



Fe-Impregnated Charcoal for Enhanced Removal of Azo Dye Reactive Blue 194: Fenton-like Oxidation Conditions and Fate of Degradation Products in Activated Sludge System



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THIS STUDY aimed to assess the effectiveness of Fe-impregnated charcoal (FIC) in removing azo dye Reactive Blue 194 (RB) under various Fenton-like oxidation (FLO) conditions, as well as investigate the fate of degradation products when discharged into an activated sludge system. The optimal FIC concentration for achieving maximum decolorization activity was found to be 0.5 to 1 g/L, resulting in a removal efficiency of over 95% within 90 minutes. However, the decolorization efficiency decreased as the initial dye concentration increased, reaching 83.6% at 0.5 g/L within 90 minutes. Other optimal reaction conditions included 80 mg/L H₂O₂ at an initial pH of 3.5 and a temperature of 25°C. The impact of tap water and chemical additives commonly used in dyeing baths, such as acetic acid and sulfonic acid, on the FLO rate was investigated. The use of tap water resulted in a 3.4% reduction in decolorization activity, while the addition of 0.3 g/L sulfonic acid led to a decrease in color removal efficiency to 84.4% within 90 minutes, although the pH was maintained at the optimum condition. The treated solutions were transferred to a pre-adapted activated sludge system, and the resulting solutions after each stage were extracted and analyzed using GC-MS. The results revealed that the de-aromatization process began during the Fenton oxidation stage and was completed in the activated sludge system. However, certain phenolic compounds originating from the degradation of the parent dye remained unchanged throughout all stages

Keywords: Azo dyes; Decolorization; Advanced oxidation; Aromatic amine.

1. Introduction

The monitoring and remediation and removal of toxic substances is of great important for survival in the earth, so several studies have been conducted for achieving this aim (Abbas et al., 2021; Abosena et al., 2021; Elbasiouny et al., 2021; El-Ramady et al., 2020). Azo dyes, commonly employed in the textile industry, pose a significant environmental challenge as they are both highly toxic and resistant to breakdown in wastewater (Wang et al., 2022). The treatment of wastewater from dyeing facilities is a primary concern in numerous countries. These dyes find extensive use in industries like textiles and leather, but they are widely recognized as carcinogenic, teratogenic, mutagenic, and xenobiotic, making them challenging to biodegrade (Le et al.,

2019; de Luna et al., 2014). Globally, over 700,000 tons of organic dyes are manufactured each year, with azo dyes accounting for around 60%–70% of the total commercial dye production (Rajeshwar et al., 2008). Given their high resistance and toxicity, azo dyes pose potential risks to both organisms and humans. Consequently, it is imperative to identify efficient treatment methods for the removal of these pollutants.

Advanced oxidation processes (AOPs) have been extensively discussed in the search for techniques capable of completely eliminating refractory organic contaminants. AOPs are favored for their operational simplicity, minimal equipment requirements, cost-effectiveness, and efficiency in reducing pollutants when compared to alternative methods (Gvonic 2022; Isarain et al., 2011; Sires et al., 2010). They

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also exhibit the capability to degrade various hazardous organic substances (Adachi et al., 2022; Kamagate et al., 2018). Fenton oxidation employs iron ions as a catalyst to stimulate the generation of highly reactive hydroxyl radicals ($\cdot\text{OH}$), which are effective at breaking down contaminants. Nevertheless, this approach has a drawback as it can lead to the generation of additional pollutants, restricting its suitability for industrial use.

In the conventional Fenton oxidation process, Fe_2^+ ions are introduced into the system to activate hydrogen peroxide (H_2O_2) and generate $\cdot\text{OH}$ in an acidic environment. However, this process results in the conversion of Fe_2^+ to Fe_3^+ (Wang et al., 2022). In this homogenous system, the inability to recycle dissolved iron salts and the generation of significant iron oxide sludge pose challenges due to the additional treatment step. Separating iron salts and sludge from the treated water demands additional effort and frequently encounters difficulties in final disposal (Park et al., 2018, Munoz et al., 2015).

