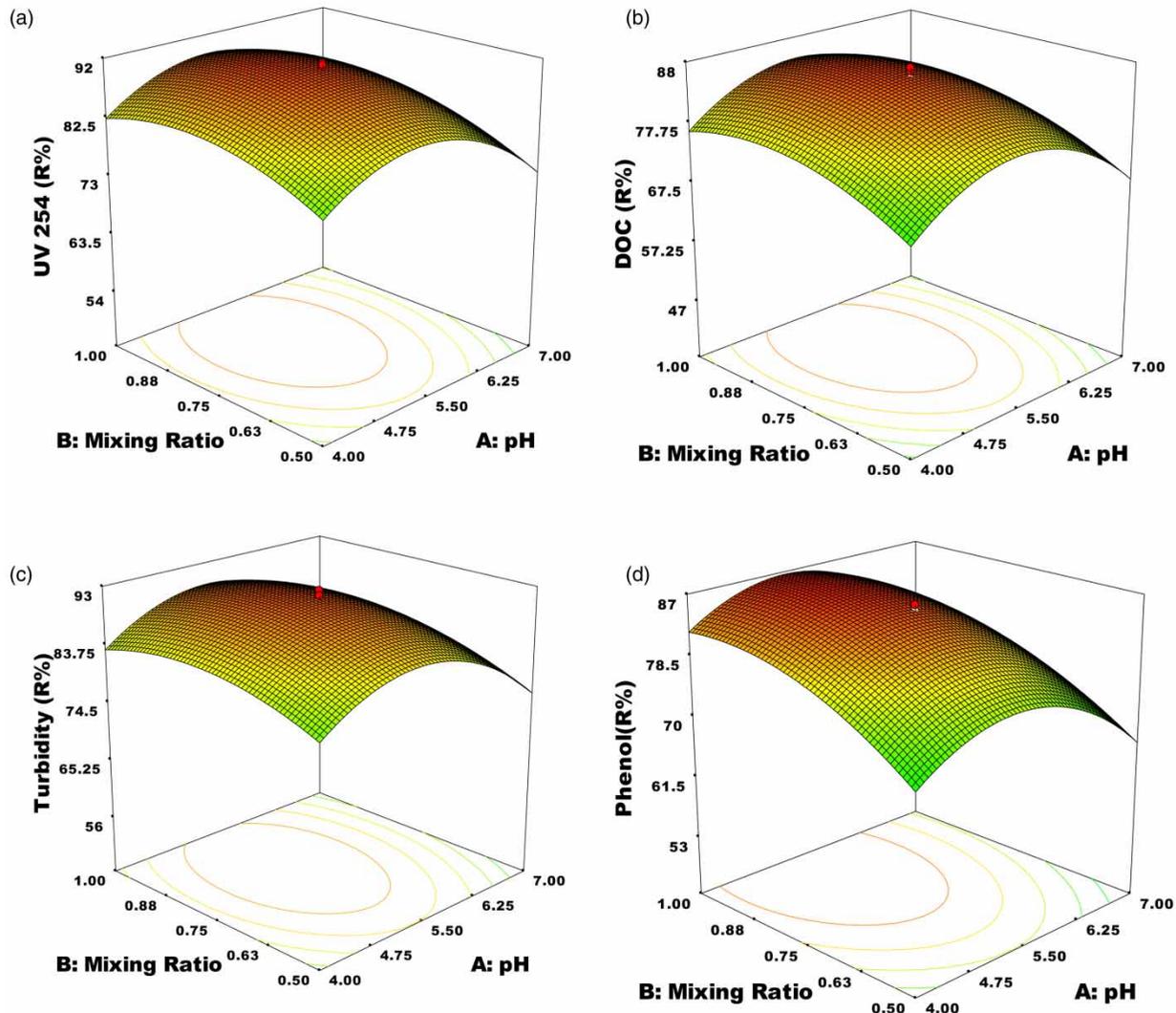


Figure 2 | Three-dimensional plot for the EC process for: (a) UV₂₅₄ reduction; (b) DOC reduction; (c) turbidity reduction; and (d) phenol reduction.

significant removal efficiency. The percentage increase of mine water in mix proportion resulted in better removal which can be attributed to an increase in multivalent cations in solution due to an increase in mine water (Zhao *et al.* 2014). The formation of an insoluble complex between NOM and coagulant species and the adsorption of NOM to freshly formed hydroxide precipitate could be the removal mechanism of NOM, thus significantly reducing the aromatic fractions of NOM (Lu *et al.* 2018). It was observed that the removal efficiency of UV₂₅₄ abs was more than DOC, which is evidence of successful aromatic removal but lower molecular weight fractions still being in solution.

