Removal of Azo Dyes From Aqueous Solution Using Fenton and Modified Fenton Processes

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Background: Fenton (Fe2+ and H2O2) and modified Fenton (Fe3+ and H2O2) are two popular methods used in advanced oxidation processes (AOP) and degradation of persistent organic pollutants (POPs), such as dye compounds. In these processes, Fe2+ and Fe3+ as catalysts and H2O2 as the oxidizing agent are added to the reactor.

Objectives: The aim of the current study is to assess the abovementioned methods for removal of Reactive Red 198 and Blue Reactive 19 from aqueous solutions.

Materials and Methods: This research was carried out using lab-scale. After preparation of RR-19 and RR-198 stock solutions (1000 ppm), optimum pH and temperature were determined within the range of (3-11) and (15°C - 40°C) respectively, and specific amounts of Fe2+ and Fe3+ (0.8, 1, 3, 7, 14 and 32 mM) were prepared by adding FeSO4.7H2O and FeCl3, and H2O2 30% W/W (2, 5, 11, 23, 47 and 94 mM) were added to the solutions to establish the H2O2/Fe2+, Fe3+ molar ratios. Standard jar tests were conducted using jar test apparatus. After sedimentation time, samples were filtered through a 0.45 µm fiber membrane, and then final dye concentrations were measured using a UV/VIS spectrophotometer.

Results: The highest dye removal efficiency in both Fenton and modified Fenton methods were obtained at the optimum pH = 3, optimum reaction time of 10 minutes, optimum temperature at 25°C and H2O2/Fe2+, H2O2/Fe3+ concentrations of 11.3 and 5.1 mM, respectively.

In the Fenton reaction the maximum efficiency was obtained at 94.70% and 99.31% for reactive red 198 and reactive blue 19, respectively.

Conclusions: Fenton and modified Fenton processes could be used as very effective methods for removal of reactive red 198 and blue reactive 19 from aqueous solutions.

Keywords: Fenton’s reagent; reactive red 198; Adsorption; Waste Water

1. Background

Textile and dyeing industrial are considered as the major sources of water consumption. According to the production rate, water consumption varies between 25 - 250 m3/ton of product. The resulting wastewater contains BOD, COD and synthetic dyes (1, 2), and discharge of contaminated effluent without any treatment into the environment creates depressed photosynthesis and aquatic plant demise which characteristics are considered as environmental threats (3). Dyes are substances with complex structures which contain atoms: electron acceptors such as chromophore or electron donors such as cocominium, which determine its strength and solubility in water (4, 5). Based on the application, dyes are categorized as Watt, reactive, direct, cation, acidic and disperse, of which Azo dyes are found in more than 50% of reactive and disperse dyes (6, 7). Azo reactive dyes are anionic and soluble in water. Because of their variety of colors, easy utilization, good stability during washing and low energy consumption, Azo dyes are applied more frequently in the textile industry (5, 8). These dyes have strong resistance to photolysis and chemical decomposition, and in some cases there are special components in their structures that have carcinogenic and mutagenic consequences (5, 9). Even the presence of a small quantity of dye (less than 1 ppm) in water has adverse effects. Synthetic dyes are used in abundance by textile (60%), paper making (10 %) and plastics industries. Now, over 10000 varied types of commercial pigments and dyes are produced annually, about 7 x 105 tons (10). Their absorption into biological masses are very weak and there is no decomposition in aerobic conditions. Reactive red 198 and blue reactive 19 are mono Azos which are used in textile plants in Iran.
Different technologies are applied to decrease absorption of these dyes into the environment such as ion exchange, chemical sedimentation, electrochemical reduction, advanced oxidation, membrane process and absorption。(13-15).

