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TECHNICAL ARTICLE

Combining Surface Water with Mine Water to Improve the Removal of Natural Organic Matter by Enhanced Coagulation

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Abstract

Mixing of near-neutral pH mine water and surface water substantially reduced the reactive portion of the natural organic matter (NOM) in the surface water by enhancing the coagulation process, using alum. The hardness and ionic moieties in the mine water improved the effectiveness of the alum in reducing the NOM concentrations. This is important because the presence of NOM can lead to the fouling of membranes and corrosion in the drinking water plant, and deteriorates drinking water quality by contributing undesirable changes in odor, taste, color. In addition, the presence of NOM can lead to carcinogenic by-products as a result of chlorination. The interactive effects of different operational conditions, i.e. pH, mixing proportion, and coagulant dose, were optimized using a statistical tool. The results affirmed that mixing of this mine water with river water would be an appropriate way to maximize the removal of the reactive part of NOM prior to disinfection and provide good quality drinking water.

Keywords Mixing ratio · NOM · Absorbance slope index · SUVA

Introduction

Natural organic matter (NOM) is defined as a heterogeneous mixture of complex organic materials that is generally present in all natural waters. This heterogeneous mixture consists of hydrophilic (non-humic acid) and hydrophobic (humic acids, fulvic acid, and humin) fractions, and represent more than 50% of the total organic carbon in source water (Thurman 1985). It is an important component in surface, ground, and rhizic (soil) waters, in terms of both reactivity and concentrations. Aquatic NOM is obtained as reaction products of microbes like algae, bacteria, and breakdown of terrestrial plants, and serves as food for various microorganisms in aquatic systems. It is also commonly found in water sources used for drinking purposes (Matilainen et al. 2010), depending on the biogeochemical cycles of the surrounding environments (Fabris et al. 2008).

The presence of NOM in treated water deteriorates drinking water quality by contributing undesirable changes in odor, taste, color, and hence seen as a carrier of hydrophobic organic compounds (USEPA 2002). It can also be observed that NOM consumes most of the disinfectant and coagulant used in water treatment. If not properly taken care of, NOM can obstruct the performance efficiency of various unit operations, which leads to clogging problems in rising rapid filters, biofilm growth on media, and rapid saturation of activated carbon beds (Matilainen and Sillanpää 2010). Another problem generated by the presence of NOM in water is corrosion and the fouling of membranes, which play the role of a substratum for bacteria in water distribution systems (Jacangelo et al. 1995; Park et al. 2002; Oh and Seock 2005). Disinfection by-products (DBPs) form primarily due to the availability of NOM (Bond et al. 2010), because chlorine has high reactivity with the aromatic fractions of NOM, causing the formation of carcinogenic chlorinated by-products, such as trihalomethanes (THMs) (How et al. 2017; Xie 2016). THMs forms dominantly in surface water (SW) and have four components: chloroform, bromoform, bromodichloromethane (BDCM), and dibromochloromethane (DBCM); of these, chloroform is the dominant species in chlorinated SW (Uyak et al. 2005). These byproducts were classified as probable human carcinogens by USEPA (1999).Thus, removing or at least reducing the amount of NOM is highly desirable.

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A wide variety of processes that have been already investigated and used to remove NOM from water, including: membrane filtration, advanced oxidation processes, adsorption, ion exchange, coagulation, electrochemical methods, and integrated methods (Sillanpää 2015; Skoronski et al. 2017; Zhan et al. 2010). As explained by Sillanpää et al. (2018), it is generally difficult to remove NOM using only a single method due to its high variability.

The removal of NOM by coagulation is selective and is affected by some water quality parameters, such as total hardness, ionic strength, the concentrations of certain cations and anions, and other parameters such as pH and coagulant characteristics (Hu et al. 2006; Matilainen et al. 2010; Wang et al. 2009). The greater the variation of NOM in water (both in composition and concentration), the less efficient conventional coagulation process becomes (Sillanpää et al. 2018). Enhanced coagulation processes have become the norm, and its optimization requires challenging operational control of conditions (mainly the pH and amount of coagulants). Alternatively, coagulation can be coupled with other water treatment techniques and technologies.

Wang et al. (2009) found that an increase in total hardness improved the removal of hydrophobic moieties, i.e. humic acid, by increasing the coagulation efficiency of aluminum salt. Further, Wang et al. (2010) reported that a combination of turbidity (using kaolin) and humic acid proportionally increased removal efficiency by increasing the total hardness and ionic strength of the solution. Zhao et al. (2014) similarly reported that increases (upto certain concentrations) in total hardness and ionic strength remarkably decreased the residual turbidity and ameliorated UV_{254} removal, confirming the reaction between the metal salts and the hydrophobic part of water.

Mine water (MW) caused by coal mining activities is also a serious concern in many parts of the world, including India (Singh 1988). The presence of mine water at mining sites creates several problems, including slope instability, corrosion of mining equipment, and acid generation due to the oxidation of sulfides (Singh et al. 2012). This MW can contaminate nearby natural water sources. To prevent both water contamination and mining problems, this MW must often be pumped out, and treated to provide good quality water for various coal cleaning operations, drinking purposes, and other domestic uses (Singh et al. 2012).