Effect of the EC process on the removal of DOC from the proportionate mixture

The DOC removal efficiency of the Al electrode during the EC process has been estimated in the range of 47.9–89% for various combinations of pH, mix ratio, current density, and contact time as shown in Figure 2(b). The process exhibited the maximum removal of DOC for the similar operating conditions as obtained for UV₂₅₄ abs removal. Researchers have reported that EC elicits the maximum efficiency of DOC removal in the pH range of 5.3–7.3 due to the formation of compact and robust flocs as found in our

research also (i.e. pH 5.5 showed the maximum removal). The removal of DOC depends on the availability of stable aluminum concentration dissolved from the electrodes. Charge neutralization and double-layer compression are the prominent mechanisms for the removal of DOC. The amphoteric behavior of aluminum hydroxide, $\text{Al}(\text{OH})_3$ might be the reason for the decline in performance at acidic condition, while the formation of $\text{Al}(\text{OH})_4$ further disturbs the enmeshment of contaminants as $\text{Al}(\text{OH})_4$ becomes soluble in alkaline pH (Adhoum & Monser 2004).

In the present study, DOC removal (47.9–89%) was more than TOC removal (40–85%). Literature suggests that DOC represents the concentration of hydrophobic NOM fractions available in the water, while the concentration of TOC shows hydrophobic, hydrophilic, and inorganic fractions of NOM in water (Mishra *et al.* 2014; Priya *et al.* 2017). Therefore, EC-based treatment is suitable for the removal of NOM from water containing more hydrophobic fractions.

Effect of the EC process on the removal of turbidity from the proportionate mixture

During the EC process, the turbidity removal efficiency of the Al electrode was estimated in the range of 56.6–95% for various combinations of pH, mix ratio, current density, and contact time. The process elicited the maximum turbidity removal for 3:4 mix proportion when current density approached 2.5 mA/cm^2 at pH 5.50 and for a contact time of 30 min as shown in Figure 2(c). Current density and contact time are the prominent parameters that determine the rate of bubble production and flocs size during the EC process. A similar reduction in turbidity during EC was reported by other researchers (Kobya *et al.* 2003).

Results showed the performance efficiency of the EC process shifted toward the negative regime in highly acidic condition. Although the performance efficiency of EC increased linearly with current density, the coagulant activity of the EC process further declined at a higher pH (pH > 5.5). The EC process interferes with the agglomeration of charged colloidal particles in water, thus increasing turbidity removal (Kobya *et al.* 2003). The formation of highly charged polynuclear hydroxyl aluminum complexes during the process of EC, such as $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$,

$\text{Al}_{13}(\text{OH})_{34}^{4+}$, and $\text{Al}(\text{OH})_7^{4+}$, would eventually entrap dispersed colloidal particles resulting in the significant reduction of turbidity from water. Higher cationic charges can also be a contributing factor for turbidity removal from water, which was imparted in the solution by adding hard mine water (Hussain *et al.* 2013).

Effect of the EC process on the removal of phenol content from the proportionate mixture

The formation of chlorinated by-products is often seen in water with a high concentration of hydrophobic groups such as phenol. There is a positive correlation between phenolic group concentration and the formation of DBPs (Criquet *et al.* 2015). In the study at hand, the phenol content of the mix was above the permissible limit due to high phenol content in the mine water (i.e. 0.1521 mg/L). Aluminum electrode performance for phenolic group removal varied from 58.9% to 87.9%, respectively, as shown in Figure 2(d). This study indicates that mixing of mine water can lead to an increase in levels of phenolic content in the mix, which has to be treated subsequently. Earlier researchers observed good DOC removal and phenol removal using the aluminum electrode (Priya *et al.* 2017). The phenolic group reduction could be one of the reasons why aluminum coagulant has drastically reduced DOC, as DOC reduction indicates a reduction in hydrophobic content (Mishra *et al.* 2014). Positively charged Al^{+3} ions might be capable of trapping phenolic molecules within aluminum hydroxide precipitates.

Regression analysis for the EC process

The regression analysis was carried out to achieve a good fit in the response function and to estimate the efficiency of the EC process. ANOVA was used to analyze the responses and to predict the relevance of the model, as shown in Table 4.