The limitations of the available technologies include dense solution disposal, high energy consumption, high operation costs, excessive production of sludge, expensive facilities (16-18). Therefore, finding new and effective alternatives is necessary to remove contaminants from aquatic environments. One effective technique is advanced oxidation which can be used to remove toxic and resistant chemicals and reprocess them into mineral form to release carbon dioxide and oxygen. Advanced chemical oxidation processes such as chemical, photochemical, photocatalytic methods and electrochemical methods (UV/O3, UV/H2O2, Fenton, modified Fenton, and ultrasound) are decapitating and produce hydroxyl radicals. In this process, hydroxyl radicals using Fe(II) and Fe(III) catalysts are generated easily as follows (19-21):

**Fenton reactions:**
1. Fe2+ + H2O2 → Fe3+ + OH- + H+  
2. Fe3+ + H2O2 → FeOOH2+ + H+  
3. FeOOH2+ → Fe3+ + O2H  
4. Fe3+ + O2H → Fe2+ + O2 + H+  
5. Fe2+ + OH* → Fe3+ + OH-  
6. H2O2 + OH* → H2O + O2H  
7. OH* + Reactive dye production

Reactions related to modified Fenton process:
1. Fe3+ + H2O2 → Fe2+ + HO2- + H+  
2. HO2- →O2- + H+  
3. HO2- + Fe3+ → Fe2+ + O2 + H+  

Efficiency of the advanced oxidation process is dependent on the oxidation rate of hydroxyl radical. These radicals have high reaction rates, oxidation potential, low selectivity for organic components and will destroy contaminants in four ways: (i) addition of OH- to the structure of contamitants (ii) hydrogen absorption (iii) electron transmission (iv) reaction between free radicals that can lead to the formation of stable compounds. Among the various processes of advanced oxidation, using the Fenton (H2O2/Fe2+) and modified Fenton (H2O2/Fe3+) methods have greater advantages, such as simple operation, low reaction time, using of coagulation and flocculation processes, non-toxic compound production, economic viability, and possibility of utilization at different scales. Disadvantages include costly treatment processes and disposal of sludge, ferrous ions are consumed faster than produced, the process is limited to low pH range, and deactivation of iron ions due to bonding of iron ions with various reagents such as anion phosphate, oxidation of the product as well as further water pollution due to existence of catalysts such as iron salt. The main steps involved in the Fenton process are: (i) oxidation, (ii) neutralization, (iii) flocculation and (iv) sedimentation.(22-24). Research shows that modified Fenton is very effective in treating colored wastewater but so far little research has been done using this method.

2. Objectives

This paper presents a brief review on the role of Fenton and modified Fenton reactions in the removal of contaminants (blue reactive 19 and reactive red 198) from aqueous solutions.

3. Materials and Methods

Reactive dyes were bought from Alvan Sabet Company (Iran); other chemical material was obtained from Merck Company (Germany). The chemical structures and a number of the physicochemical properties of the dyes used are listed in Table 1.

This research was carried out using lab-scale in chemistry laboratory of Zahedan University of Medical Sciences. The advanced oxidation experiments were started in a Plexiglas reactor (1 L) as batch system. Ranges of experimental parameters are given in Table 2. After preparation of RB-19, RR-198 Stock solutions (1000 ppm), working solutions were made by dissolving stock solution in deionized water. After determination of optimum pH within range of (3-11) and temperature (15°C - 40°C), specific amounts of Fe2+ and Fe3+ (0.8, 1, 3, 7, 14 and 32 mM) were prepared by adding FeSO4·7H2O and FeCl3, and determined amounts of H2O2 30% W/W (2, 5, 11, 23, 47 and 94 mM) were added to the solution to create the H2O2/Fe2+ and H2O2/Fe3+ molar ratios. Standard Jar Tests were conducted using jar test apparatus (model OSK8996). After sedimentation time, supernatant samples were collected from the solution using a 50 mL pipet. Collected samples were filtered through a 0.45 µm fiber membrane, then final dye concentrations were measured using a UV/VIS spectrophotometer (optima SP-3000 plus) at 590 nm for RB-19 and 518 nm for RR-198. The dye removal percentage (R%) was calculated as follows (Equation 1):

\[
R(\%) = \left(\frac{C_0 - C}{C_0}\right) \times 100
\]

Where \(C_0\) is the initial concentration (mg/L) and \(C\) is the final dye concentration (mg/L).

4. Results

It has been established that pH has a significant influence on the performance of oxidation processes. In the present study the effect of pH (3-11) on removal of two dyes, reactive red 198 (RR98) and blue reactive 19 (RB 19), were investigated. Figure 1 shows that the highest removal efficiency for the dyes studied occurred at pH 3 for both processes, modified Fenton and Fenton. Final values of pH samples at the end of the experiments are presented in Figure 2.
Optimum reaction time for Fenton and modified Fenton methods depends on the initial concentration and variance of catalyst dosage. Dye removal efficiency was investigated at fixed pH and $H_2O_2/Fe^{2+}$, $Fe^{3+}$ ratio conditions. As it can be seen in Figure 3, optimum reaction time for both processes was obtained at 10 minutes.