To address the shortcomings of the traditional Fenton reaction, a Fenton-like reaction (Heterogeneous Fenton reaction) employing solid support catalysts impregnated with iron, such as goethite and clay minerals, has been developed (Park et al., 2018, Costa et al., 2008; Pouran et al., 2014). Iron-impregnated carbon materials like activated carbon, graphene, and carbon nanotubes have also been created, demonstrating high degradation efficiency and stability (Munoz et al., 2015; Bounab et al., 2016). Nevertheless, these materials involve a two-step process of initially obtaining carbonaceous material through pyrolysis and then subjecting it to iron impregnation and additional pyrolysis (two thermal steps).

The activated sludge process is one of the most commonly used systems for secondary wastewater treatment (Archana et al., 2017; Salaudeen et al. 2018; Ladha et al., 2007). Although it well established as the most cost-effective technology, it has been demonstrated ineffective for the degradation of azo dyes. This is related to presence of the molecule of azo dyes possess strong electronegativity because of the presence of azo bonds ($-\text{N}=\text{N}-$) in addition to low BOD to COD ratios (Ladha et al., 2007). To achieve a combination of both economic and environmental advantages, the combination between chemical and biological processes can be an efficient solution for the removal of toxic compounds from effluents (Garcia-Montano et al., 2006).

Most of the previous studies conduct Fenton reactions in order to break down the textile dyes in a solution consisting of distilled water with the dye to be degraded only. In this study, the effect of some chemical additives used in the dyeing process in low-tech dyeing houses in the city of Al-Mahalla Al-Kobra, Gharbia Governorate, Egypt, and the effect of using tap water in dyeing houses on the efficiency of the reaction were studied through Fe-impregnated charcoal to achieve decolorization of Reactive blue 194 and detect the fate of the degradation products in activated sludge treatment systems through GC-MS analysis.

2. Materials and Methods

2.1. Preparation of Fe-impregnated charcoal (FIC)

Impregnation of charcoal was conducted according to the method described by Micháleková-Richveisová et al. (2017) with some modifications, to prepare, 100 grams of charcoal was combined with a saturated ferrous sulfate solution and stirred magnetically at room temperature for 12 hours. Afterward, the mixture was dried at 105°C for 12 hours. The dried composites were thoroughly rinsed with deionized water to eliminate any surface iron hydroxide that had formed. They were then dried overnight at 105°C . The resulting products were sieved to achieve a particle size range of 0.2 to 1 millimeter and stored in polypropylene containers for future utilization. (All chemicals were purchased from El-Gomhoria for chemicals)

2.2. SEM and XRD analysis of prepared FIC

The morphology and structure of FIC were observed by scanning electron microscope (SEM, FEI-QUANTA 250, USA). XRD measurements were conducted using a Cu target X-ray tube at 40.0 kV and 30.0 mA. Slits controlled the X-ray beam, and a Theta-2Theta scan covered 5.0000 to 80.0000 degrees. Data processing included manual smoothing, background subtraction, and automated peak search with specific parameters. The FWHM threshold was 0.050 degrees, and the intensity threshold was 30 parts per million. The FWHM ratio used for peak analysis was $(n-1)/n = 2$. No system error correction or precise peak correction was applied. These conditions were chosen to ensure accurate and reliable XRD data collection for the sample

2.3. Catalytic activity of FIC

The catalytic effectiveness of FIB in the Fenton-like oxidation reaction was assessed under various conditions. These conditions included different initial FIB concentrations ranging from 0.1 to 1.0 g/L, varying initial H₂O₂ (37%) concentrations from 50 to 1000 mg/L, adjusting the initial solution pH within the range of 2.5 to 6, and changing the initial concentration of Reactive blue 194 between 100 and 500 mg/L. The degradation of Reactive blue 194 by the FIB catalyst was carried out as follows: 0.1 g/L of FIB was placed in glass Erlenmeyer flasks, followed by the addition of 100 mL of a solution containing 0.1 g/L of Reactive blue 194. In addition to the effect of tap water in reaction mixture, different concentrations of acetic acid (0.25, 0.5 and 1%) and different concentrations of sulfonic acid (1 and 3 g l⁻¹) were also studied.