In this regard, MW generally has greater hardness and ionic strength than SW, which should aid NOM removal (Miller et al. 2008; Wang et al. 2010; Zhao et al. 2014). Mine water also has little hydrophobic NOM content and less turbidity than SW. However, MW contains contaminants that might detrimentally affect the coagulating water and generated sludge. Nevertheless, the presence of the anions in the MW, if not in excess, could support the coagulation process and subsequently be removed with the formed flocs. Apart from this, several studies have already been reported that aluminum salts, in either monomeric or polymeric form, can act as an effective coagulant for treating metals in wastewater (Sakhi et al. 2018; Chu 1999; Fan et al. 2003). Hence, using the abundant, unutilized MW to treat high NOM-containing SW could be an efficient way to remove hydrophobic as well as hydrophilic NOM fractions.

Thus, the present research work investigated co-treatment of MW and surface water SW. Enhanced coagulation experiments were conducted with MW samples mixed with a wide range of NOM-containing SW in different ratios to understand the influence of organic and inorganic substances of different molecular weights on coagulation performance. The mixing of MW and SW was systematically evaluated, and the process parameters were optimized using a statistical tool, RSM. Finally, the absorbance slope index (ASI) was applied over the TOC/DOC removal to better understand the removal of the reactive part of the NOM.

Material and Methods

Water Sample Collection and Preparation of Coagulant Solution

Samples of SW were collected from the Damodar River, Jamadoba (23° 42′ 18.00″ N, 86° 22′ 26.40″ E), Dhanbad district of Jharkhand, India. Mine water samples having pH around neutral were collected from pit no. 2 of the TATA Jamadoba Colliery; (23° 42′ 28.80″ N, 86° 24′ 3.60″ E) Jamadoba, Dhanbad. Samples were collected in October, 2019, which is a post-monsoon season in India. Collected samples were left overnight in the laboratory to allow larger particles to settle, particularly for the Damodar River samples, and were maintained at room temperature (27 °C) before use. The physiochemical properties of the MW and SW have been summarized in Table 1. The MW and SW samples were mixed in different proportions for enhanced coagulation. Adopted coagulant alum [$Al_2(SO_4)_3·18H_2O$], HCl, and NaOH were procured from Loba Chemie Pvt Ltd., India, and Merck, India, respectively. Analytical grade chemicals were used. The coagulant solution of 1000 ppm aluminum sulphate was prepared by dissolving 1 g of coagulant salt in 1000 mL of deionized water and mixed to obtain a homogenized solution. The solution was then stored at 4 °C.

Analytical Methods

The analysis of treated water for various parameters like pH, electrical conductivity (EC), total dissolved solids (TDS), salinity, chloride, sulphate, turbidity, phenol, total organic carbon (TOC), dissolved organic carbon (DOC), total hardness, alkalinity UV_{254}, and metal analysis were

Table 1 Physiochemical characteristics of river water and mine water

Parameters	Surface water	Mine water	BIS (2012) IS:10500 (μg/L)
pH	7.9	8.5	6.5–8.5
Conductivity (μS/cm)	461.5	893	–
Total dissolved solids (ppm)	220	447	500–2000
Salinity (%)	0.8	1.6	–
Chloride (mg/L)	29.99	59.98	250–1000
Total alkalinity (mg/L)	104	420	200–600
Turbidity (NTU)	15	2.2	1–5
Total hardness (mg/L)	152	376	200–600
Sulphate (mg/L)	48.1	198	200–400
Fe	0.21	0.28	0.3–1.0
As	0.02	0.01	0.050
Cd	0.24	0.008	0.010
Pb	0.018	0.019	0.050
Zn	0.204	0.198	5.0–15.0
Mn	0.064	0.085	0.1–0.3
Cu	0.041	0.048	0.050–1.5
Total organic carbon (mg/L)	5.436	3.575	–
Dissolved organic carbon (mg/L)	5.164	3.315	–
UV_{254} absorbance	0.340	0.043	–
SUVA	6.584	1.297	–
Phenol (mg/L)	0.0826	0.1682	0.001–0.002

carried out per the APHA standard protocols (APHA 2017). The pH, EC, salinity, and TDS were measured using a bench-scale pH meter (Hanna Instruments, Germany) and turbidity was measured using digital turbidity meter (E.I, India). TOC and DOC were analyzed using a TOC analyzer (Shimadzu, Japan). Ultraviolet (UV) absorbance was measured using a UV–Vis spectrophotometer (Labtech, Model: UV 9100/A, China) at different wavelengths depending on the specification of spectral indices. Different metal analysis were carried out using an atomic absorption spectrophotometer (AAS; model: Avanta, GBC, Australia). The specific ultraviolet absorbance (SUVA) is equivalent to the 100-fold DOC-normalized UV absorption coefficient at 254 nm(Mishra et al. 2016). It is considered to be a simple representative parameter expressing dissolved organic matter (DOM) aromaticity, an important property associated with its reactivity with chlorine and DBPs formation potential (Kitis et al. 2002; Reckhow et al. 1990; Weishaar et al. 2003). The rate of chlorine consumption (differential spectroscopy) and spectroscopic indices were used to investigate the residuals NOM as ASI, per Korshin et al. (2009). All experiments were conducted in triplicate for reproducibility purposes.