Temperature has a positive effect on treatment efficiency; hence, six temperatures were investigated in this study. As shown in Figure 4, the best removal efficiency for both methods was obtained at 25°C. In addition, this effect was studied in various molar ratios. Maximum dye removal in optimum molar ratios in Fenton and modified Fenton methods were obtained at $H_2O_2/Fe^{2+} = 11.3$ and $H_2O_2/Fe^{3+} = 5.1$, respectively (Figures 5 to 8). To determine the effect of dye concentration on removal efficiency, mentioned dyes were examined at three concentrations (10, 50 and 500 mg/L). Figures 5 to 8 reveal dye removal efficiency in various concentrations. As can be seen, removal efficiency was increased by increasing dye concentration.

| Characteristics          | Reactive Red 198 | Reactive Blue 19 |
|--------------------------|------------------|------------------|
| Chemical structure       | ![Chemical structure of Reactive Red 198](image1) | ![Chemical structure of Reactive Blue 19](image2) |
| Molecular formula        | $C_{27}H_{18}ClN_7Na_4O_{15}S_5$ | $C_{22}H_{16}O_5N_2S_3Na_2$ |
| Molecular weight, g/mol  | 967.5            | 626.5            |
| $\lambda_{max}, nm$      | 520              | 592              |

Table 1. Characteristics of Dyes Used

Table 2. Ranges of Experimental Parameters*

| Parameters                              | Ranges of Experimental |
|-----------------------------------------|------------------------|
| Mixing speeds, rpm                      |                        |
| 1 min                                   | 80                     |
| 80 min                                  | 30                     |
| Temperatures, °C                        | 15, 20, 25, 30, 35, 40 |
| Sampling Times, min                     | 10, 20, 40, 80         |
| Initial dyes concentrations, Mg/L       | 10, 50, 500            |
| $H_2O_2$ concentrations, mM             | 2, 5, 11, 23, 47, 94   |
| $Fe^{3+},Fe^{2+}$ concentrations, mM    | 0.8, 1.3, 7.14, 32     |
| pH                                      | 3, 5, 7, 9, 11         |

*Abbreviation; rpm, revolutions per minute.

Figure 1. Effect of pH on Reactive Red 198 and RB-19 Removal Percentage in Fenton and Modified Fenton Methods

Figure 2. Final pH in Dye Removal in Different Concentration of $H_2O_2$/Fe$^{2+}$ and $H_2O_2/Fe^{3+}$ in Fenton and Modified Fenton Methods

Temperatures 25°C, reaction time of 20 minutes, dyes concentrations 50 mg/L, $H_2O_2/Fe^{2+}, Fe^{3+} = 11.3$.
Figure 3. Effect of Contact Time on Reactive Red 198 and Reactive Blue 19 Removal Percentage in Fenton and Modified Fenton Methods

Temperatures 25°C, pH = 3, dye concentration 50 mg/L, H$_2$O$_2$/Fe$^{2+}$, Fe$^{3+}$ = 11.3.

Figure 4. Effect of Temperature on Reactive Red 198 and Reactive Blue 19 Removal Percentage in Fenton and Modified Fenton Methods

pH = 3, reaction time of 10 minutes, dyes concentrations 50 mg/L, H$_2$O$_2$/Fe$^{2+}$, Fe$^{3+}$ = 11.3.

Figure 5. Removal Percentage and Residue Concentration of reactive red 198 in Different Dye Concentrations and Molar Ratios of H$_2$O$_2$/Fe$^{2+}$ in Fenton Method

Temperatures 25°C, pH = 3, reaction time of 10 minutes.

Figure 6. Removal Percentage and Residue Concentration of Reactive Blue 19 in Different Dye Concentrations and Molar Ratios of H$_2$O$_2$/Fe$^{2+}$ in Fenton method

Temperatures 25°C, pH = 3, reaction time of 10 minutes.
**Figure 7.** Removal Percentage and Residue Concentration of Reactive Red 198 in Different Dye Concentrations and Molar Ratios of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ in Modified Fenton Method

Temperatures $25^\circ\text{C}$, $\text{pH} = 3$, reaction time of 10 minutes.