2.4. Effect of charcoal particle size

The prepared charcoal was sieved to obtain particle sizes of 0.2 and 1 mm and the effect of the two size levels on the rate of dye decolorization was estimated. The optimum results from each experiment were applied in the next one.

2.5. Analytical methods

After the Fenton-like reaction, the samples were subjected to centrifugation at 4000 rpm for 10 minutes. Subsequently, the supernatant was carefully collected and analyzed to ascertain the remaining concentration of Reactive blue 194. This analysis was performed using a spectrophotometer, specifically the Jenway 6705 model, at a wavelength of 600 nm.

For determining the decolorization of dye, color removal efficiency was calculated using Eq. given below.

$$\text{Color Removal Efficiency (\%)} = \frac{R_0 - R_t}{R_0} \times 100$$

Where R₀ and R₁ represent the absorption reading at 600 nm at an initial time (t = 0) and at time 't' respectively

2.6. Biological treatment by activated sludge

2.6.1. Source of activated sludge

The Activated Sludge utilized in this study was obtained from a conventional activated sludge facility located in Sakha, Kafr El-shikh. To eliminate any remaining carbon or mineral nutrients, the sludge underwent multiple washes. This process involved using a phosphate buffer with a pH of 7, followed by successive steps of centrifugation, extraction of the supernatant, and resuspension of the pellet in water.

Preparation of synthetic waste water

Synthetic wastewater was prepared according to de Kreuk et al. (2005) as described in table (1)

Table 1. Composition of synthetic wastewater.

Solution A	Concentration (mM)	Solution B	Concentration (mM)
CH ₃ COONa	65.1	NH ₄ Cl	35.2
MgSO ₄ .7H ₂ O	3.7	K ₂ HPO ₄	4.4
KCl	4.8	KH ₂ PO ₄	2.2
		Trace element*	10 mL L ⁻¹

*Trace element solution contained (mmol L⁻¹): EDTA 342.2, ZnSO₄.7H₂O 15.3, CaCl₂.2H₂O 111.3, MnCl₂.4H₂O 51.1, FeSO₄.7H₂O 35.9, Na₂Mo₇O₂₄.2H₂O 2.7, CuSO₄.5H₂O 12.0, and CoCl₂.6H₂O 13.5.

Solution A and B were prepared in minimum quantity of distilled water and the dye solution resulted after Fenton-like treatment was used to dilute the concentrated synthetic wastewater solution to the concentration mentioned in table (1).

2.6.2. System operation

The experiment was carried out using 500 mL serum bottles with a working volume of 250 mL. The initial pH of the solution was set at 7. Activated sludge was introduced to achieve an initial concentration of 1 g/L of dry matter. The cultures were mixed by placing them on a rotary shaker operating at 150 rpm and were maintained at room temperature, which was 25°C, the system was operated for three cycles before sample needed for GC-MS analysis was taken. The operating cycle

consists of agitation for 12 hours the agitation was stopped to permit sludge settling the supernatant was removed and replaced with fresh solution containing dye degradation metabolites resulting from fenton-like oxidation as mentioned earlier. The concentration of sludge concentration was kept constant during the experiment through removing the excess sludge.

2.7. Identification of degradation products

The degradation products at three different stages of RB 194 treatment (after 10 minutes of the Fenton reaction, after 90 minutes, and following the completion of biological treatments) were extracted using dichloromethane. Subsequently, the compounds were identified using a Trace GC-TSQ

Quantum mass spectrometer manufactured by Thermo Scientific in Austin, TX, USA. A direct capillary column TG-5MS (30 meters in length, 0.25 mm diameter, and 0.25 μm film thickness) was employed.