Jar Test Experiment

To study the coagulant behavior of aluminum sulphate under different operational conditions, bench-scale coagulation/flocculation experiments were carried out using ajar test apparatus (Scientific Engineering Corp., India). The samples were prepared by mixing the SW and MW in different proportions. The pH of the samples prepared for coagulation was adjusted using 0.1 M of HCl and NaOH. The prepared samples were subjected to the coagulation process in the jar test apparatus: rapid mixing of the samples at 200 rpm for 2 min, followed by slow mixing at 40 rpm for 15–20 min. The optimized dose of coagulant was added before rapid mixing. The treated samples were kept in the quiescent state for 30 min. Later on, 200 mL of the supernatant sample was taken from 2 cm below the surface of the treated water using a water syringe for further analysis.

Experimental Design using Central Composite Design (CCD)

RSM’s central composite design (CCD) tool was used to study the interaction between variables to optimize the independent variables with different sets of experiments to achieve the maximum removal efficiency using aluminum sulphate as a coagulant. RSM was chosen as a convenient statistical approach for the optimization process due to the perspective it provides (Priya et al. 2018a; Sonal et al. 2018). In the face-centered CCD model, different variable factors were selected along with responses. Before selecting different independent factors and their variables, a set of experiments were conducted manually to narrow the range of factors (Sonal et al. 2018). A narrow range of all of the independent variables were determined by keeping two factors constant at a specific set of conditions and altering one variable at a time**.** Based on manual observations, three independent factors, pH, mixing ratio, and coagulant dose, were selected for the three-level full factorial CCD (Table 2) and examined for optimization of the coagulation process. After this, a set of 20 experiments were carried out for three factorial designs, for factorial, axial, and central points.

Results and Discussion

Effect of Varying the Ratio of Mine Water and Surface Water

The interaction of SW and MW plays an essential role in the adaptation of this treatment method for effective and efficient removal of NOM. In the first step, the physicochemical parameters of the SW and MW were analyzed to check the suitability of the considered treatment approach to the samples collected (Table 1).The MW contains greater concentrations of total hardness, EC, TDS, salinity, chloride, sulphate, and total alkalinity compared to SW, which is desirable for balancing the low hardness and ionic composition of the SW during coagulation, while the SW has greater concentrations of UV_{254}, TOC, DOC, and SUVA, resembling the reactive part of NOM, than the MW. The MW also contains a greater concentration of sulphate and metals than the SW, but these parameters were under the permissible limits so their effects will be negligible. The higher concentration of phenol in the MW will be balanced during mixing and subsequently eliminated during the treatment process.

Researchers have reported that treating SW with alum does not substantially remove the reactive part of NOM, causing carcinogenic THMs to form after tertiary treatment (Jarvis et al. 2012; Priya et al. 2018b). However, mixing of these two waters was found to produce better coagulation results.

Simultaneously, the effects of mixing ratio on parameters considering the physicochemical characteristics and reactive part of NOM have also been examined (Table 3 and 4). The results show that mixing the MW with the SW improved the pH, EC, TDS, salinity, sulphates, chlorides, total alkalinity, turbidity, and total hardness, by accelerating the coagulation process. Likewise, all of the NOM-contributing parameters, such as UV_{254}, TOC, DOC, and SUVA concentrations were also improved (Table 4). Although the phenol concentrations increased, it was not enough to substantially increase the concentration of the reactive part of the NOM, and it was subsequently removed by coagulation/flocculation process.

The NOM present in natural water generally has both high molecular weight, aromatic hydrophobic groups, and lower molecular weight, aliphatic hydrophilic groups (Liang and Singer 2003) with corresponding greater SUVA values

Table 2 Experimental design summary using RSM

Variable	Unit	Symbol	Low actual	High actual	Low coded	High coded	Mean	Std. Dev
pH	–	A	4.00	8.00	– 1.000	1.000	6.000	1.414
Coagulant dose	mg/L	B	1.00	5.00	– 1.000	1.000	3.000	1.414
Mixing ratio (MW:SW)	–	C	0.25	1.00	– 1.000	1.000	0.625	0.265

Table 3 Effect of changing mix ratio (MW: SW) on physicochemical parameters

Mix ratio	pH	Electrical conductivity (µS/cm)	TDS (ppm)	Salinity (%)	Chloride (mg/L)	Sulphate (mg/L)	Total alkalinity (mg/L)	Turbidity (NTU)	Total hardness (mg/L)
0:1 (SW)	7.9	461.5	220	0.8	29.99	48.1	104	15	152
1:4	8	518.2	259.9	0.9	33.99	60.3	168	8	208
1:3	8.1	550	276.5	1.0	35.98	81.4	196	7.4	210
1:2	8.2	572.7	287	1.1	39.98	92.4	212	6.6	236
1:1	8.4	658.4	332.5	1.3	43.98	119.9	240	5.8	284
1:0 (MW)	8.5	893	447	1.6	59.98	198	420	2.2	376

Table 4 Effect of mixing ratio on different parameters considering reactive part of NOM