**Figure 8.** Removal % and Residue Concentration of Reactive Blue 19 in Different Dye Concentrations and Molar Ratios of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ in Modified Fenton Method

Temperatures $25^\circ\text{C}$, $\text{pH} = 3$, reaction time of 10 minutes.
5. Discussion

The present study has evaluated a number of parameters such as pH, contact time, temperature, initial hydrogen peroxide H₂O₂ concentration and iron (II), iron (III) concentrations.

5.1. Effect of pH

pH is one of the effective parameters on dye removal efficiency in Fenton and modified Fenton processes. pH plays an important role in production of radicals that are effective in increasing oxidation efficiency. It has been proven that the Fenton reactions in acidic pH are more effective than neutral pH (25). On the other hand, oxidation reactions are slower in neutral pH due to hydroxyl ion of iron (26). Figures 1 and 2 show that the maximum removal percentage reached is 95% in pH = 3, thus the optimum pH was obtained as 3 for all of samples. In pH > 3, because of Fe(III) sediments, Fenton efficiency decreases, the synthetic hydroxide produced can hydrolyze the available hydrogen peroxide to other products (O₂ and H₂O) that subsequently cause oxidation and hydroxyl ions decline. Moreover in pH > 3, the Fe(II) [Fe(II) (H₂O)₆]²⁺ substance can react with hydrogen peroxide better than the Fe(II) [Fe(II) (OH) (H₂O)₅]²⁺ substance (27, 28). In lower pH, the additionally produced hydroxyl ions react in reverse which leads to further Fe(III) production. As shown in Figure 8 below (27).

8. Fe³⁺ + H₂O₂ → Fe - OOH²⁺ + H⁺

As shown above, the generation of Fe(III) to Fe(II) is prohibited and as a result the available Fe(II) concentration producing hydroxyl radical was declined. These results are in accordance with other reported research (29). In the Fenton method, iron ions will become sediment in higher pH in the form of ferric hydroxide. In low pH iron ions can form a stable substance with hydrogen peroxide leading to the inactivation of the catalyst and subsequently removal efficiency decreases. Acidic solutions have a propensity to produce hydrogen peroxide (Equation 9), but according to equation 10, in low pH, the number of active sites for hydrogen peroxide is declined. In pH < 3 hydrogen peroxide forms econium and remains constant. According to other research, pH = 3 because of renewed production of Fe(II) via reaction between Fe(III) and hydrogen peroxide, the Fenton process has less effect (10, 22, 23).

9. O₂+ 2H⁺+ 2e⁻→ H₂O₂
10. H₂O₂+ 2H⁺+ 2e⁻→ 2H₂O
11. H₂O₂+ H⁺→ H₂O₂⁺

Figure 5 shows the final pH of the solution and it can be concluded that by increasing the iron concentration, the pH decreases from 4 to 2.5; this may be due to the hydrolysis of water and production of further H⁺ ions (28). Yung et al. obtained optimum pH = 2 - 4 for treatment of pharmacy wastewater; also the optimum pH for dye removal was 3 - 4 (30, 31).

5.2. The Effect of Contact Time

To study the optimum time and its effect in the Fenton and modified Fenton processes, experiments were performed for 10 to 80 minutes to determine optimum time of the Fenton and modified Fenton efficiency in dye removal. As shown in Figure 3, maximum efficiency was attained at 10 minutes for both of the processes which was more than 94%. It is clear that removal efficiency increase was linear and slow thereafter. Linear increase of dye removal efficiency can be related to chemical oxidation of dye by OH. In advanced chemical oxidation, with methods other than the Fenton process, OH production in the environment is continuous, but in the Fenton process high concentrations of OH are produced in the first minutes of the process (29). Fenton oxidation of organic compounds showed that in the early stages the initial rate of mineralization was fast with Fenton reagents, due to the immediate formation of hydroxyl radicals, where the color could obviously be reduced. It demonstrated that the recalcitrant organic compounds which were in the wastewater had been oxidized by HO⁻ after reaction time of 60 minutes, resulted in the curve slightly ascending (21). In the Fenton oxidation system, the hydroxyl radicals made, which had extremely high oxidizing ability, could oxidize into hardness with the decomposition of organic compounds in a short time. Also after the rapid and slow mixing, large amounts of pinpoint flocs were consistently observed and took a very long time to settle down. These tiny amounts of floc frequently interfered with color and measurement. The majority of color was generally removed after rather short oxidation times: one minute (26), 10 minutes (18), and 15 minutes (27).