The temperature profile for the column oven was as follows: it started at 50°C, then increased at a rate of 5°C per minute until reaching 200°C, where it was held for 2 minutes. Afterward, the temperature was raised to a final value of 290°C at a rate of 30°C per minute, and again held for 2 minutes. The injector and mass spectrometer transfer line were maintained at temperatures of 270°C and 260°C, respectively. Helium gas was employed as the carrier gas at a constant flow rate of 1 ml/min. There was a 3-minute solvent delay, and 1 μl diluted samples were automatically injected using an Autosampler AS1300 in split mode.

Mass spectra were collected with an ionization voltage of 70 eV across the m/z range of 50 to 500 in full scan mode. The ion source temperature was set at 200°C. To identify the components, their retention times and mass spectra were compared with those present in the WILEY 09 and NIST 11 mass spectral databases.

3. Results and Discussion

The prepared Fe-impregnated charcoal (fig 1) was used to conduct a Fenton like reaction.



Fig. 1. The iron- Impregnated charcoal particles are attracted to the magnet, indicating the success of the production process

The reaction mixture component properties as H_2O_2 decomposition, charcoal surface properties, and degradation of organic molecules are affected by the pH value (Yang et al., 2022; Murphy and Strongin 2009; Kantar et al., 2015).

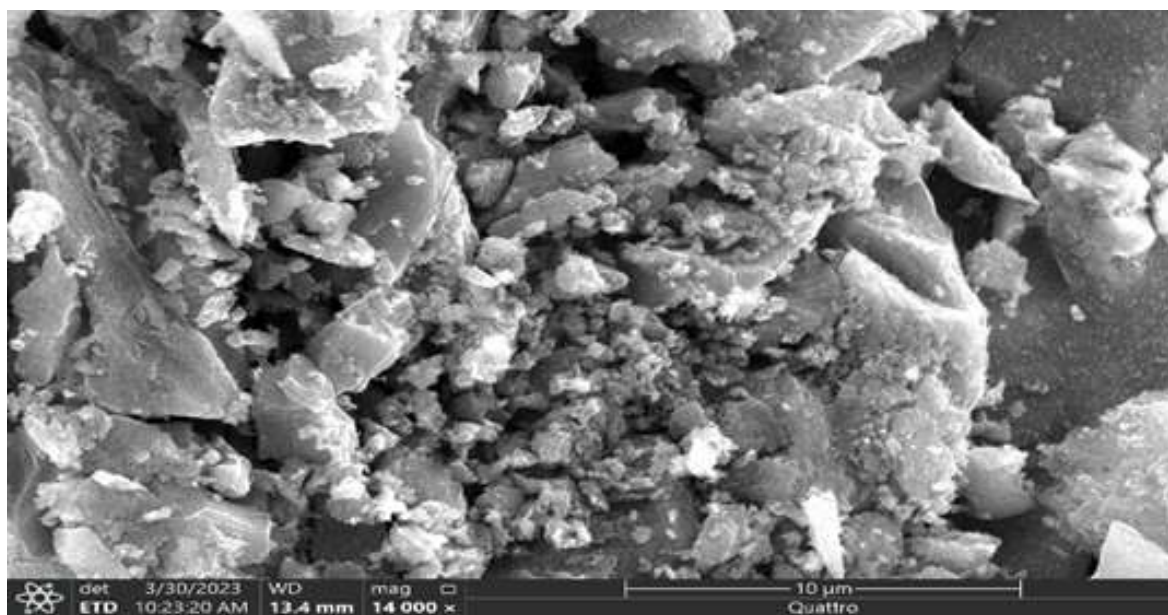


Fig. 2 – Scanning electron microscopy (SEM) images of FIC.