Mix ratio	UV_{254} absorbance	TOC (mg/L)	DOC (mg/L)	SUVA	Phenol concentration (mg/L)
0:1 (SW)	0.340	5.436	5.164	6.584	0.0826
1:4	0.072	4.710	4.316	1.668	0.0991
1:3	0.071	4.656	4.155	1.709	0.1038
1:2	0.070	4.573	4.075	1.718	0.1092
1:1	0.065	4.237	3.748	1.734	0.1112
1:0 (MW)	0.043	3.575	3.315	1.297	0.1682

for hydrophobic fractions and less for hydrophilic fractions of NOM (Uyak and Toroz 2007). The SUVA value of the SW exceeded those of the MW, but on mixing, the value declined to less than 2, which shows that the mixed water has low hydrophobicity and mostly non-humic NOM (Mishra et al. 2016; Uyak and Toroz 2007). Hence, the trend of SUVA values helps to validate the proposed treatment methodology. In addition, the moderate alkalinity acts as a buffer, maintaining the pH at an appropriate level for the coagulation process using alum, which hydrolyses in the aqueous medium and releases hydrogen ions along with coagulating species. These hydrogen ions neutralize the alkalinity. Similarly, the total hardness (including chlorides, sulphates) aids the coagulation process by compressing the double layer of colloidal particles, thereby reducing the repulsive forces. When alum hydrolyses in water, it undergoes complexation: the inorganic anions in the water form complexes with the Al, producing a metal precipitate (Van Benschoten and Edzwald 1990).The coordinative requirement of alum is influenced by type and concentration of anions in the water, and it was found that anions such as OH^-, SO_4^{2-}, F^-, PO_4^{3-}, bicarbonate, and chloride have a considerable effect on the coordinative requirements for Al complexes formation (Duan and Gregory 2003; Stumm and Morgan 1962). Hence, mixing the two waters can aid water treatment. Moreover, this treatment is a novel approach that can be applied to generate potable water using other forms of MW, such as treated acid MW, which contains high TDS, even after treatment (Masindi et al. 2020; Saha et al. 2019), though implementing the process would require experimental observations and process optimization.

Performance Assessment of the Coagulation Process

Effects of Coagulant on Turbidity Reduction of Mixed Water

The efficiency of alum was studied in terms of turbidity removal (Fig. 1a–c). The turbidity removal efficiency of alum was estimated to range from 53.4 to 92.1% at different levels of pH, alum doses, and mix ratios. The optimum coagulant and coagulant aid dose varied greatly for both the types of raw water (Jarvis et al. 2012; Priya et al. 2018b). But as the raw surface and mine water was mixed together (at a ratio of 1:1.6 SW:MW), the maximum turbidity removal efficiency of 92.1% was achieved at an alum dosage of 3 mg/L at a pH of 6. The coagulant dosage needed to achieve the optimum turbidity removal decreased as the proportion of MW increased in raw SW (Fig. 1a–c), indicating that mixing enhances the turbidity removal of SW. Although, the coagulant efficiency decreases as the pH of the solution increases (pH > 6) at a low doses of coagulant (Yan et al. 2008). The maximum turbidity removal efficiency (88.9%) was observed at pH 6. At higher coagulant dosages, more counter ions will be generated, which leads to restabilization of suspended colloidal particles and less turbidity removal.

Effect of Coagulation Process on Phenol Removal

In NOM enriched water, the presence of hydrophobic group such as phenol makes the water more susceptible to forming chlorinated by-products after chlorination. Researchers have already established the proportional correlation between the available concentration of phenolic groups and the rate of formation of DBPs in disinfected water (Criquet et al. 2015; Priya et al. 2018b). The present study examined phenolic group segregation from NOM-enriched, low-turbidity water, formed by mixing MW with SW using alum as a coagulant. The performance of alum for phenolic group removal ranged from 57.3 to 90.8% (Fig. 1a–c). The highest removal (90.8%)was observed at a pH, dose, and mixing ratio as 6, 3 mg/L, and 0.63, respectively. The result clearly suggests that the removal of phenolic groups in mixed water surpasseswhat occurs in traditional treatment of SW. Also, the removal of these phenolic group from the water might be responsible for the drastic reduction in DOC (Priya et al. 2018a). The reduction in phenol in the mixed water might be due to the destabilization of colloidal particles by enhanced electrostatic attraction between the particles,asthe positively charged alum flocs are robust and compact,allowing the hydrolyzed alum precipitates to trap the phenols and settle them with the flocs.