A quadratic model was developed to predict the reduction of turbidity, DOC, UV_{254} abs, and phenol based on pH (A), mix ratio (B), current density (C), and contact time (D); and calculated as 4 first-order effect (in terms of A, B, C, and D), 6 interaction effects (AB, AC, AD, BC, BD, and CD), and 4 second-order effects (A^2 , B^2 , C^2 ,

Table 4 | ANOVA analysis for the EC treatment

Variable	UV ₂₅₄	DOC	Turbidity	Phenol
R^2	0.99	0.99	0.99	0.97
R^2 adjusted	0.98	0.98	0.98	0.95
Regression (degree of freedom – 14)				
Sum of squares	2,775.86	3,602.24	2,568.55	3,085.7
Mean square	198.28	257.3	183.47	220.41
P -value	<0.0001	<0.0001	<0.0001	<.0001
F -value	123.96	119.59	101.34	41.59
Lack of fit (degree of freedom – 10)				
Sum of squares	20.64	22.27	23.91	77.34
Mean squares	2.06	2.23	2.39	7.73
P -value of lack of fit	0.11	0.48	0.08	0.002
F -value of lack of fit	3.08	1.11	3.68	17.86
Pure error (degree of freedom – 05)				
Sum of squares	3.35	10	3.25	2.17
Mean square	0.67	2	0.65	0.43
Coefficient of variance (CV) %	1.61	2.04	1.68	3.16
Standard deviation	1.26	1.47	1.35	2.30

and D^2) as shown in the following equation:

$$\text{UV}_{254} \text{ reduction } \gamma = 90.38 - 2.03 * A + 2.29 * B + 3.62 * C + 1.96 * D + 0.029(A * B) + 0.096(A * C) + 0.029(A * D) - 0.011(B * C) - 0.029(B * D) + 0.096(C * D) - 8 * A^2 - 3.87 * B^2 - 3.15 * C^2 + 0.18 * D^2$$

$$\text{DOC reduction } \gamma = 85.82 - 1.29 * A + 2.76 * B + 4.10 * C + 1.68 * D - 0.17(A * B) - 0.052(A * D) + 0.21(B * C) + 0.015(B * D) - 0.060(C * D) - 9.24 * A^2 - 4.28B^2 - 4.24C^2 + 0.15D^2$$

$$\text{Turbidity reduction } \gamma = 91.21 + 1.82 * A + 1.59 * B + 3.53 * C + 1.75 * D + 0.22(A * B) + 0.10(A * C) + 0.15(A * D) + 0.27(B * C) - 0.22(B * D) + 0.18(C * D) - 7.86A^2 - 3.37B^2 - 3.31C^2 + 0.36D^2$$

$$\text{Phenol reduction } \gamma = 84.98 - 2.72 * A + 4.93 * B + 4.12 * C + 1.78 * D - 0.35(A * C) - 0.15(A * D) - 0.35(B * C) - 0.051(B * D) + 0.051(C * D) - 7.50A^2 - 3.58B^2 - 3.28C^2 - 0.86D^2$$

The F -test was used to understand the model's significance. The condition for a good relevance of model terms

is that the F -value must be large and the P -value must be small. The large modal F -value of 123.96, 119.59, 101.34, and 56.01 for the reduction of UV₂₅₄ abs, DOC, turbidity, and phenol, respectively, indicated a good significance of the model. The P -value for all the four responses has been estimated as <0.0001 in the present study, which also suggested that the model developed is significant. The value of R^2 was used to learn about the quality of the model. The high R^2 value indicates a good model and ensures adjustment to experimental data. The R^2 values for the responses were 0.99, 0.99, 0.98, and 0.97, respectively, which implies approximately 99%, 99%, 98%, and 97% correlation in actual and predicted values of UV₂₅₄ abs, DOC, turbidity, and phenol reduction. However, the relatively low value of the coefficient of variance (CV) (i.e. 1.61%, 2.04%, 1.68%, and 3.16%) for UV₂₅₄ abs, DOC, turbidity, and phenol reduction, respectively, indicated a precise and accurate data set. The regression analysis has, therefore, affirmed the relevance of model terms adopted during the EC process.

Validation of the model

The efficiency of EC at reducing NOM fraction from water depends on many factors such as electrode type, current density, mixing conditions, pH, temperature, and the presence of divalent cations and concentrations of destabilizing anions (bicarbonate, chloride, and sulfate). Many researchers have correlated high SUVA values to increased reactivity of NOM in water sources (Edzwald & Tobiason 1999). The effects of four variables, namely pH, mix ratio, current density, and contact time, were studied to reach the maximum efficiency of the EC process using aluminum electrodes. Based on the 30 runs designed, the validity of the predicted model was analyzed. The relation between the actual and predicted values has been shown graphically using the RSM. The optimized conditions came out to be pH = 5.35, mixing ratio = 0.81, current density = 3.07 mA/cm², and contact time 25 min. The theoretical predictions at the optimum condition were assumed as 93.9%, 89.1%, 94.6%, and 88.3%, respectively, whereas the experimental coagulant activity has been estimated as 92.3%, 88.6%, 95.1%, and 89.2% for the reduction in UV₂₅₄ abs, DOC, turbidity, and phenol,

respectively. Predicted values of the responses chosen were found to be relevant, as the experimental values were within 3% of the predicted value. Thus, RSM proved to be an appropriate and effective statistical tool for optimizing the treatment process.