3.1. SEM and XRD Characterization

The SEM image was obtained at a magnification of 10,000x, with a scale bar indicating a length of 10 μm . The image reveals the surface and internal structure of the Fe-impregnated charcoal, and the smooth surface of charcoal indicate the success of

impregnation process which was further confirmed by XRD (fig.2). In the XRD analysis of charcoal impregnated with iron, the three strongest peaks were identified at 2θ angles of 47 degrees (d-spacing: 3.32099 Å, intensity: 100% relative to the strongest peak, FWHM: 0.44750 degrees, integrated intensity: 94 counts), 46 degrees (d-spacing: 3.35584 Å, intensity: 49% relative to the

strongest peak, FWHM: 0.30400 degrees, integrated intensity: 46 counts), and 45 degrees (d-spacing: 3.41141 Å, intensity: 35% relative to the strongest peak, FWHM: 0.35000 degrees, integrated intensity: 33 counts). These peaks reveal the presence of well-defined crystallographic planes in the sample, with variations in intensity and width offering insights into the material's crystal structure and degree of crystallinity. Further analysis and comparison with reference data can aid in characterizing the specific phases and composition of the charcoal impregnated by iron. fig 3.

3.2. Effect of initial pH

The impact of varying pH levels from 3 to 5 was examined (as shown in Figure 4). The catalytic activity of magnetite in the Fenton reaction

demonstrated an increase as the pH decreased. Specifically, at pH values of 4.5 and 5.0, there was minimal removal of RB194. However, at pH levels of 3 and 3.5, RB194 was nearly entirely degraded. This behaviour is likely linked to the creation of a more acidic environment, which promotes the decomposition of H_2O_2 into hydroxyl radicals ($\cdot OH$) (Chen et al., 2021). In addition, the oxidation potential of $\cdot OH$ radical inversely proportional with pH value (Xu et al., 2017; Nguyen et al., 2021); also, the lower pH values stimulates the interactions between electrostatic positive charge of catalyst (Charcoal) surface and negative charge of RB194, which lead to accelerating the degradation rate (Nguyen et al., 2021; Liu et al., 2017). Therefore, the optimum pH value was 3.5 for FIC/ H_2O_2 oxidation.

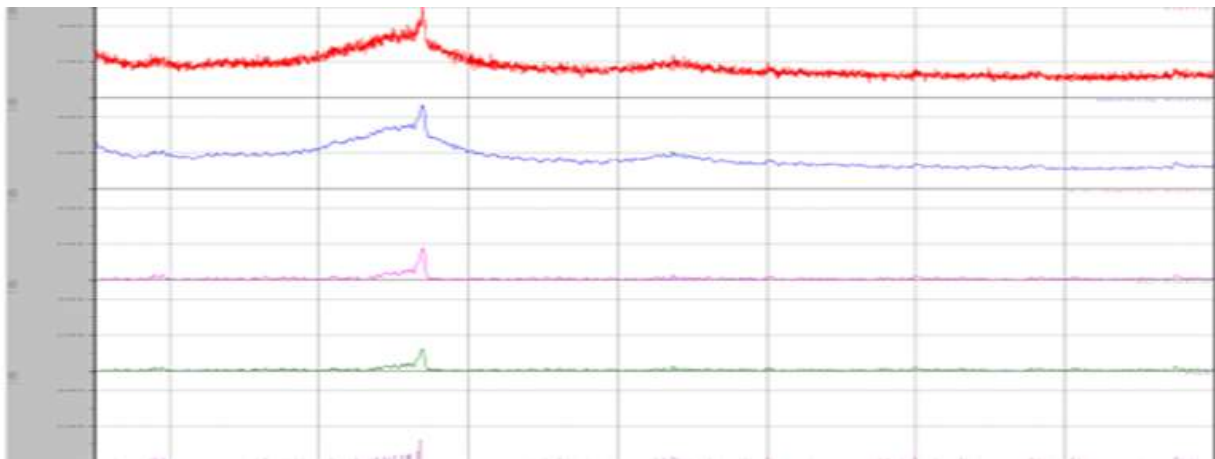


Fig. 3. – X-ray diffraction (XRD) profiles for FIC.