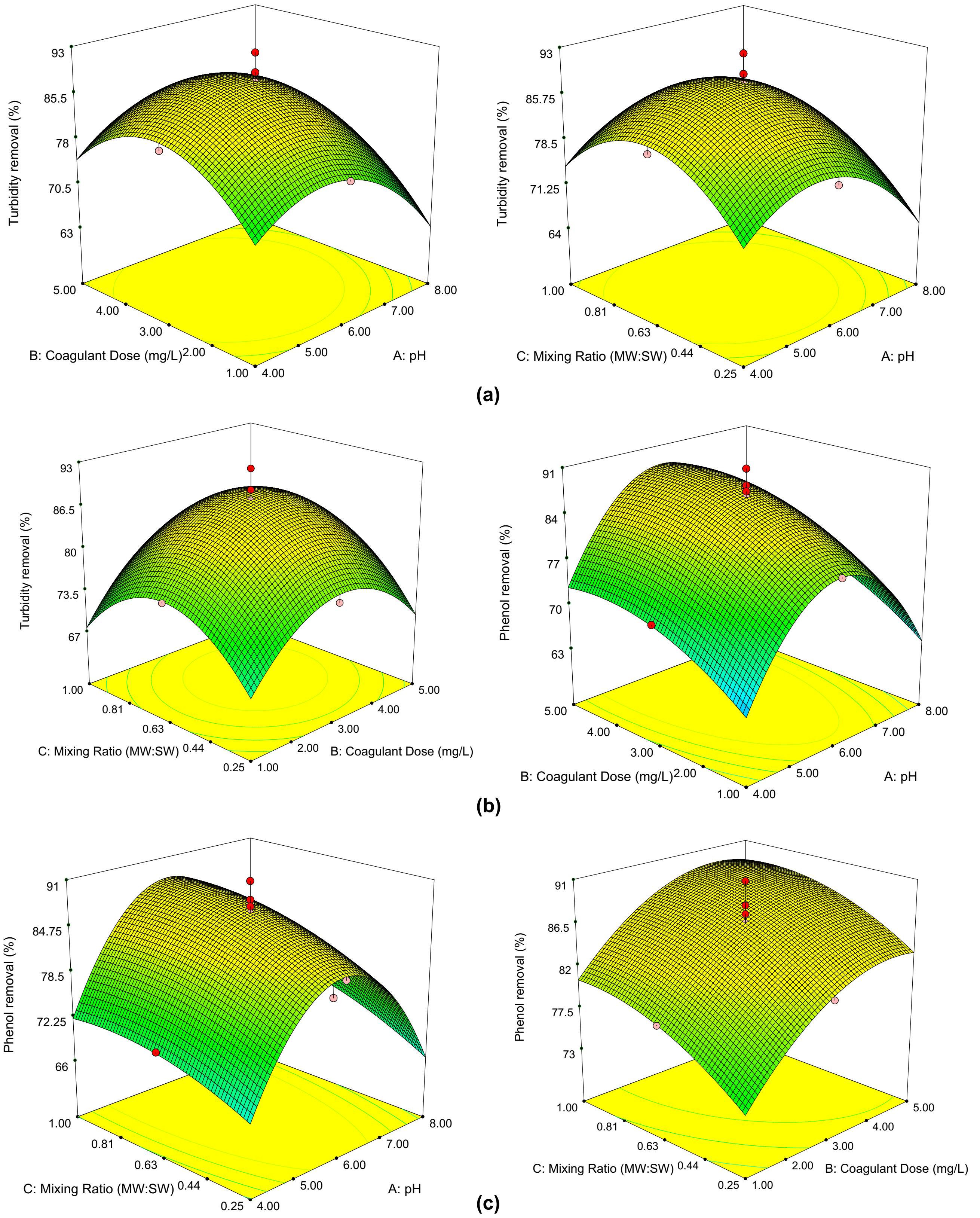

Fig. 1 3-D response surface plots showing the use of alum for turbidity and phenol removal as a function of: (**a** & **d**) pH and alum dose (**b** & **e**) pH and mixing ratio and (**c** & **f**) alum dose and mixing ratio.