5.3. The Effect of Temperature

Although temperature has a positive effect on treatment efficiency in the Fenton process, it has a less effect than other factors. Very low or high temperature has adverse results on the efficiency process (28). Figure 5 shows the highest removal efficiency at 25°C. Goi et al. (32) reported that 30˚C is as an optimum temperature for decomposition of silicic acid. Also it has been proven that temperatures between 20°C - 30°C can be used as the best temperature because of high efficiency (32). Zhang et al. concluded that COD removal efficiency was increased gradually by varying temperature from 15°C - 35°C (28). Weng et al. reported that dye decomposition rate was less at lower temperatures (33). The optimum temperature was estimated to be 45°C (31). During the process, temperature had two effects on accumulation of hydrogen peroxide: a) when temperature is increased, dissolving of oxygen decreased; b) peroxide had a low solubility in higher temperature. When temperature increased to more than 30°C, dye decomposition declined because of decomposition of hydrogen peroxide. Also the negative effect of temperature on contaminant re-
removal can be described as low concentration of dissolved oxygen (DO) and spontaneous decomposition of peroxide in high temperatures (20). Usually when temperature increases, hydrogen peroxide concentration decreases, because increasing the temperature reduces DO to wastewater. Devi et al. reported that by increasing temperature from 30 to 50°C, Alizarin Red decomposed very well (34). Ayodele et al. (19) showed that phenol decomposition increased with varying the temperature from 22°C to 27°C; it also proved that by increasing the temperature, oxidation and mineralization rates improved by decreasing the hydrogen peroxide and Fe(II). This phenomenon can be due to the increasing reaction between hydrogen peroxide and any sort of iron ions that finally lead to generation of hydroxyl radicals or a high capacity of iron species (19).

5.4. The Effect of H2O2

In the Fenton process, hydrogen peroxide plays an essential role in contaminant removal efficiency. Figure 3 shows the effect H2O2 concentration on reactive dye removal percentage from colored solutions. An increase in H2O2 concentration from 2 to 5 mM causes an increasing in the dye removal percentage. Improvement in dye removal can be attributed to increase of hydroxyl radicals as a result of growing growth (31). When H2O2 concentration increases, the reaction time gets shorter. Minimum removal efficiency was observed in higher concentrations of H2O2 (> 5 mM). The slow decomposition of reactive dye at higher concentrations of H2O2 was due to the conversion of the generated hydroxyl radicals to hydroxyl ions, reaction of hydroxyl radicals, prohibition of its formation and H2O2 dissociation with oxygen and H2O that change precipitate Fe3+ ions. The sequences above are in accordance with the following equations (35):

12. H2O2 → HO• + HO•
13. Fe2+ + HO• → Fe3+ + OH•
14. [Fe3+] [OH•] → Ksp Fe(OH)3

In other words, the deactivation of Fe2+ takes place at higher dosages of H2O2, thus giving a brownish yellow precipitate at higher dosages (29). Zhang et al. (28) reported that efficiency of hydrogen peroxide for removing organic materials in the leachate decreased with the increase of Fenton’s reagent dosage. At a high dosage of H2O2, the decrease in removal efficiency was due to the hydroxyl radical scavenging effect of H2O2 (Equations 15 and 16) and the recombination of the hydroxyl radical (Equation 17) (10):

15. HO• + H2O2 → HO2• + H2O
16. HO2• + HO• → H2O + O2
17. 2HO• → H2O2

According to the literature, stepwise H2O2 addition could be more effective than applying a large initial dose. This could be due to scavenging of OH• by H2O2, according to reaction 18 (36):

18. OH• + H2O2 → HO2• + H2O

Reaction 18 contends better with reaction seven at higher concentrations of H2O2, reducing the oxidation rate of the target dye compound. Hydroxyl radical concentration increased when the H2O2/Fe2+ ratio increased that led to greater oxidation of dye. In this study, H2O2 dosage in the Fenton and modified Fenton processes were chosen as 11 and 5 mM as the optimum dosage, respectively.