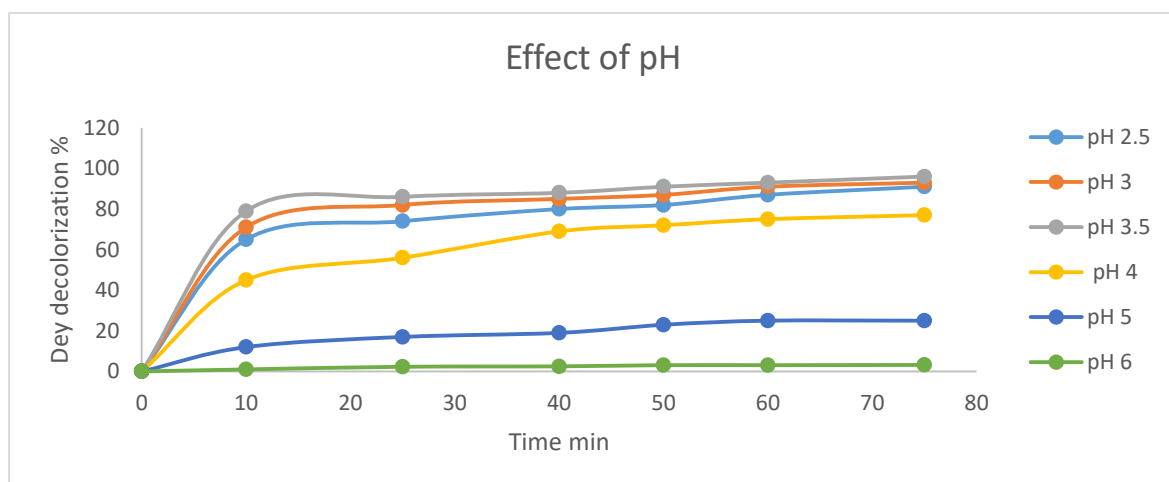


Fig. 4. Effect of initial pH values on removal rate of RB 194 using FIC.

3.3. Effect of catalyst dosage

The impact of varying the catalyst dosage on the degradation efficiency was studied using FIC dosages ranging from 0 to 1.0 g/L. Clearly, as the catalyst dosage increased (as depicted in Figure 5), the efficiency of RB 194 degradation also increased. The degradation efficiency of RB 194 rose from 69.2% to 97.8% as the magnetite dosage

increased from 0.1 to 1.0 g/L. This can be attributed to the greater number of active sites available on the catalyst surface, which enhances the activation of H_2O_2 and the degradation process (Wang et al., 2022). Notably, the degradation efficiency of RB 194 started to exceed 90% when the (FIB) dose was 0.3 g/l.