For understanding the significance of mixing mine water with surface water, it is imperative to discuss the test results of both the water samples separately. Testing of surface water and mine water was done at optimum conditions as obtained using the RSM tool, and results suggested that the efficiency of EC has increased in comparison to the individual treatment given to the surface and mine water, and the test results for surface water and mine water are shown in Table 5.

Results obtained were in line with previous studies on EC using aluminum electrodes (Ulu *et al.* 2015).

Effect of the EC process on the ASI

ASI values establish a relation between the presence of aromatic groups and variation in NOM concentration (Korshin *et al.* 2009). The ASI has been correlated with the ability of chlorinated water to form THMs by the researchers (i.e. higher ASI values denote more chances of THMs formation) (Priya *et al.* 2017).

Chlorination in the surface water, mine water, and the optimum mix were carried out at optimum conditions to observe the variations in chlorine demand and estimate the THMs formation potential in terms of ASI. Chlorine demand of surface water, when tested individually, was obtained as 8 mg/L and residual chlorine was 0.2 mg/L, whereas mine water had chlorine demand of 3.5 mg/L and residual chlorine was 0.2 mg/L. A high level of chlorine demand in surface water indicated a high level of NOM content also correlated with high DOC and TOC readings. This high dose of chlorine in water treatment can lead to THMs formation as higher disinfectant doses increase the DBP formation potential in water. This could be correlated from the

ASI value of surface water as 0.84Ab and mine water ASI reading as 0.70Ab, as ASI showed linear (positive) correlation with a chloroform formation rate in water-containing chlorine. (Korshin *et al.* 2009).

Chlorine demand reduced to 2 mg/L when the mixture was treated at optimum conditions such as pH = 5.35, current density = 3.07 mA/cm², and contact time of 25 min for the water mix of 0.81 ratio. The ASI value of water mix was observed as 0.42Ab, which also indicated a decrease in THM formation potential of the water on mixing mine water. Mixing of mine water has led to increasing multivalent cations in the mixture owing to the high hardness of mine water, which aids the removal of organic matter from water (Zhao *et al.* 2014). Thus, aluminum-based EC treatment after mixing mine water with surface water under optimum conditions can be an effective treatment method for reducing TOC and DOC from water containing NOMs.

CONCLUSION

The aluminum-based EC treatment method has been found to be an effective remediation approach to remove aromatic and hydrophobic fractions from NOM-enriched water. Mixing of mine water and surface water at optimum conditions significantly increased the efficiency of treatment. The increase in multivalent cations in the mixture due to the addition of mine water led to effective removal of aromatic moieties and hydrophobic fractions of NOM from water which elicited the impact in control of THMs formation in chlorinated water. However, the process was highly governed by the effects of pH, current density, mix proportion, and operating time. Optimum conditions, which showed the maximum efficiency, were pH = 5.35, current density = 3.07 mA/cm², and contact time of 25 min for 0.81 proportionate mixes. The EC process showed that TOC and DOC removal efficiencies increased about 1.2

Table 5 | Removal efficiencies for water samples

Sample	UV ₂₅₄ (cm ⁻¹)	% Removal (UV ₂₅₄ abs)	DOC (mg/L)	% Removal (DOC)	Turbidity (NTU)	% Removal (turbidity)
Surface water	0.06	80 ± 1.2	1.31	75 ± 1.4	1.78	88 ± 1.5
Mine water	0.006	86 ± 1.0	0.61	82 ± 1.2	0.46	79 ± 1.3

times after the addition of mine water, which indicated more effective removal of hydrophobic fractions during treatment. An appreciable reduction in UV₂₅₄ absorbance was observed, which suggested that aromatic fraction can be removed significantly just by the addition of mine water. Turbidity reduction was also increased, which indicated that adding mine water helped in the destabilization of suspended solids present in the water mix, thus reducing turbidity levels in mix proportion. An increase in phenolic content could be easily checked by treatment using the EC method as removal efficiency of phenol was found to be good using aluminum electrodes. Reduced chlorine demand and ASI values indicated that the NOM content of both the waters underwent spontaneous reaction, which led to a reduction in organic content of the mix, thus also reducing the THMs formation potential of chlorinated water.

ACKNOWLEDGEMENTS

This work was supported by the Science and Engineering Research Board, Department of Science and Technology, Government of India (SR/S3/CEE/0004/2013) for the grant received for research projects. The authors thank the Department of Environmental Science and Engineering, Indian Institute of Technology (ISM) Dhanbad for providing technical support to carry out this research work.

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First received 6 May 2019; accepted in revised form 30 September 2019. Available online 14 October 2019