5.5. The Effect of Iron Concentration

There are no hydroxyl radicals devoid of ions, so the iron ion concentration is essential because increasing the hydroxyl radicals and the coagulation phenomenon lead to a decrease of contaminants. Fenton efficiency can be enhanced by increasing the Fe(II) and Fe(III) concentration, since hydroxyl radical concentration [the same key oxidant] was increased by increasing the Fe(II) concentration. Hydrogen peroxide is not strong enough to oxidize big molecules such as pigments in wastewater dye without the presence of Fe(III) (37). By adding a quantity of Fe(III), removal efficiency will increase. Wang et al. reported that Fe(II) ions reduce COD amount by increasing Fe(II) (0.33 mM), where COD removal efficiency reached 43% from 19% (38). Zhou et al. found that methylene red removal was increased from 45% to 75% in presence of Fe(II) at 10 minutes (39). The effect of ferric and ferrous dosage on removal efficiency is shown in Figures 3 and 4; the plots illustrate that an increase in iron ion concentration, results in a decrease in the percentage of dye removal. The use of high concentrations of Fe2+ (for a given hydrogen peroxide concentration) accelerated the rate of decomposition of the hydrogen peroxide generated hydroxyl radicals [HO2•] which is considered to be the rate limiting step, while lower doses of Fe2+ favored the reaction to generate OH• which is more reactive than HO2• radicals. Beyond the dosage, 2 mM inactivation of the Fe2+ occurred owing to instantaneous formation of hydroxyl ion in accordance with the following reaction (33):

19. OH• + Fe2+ → OH• + Fe3+

This takes place at a faster rate than the formation of hydroxyl radical from Fe2+ and peroxide. In conclusion, more reduction in dye removal was observed as more catalyst was added early in the reaction. The Fenton reaction occurred during the first 10–40 minutes. Then, the rate of Fenton reaction due to production of Fe3+ by Fe2+ became slower and decolorization stopped (37). By increasing the iron ions above these values, removal efficiency did not increased because of the tendency of the hydroxyl radicals to react with Fe3+ and H2O in the oxidation-reduction reaction (29). In this paper, Fe2+ and Fe3+ dosage of 3 and 1 mM were selected as the optimum dosage respectively.

5.6. The Effect of Dye Concentration

Dye concentration is effective on dye removal percentage. Figure 8 shows the effect of various dye concentra-
tions (10, 50, 500 mg/L) on removal efficiency [pH = 3, Fe(II) and Fe(III) concentration 50 mg/L, contact time of 10 minutes]. The line reveals that an increase in the dye concentration from 10 to 500 mg/L, reduces the percentage of dye removal, because by increasing the concentration and keeping the H$_2$O$_2$ value stable, the hydroxyl radicals produced also become stable, thereby the removal percentage will reduce (29, 36). RR-198 and RB-19 removal percentage was determined in 50 mg/L of dye. The Present study was performed with the aim of evaluating the Fenton and modified Fenton processes in removal of reactive red 198 and Reactive Blue 19 from aqueous environments. The effect of various operating parameters such as H$_2$O$_2$/Fe$^{2+}$, H$_2$O$_2$/Fe$^{3+}$, pH, reaction time, temperature and initial concentration of dye was investigated. The results of this study showed that the most effective dye removal agents are H$_2$O$_2$/Fe$^{2+}$, H$_2$O$_2$/Fe$^{3+}$, equal to 11/3 and 5/1 mM at pH = 3 respectively. Dye removal efficiency for reactive red 198 and Reactive Blue 19 utilizing the Fenton and modified Fenton processes were 99.43, 99.31, 94.8 and 90.98%, respectively (initial dye concentration 50 mg/L and reaction time of 10 minutes). The findings of this study showed that removal efficiency reduced with increase of dye concentration in fixed conditions for other parameters. Finally, it can be concluded that the modified Fenton process is superior to the Fenton process for dye removal from aqueous solutions.

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Authors' Contribution

The overall implementation of this study including design, experiments and data analysis, and manuscript preparation which were the results of joint efforts by individuals who are listed as co-authors of this paper. All authors have made extensive contribution in the review and finalization of this manuscript.

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