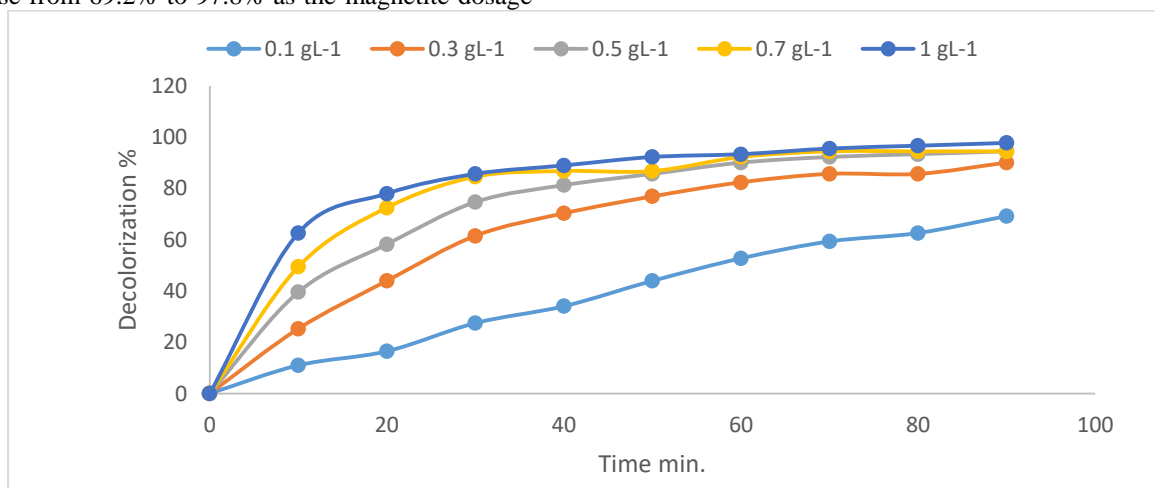


Fig. 5. Effect of catalyst concentration (FIC) on removal rate of RB 194.

3.4. Effect of RB194 concentration

Pollutant concentration plays a crucial role in textile wastewater treatment. To assess the decolorization capability of Fenton's reagent, various concentrations of RB 194 dye were employed. Specifically, the concentrations tested in this study were 100, 300, 400, and 500 mg/L. It was observed (as shown in Figure 4) that a decolorization percentage exceeding 90% was achieved for dye concentrations up to 300 mg/L. In contrast, the removal percentage was proportionally decreased

as the dye initial dye concentration increased Fig. (6). (Liu et al., 2014) Stated that, the degradation of RB 194 with FIC includes mainly the adsorption of dye molecules onto the catalyst surface and subsequent surface reaction. The increase in dye concentration with fixed catalyst concentration would lead to accumulation of dye molecules onto the catalyst surface leading to hindering other dye molecules in the bulk solution to be adsorbed and decomposed.

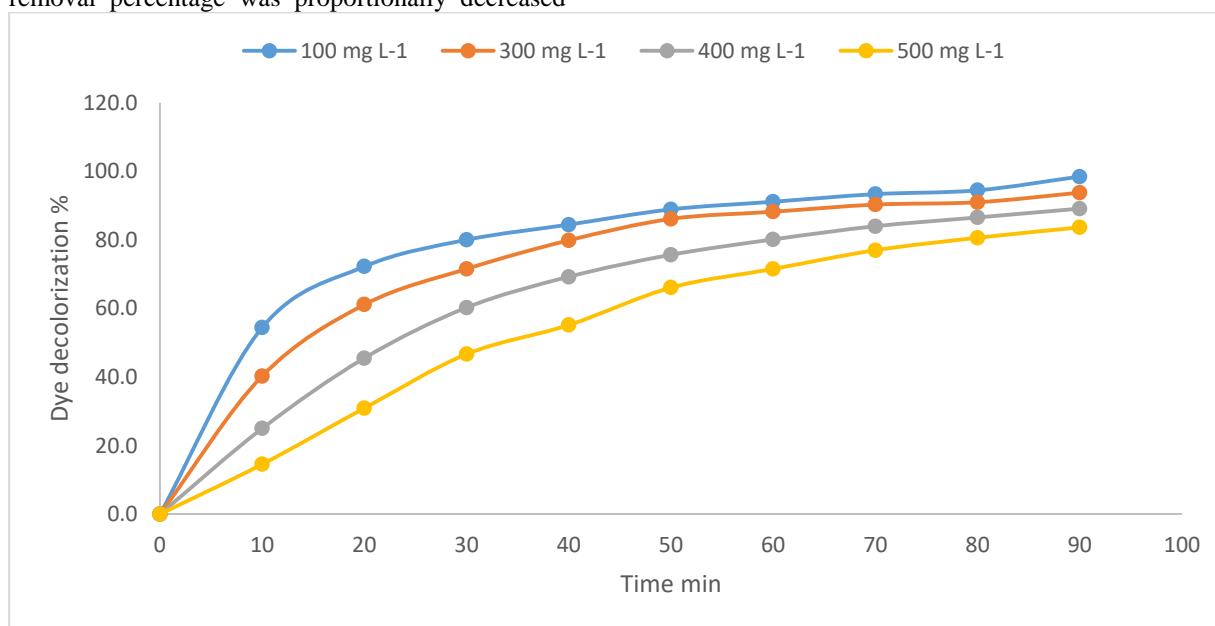


Fig. 6. Effect of initial dye (RB194) concentration on removal rate using (FIC).