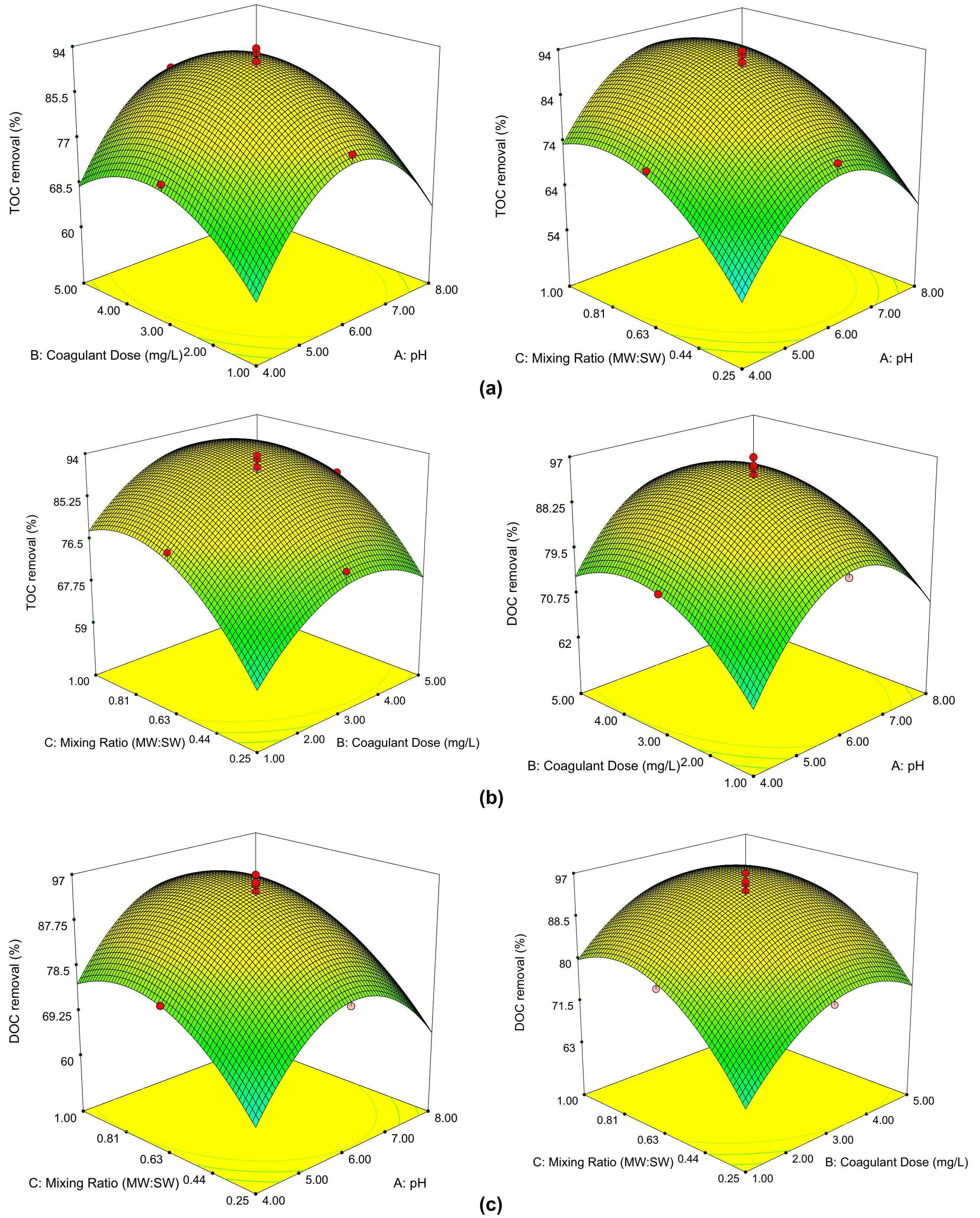

Fig. 2 3-D response surface plots showing the use of alum for TOC and DOC removal as a function of: (**a** & **d**) pH and alum dose (**b** & **e**) alum dose and mixing ratio and (**c** & **f**) alum dose and mixing ratio

Effect of Coagulant on DOC and TOC Reduction

The levels of DOC and TOC in the treated water were reduced by the coagulation/flocculation process (Fig. 2a–c). DOC and TOC removal improved at moderate coagulant dosages. This removal of organic matter by the coagulation process is attributed to the considerable influence of pH, alkalinity, and the NOM composition (Bratby 2016). The hydrophobic nature of the colloidal particles decreased as the metallic coagulant hydrolyzed, allowing the organic content to interact with their positively charged surfaces of the colloidal particles and be removed as micro-flocs (Duan and Gregory 2003). The highest observed DOC and TOC removals were 95.3% and 93.1%, respectively. Figure 2a–c show that the effect of alum on TOC removal ranged from 40.5 to 93.7%, whereas DOC removal (Fig. 2d–f) ranged from 44.7 to 96.9%. This clearly supports NOM removal, which leads to appreciable retardation in THM formation in treated water (Priya et al. 2017). The highly charged precipitated particles of aluminum also trap a considerable amount of organic carbon, which consequentially improves the removal of DOC and much of the aromatic fraction.

Effect of the Coagulation Process on the SUVA

The alum notably reduced the NOM concentrations, based on the SUVA values (Table 4). The DOC and UV absorbance at 254 nm were reduced by 95.3%, and 92.1%, respectively, and the corresponding SUVA value was 1.6. This low residual value has little influence on the treated water. The enhanced coagulation behavior might be due to the rapid hydrolysis rate of alum and the strong affinity of the positively charged Al precipitates toward the organic carbon (Priya et al. 2018b).

Statistical Validation

The working conditions that influenced the coagulation process were examined for 20 distinct experimental conditions based on the CCD analysis. The percentage turbidity reduction (R_1), TOC reduction (R_2), DOC reduction (R_3), and phenol reduction (R_4) were the functions of pH (A), coagulant dose (B), and mixing ratio (C). Analysis of variance (ANOVA) checked the adequacy and significance of the model. The F-test of the regression indicates that the model results for reduction of all of the selected parameters was significant, which is a desirable ANOVA result (Moghaddam et al. 2010; Sonal and Mishra 2019).The values of the regression coefficient (R^2) for all of the responses

Table 5 ANOVA analysis of Turbidity, DOC, TOC and phenol removal using response surface quadratic model

Responses	Sources	Sum of squares	df	Mean square	F-value	P > F
Turbidity removal	Model	2820.02	9	313.34	71.46	< 0.0001 (significant)
	Residual	43.85	10	4.38	–	
	Lack of fit	20.34	5	4.07	0.87	0.5609 (not significant)
	Pure error	23.50	5	4.70	–	–
SD: 2.09; CV %: 2.82; PRESS: 299.31; R^2: 0.98; adj R^2: 0.97; Pred R^2: 0.89; Adeq precision: 22.84						
DOC removal	Model	4596.72	9	510.75	152.71	< 0.0001 (significant)
	Residual	33.45	10	3.34		
	Lack of fit	14.92	5	2.98	0.81	0.5909 (not significant)
	Pure Error	18.52	5	3.70	–	–
SD: 1.83; CV %: 2.36; PRESS: 162.22; R^2: 0.99; adj R^2: 0.98; Pred R^2: 0.96; Adeq precision: 37.19						
TOC removal	Model	5195.97	9	577.33	68.12	< 0.0001 (significant)
	Residual	84.75	10	8.48	–	–
	Lack of fit	18.49	5	3.70	0.28	0.9062 (not significant)
	Pure error	66.26	5	13.25		
SD: 2.91; CV %: 3.94; PRESS: 214.92; R^2: 0.98; adj R^2: 0.96; Pred R^2: 0.95; Adeq precision: 24.08						
Phenol removal	Model	2010.37	9	223.37	68.73	< 0.0001 (significant)
	Residual	32.50	10	3.25		
	Lack of fit	13.47	5	2.69	0.71	0.6431 (not significant)
	Pure error	19.03	5	3.81	–	–
SD: 1.80; CV %: 2.35; PRESS: 167.36; R^2: 0.98; adj R^2: 0.96; Pred R^2: 0.91; Adeq precision: 23.77						

were higher, i.e. ≈ 0.9, which indicates a good fit for the model. The values of the adjusted determination coefficient also proved the significance of all the parameters' removal.

The model F-values and low probability values showed the significance of the design for the coagulation process (Table 5). The quadratic model regression Eqs. 1, 2, 3 and 4 obtained by Design Expert 7.0.0 are given below:

Final equation for turbidity removal in terms of coded factors:

$$R_1 = 87.68 - 3.34A + 2.37B + 1.30C + 1.08AB + 0.3AC + 1.31BC - 8.90A^2 - 8.90B^2 - 8.89C^2 \quad (1)$$

Final equation for TOC removal in terms of coded factors:

$$R_2 = 90.81 + 1.91A + 3.84B + 8.67C - 0.022AB - 0.66AC - 0.67BC - 15.84A^2 - 9.01B^2 - 8.95C^2 \quad (2)$$

Final equation for DOC removal in terms of coded factors:

$$R_3 = 93.52 + 1.76A + 4.24B + 6.85C - 1.45AB - 0.25AC - 1.20BC - 14.94A^2 - 8.40B^2 - 9.00C^2 \quad (3)$$

Final equation for phenol removal in terms of coded factors:

$$R_4 = 86.91 + 0.32A + 4.57B + 3.11C + 0.23AB + 0.93AC - 0.41BC - 14.83A^2 - 3.43B^2 - 1.93C^2 \quad (4)$$

where A, B, and C represents the pH, coagulant dose, and mixing ratio, respectively. Apositive sign demonstrates synergistic effects, while a negative sign shows hostile effects of the components on the individual responses. The results were validated statistically using ANOVA.

Optimization of Experimental Conditions

The process of coagulation using alum as a coagulant was studied using a statistical tool, RSM, for different factors, and the optimal values of the independent variables, i.e. pH, coagulant dose, and mixing ratio, were determined. For these optimized values, the independent variables were individually arranged to obtain better results. In this study, each factor was chosen within a range, and each response was selected to be the maximum. After this, the optimized independent variables and predicted responses were recorded (Fig. 3). Subsequently, experimental responses were determined using the optimized independent values of the modelled variables. The experimental and model-predicted values for all responses were found to be in good agreement, suggesting that the optimization process was sound (Table 6).The optimized study showed that the coagulant activity of alum reached its maximum at pH 6. This might be due to more efficient entrapment of negatively-charged colloidal particles by the Al precipitate (Jarvis et al. 2012).However, at a higher pH, the coagulant activity of alum deteriorates, which might be due to the increase in hydroxyl (OH^-) ions. The optimal doses of alum in this study were 3.5 mg/L; at higher doses, the coagulant's hydrolyzing activities declined, which may be due to the possible restabilization of the colloidal particles, as already discussed. Similarly, the mixing ratio of 0.76 (1:1.32) was found to be the most appropriate mixing ratio of mine and surface water for the removal of turbidity, TOC, DOC, and phenol, suggesting that this mixing of two different waters benefits the coagulation process.

Assessing the Removal of the Reactive Part of NOM Using the Spectral Approach

The ASI of water represents the rate of variation in NOM concentrations because of the effect of the aromatic fraction on NOM reactivity (Korshin et al. 2009). The ASI can be represented as:

$$ASI = \left(\frac{A_{254} - A_{272}}{A_{220} - A_{230}}\right) \times 0.56 \quad (5)$$

The reactive fractions of NOM were determined after the coagulation treatment. The ASI value was considered as the metric of potential formation of disinfection by-products (DBPs). The chlorine demand for the SW and MW was found to be 8 mg/L and 3.5 mg/L, respectively. The ASI values for the SW and MW were 0.62 and 0.68. The optimum RSM result for the mixed water showed a chlorine demand of 2 mg/L and an ASI value of 0.29, representing a 52.3% ASI reduction compared to the SW alone, and a 56.7% reduction compared to the MW alone. The remarkable reduction in ASI and SUVA values (<2) in the optimized results affirmed that this treatment method achieved desirable NOM removal.

Conclusion

This study showed that co-treating MW with SW substantially reduced the concentrations of the reactive component of the NOM in the SW, making the water much more appropriate for consumption. The experimental results revealed that the best results for the removal of the reactive part of NOM were obtained at a pH of 6, a coagulant dose of 3.5 mg/L, and a mix ratio 0.76 (MW:SW), although these would differ for different water sources. The high degree of DOC, TOC, and phenol removal would virtually eliminate the chances of carcinogenic by-products forming during disinfection. Thus, the present study provides a novel co-treatment approach. Although this research was

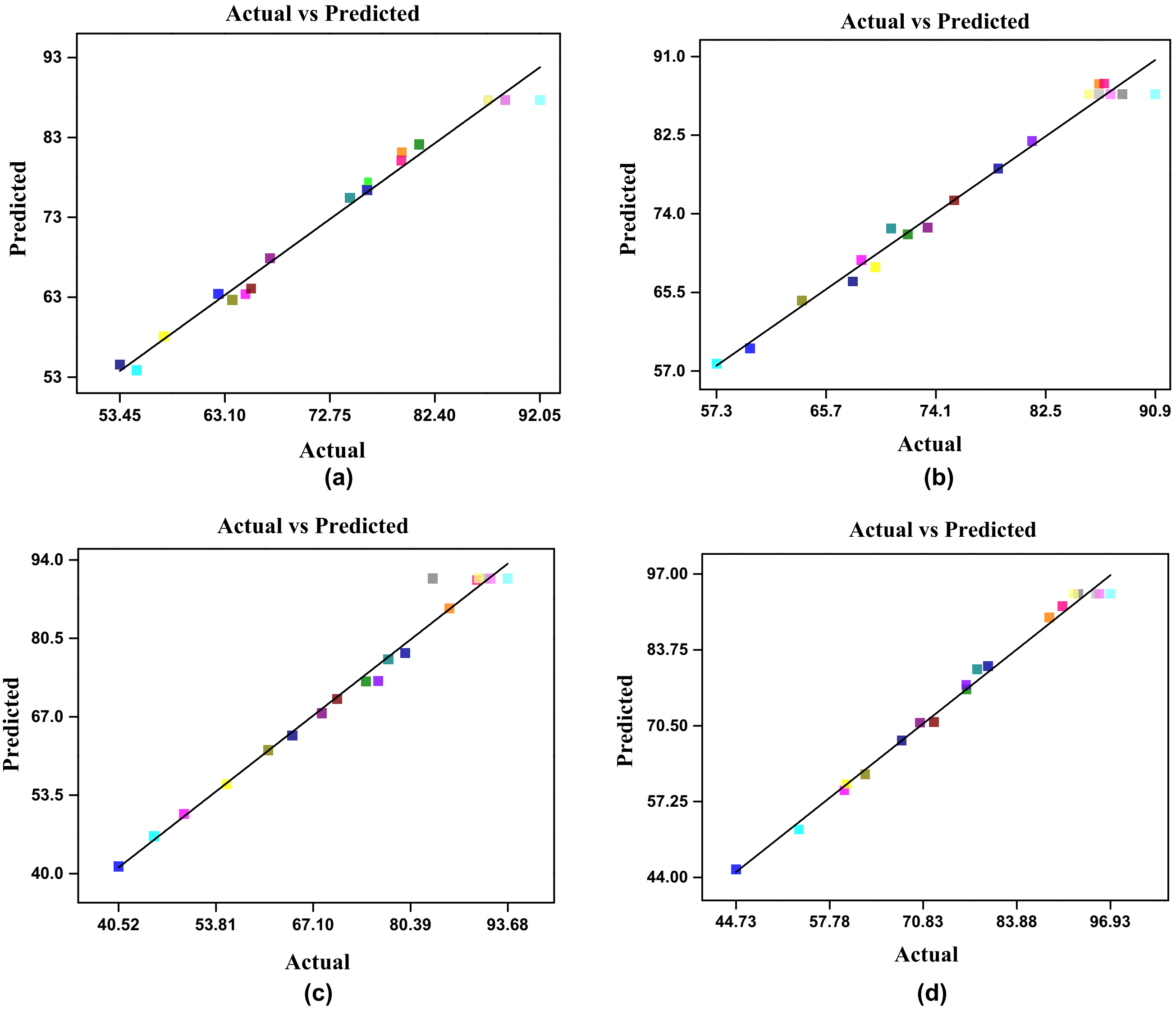

Fig. 3 Actual vs. predicted diagnostic of: **a** turbidity reduction, **b** phenol reduction, **c** TOC reduction; and **d** DOC reduction

Table 6 Optimized predicted vs experimental results for percentage reduction in selected responses

	Independent variables			Responses			
	pH (A)	Coagulant dose (mg/L) (B)	Mix ratio (C)	Turbidity removal (%)	TOC removal (%)	DOC removal (%)	Phenol removal (%)
Predicted values	6.02	3.50	0.76	87.15	93.11	95.26	88.66
Experimental values	6.02	3.50	0.76	88.88	92.64	96.83	90.13

conducted with MW that was naturally circumneutral, it is likely that the effluent of an acid MW treatment plant could also be used, though this would, of course, have to be demonstrated.

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