3.5. Effect of the H₂O₂ dosage

The effect of the H₂O₂ dosage (0–1000 mg/L) on the degradation rate of RB 194 was investigated (Fig.7) in the presence of catalyst alone, RB194 removal was negligible. The removal efficiency of RB194 increased from 93.3% to 98.9% with increasing H₂O₂ dosage from 50 mg/L to 1000 mg/L. At low H₂O₂ dosages, the amount of

hydroxyl radical liberated was not enough to achieve competitive degradation of RB 194 (Shoueir et al., 2018).

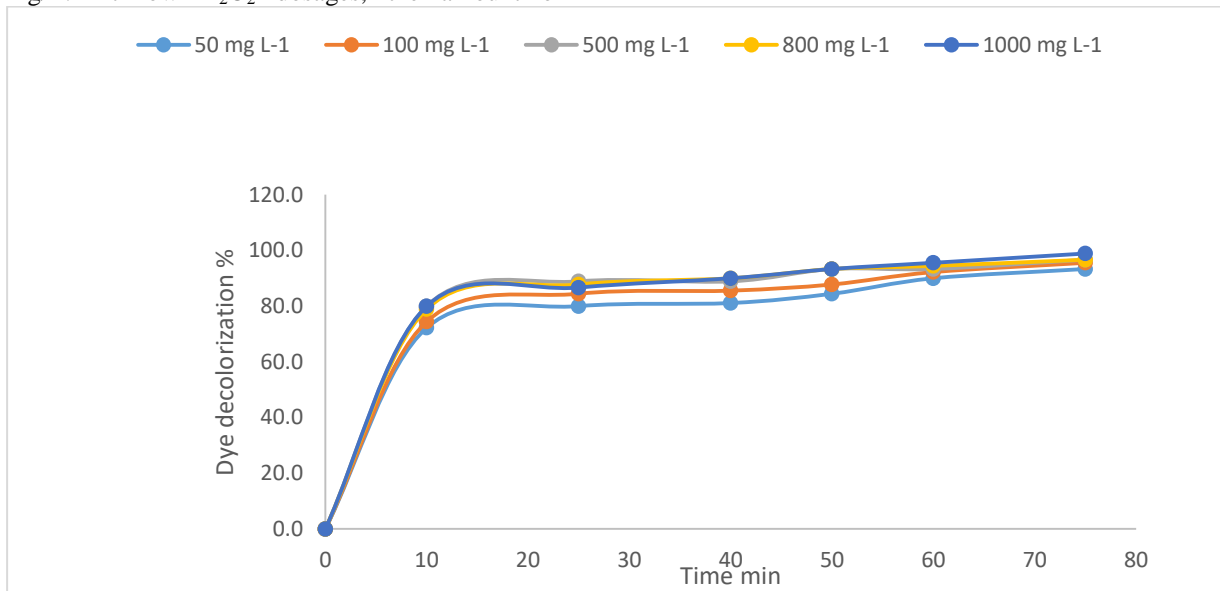


Fig. 7. Effect of H₂O₂ concentration on removal rate of RB 194.

3.6. Effect of charcoal particle size

The small size of the catalyst particles is followed by an increase in the surface area and thus an increase in the reaction rate. It was observed that the dye removal rate increased from 79% to 98% when the catalyst particles were reduced from 1

mm (L2) to 0.2 mm (L1), respectively, after ten minutes of the beginning of the interaction Fig (8). The relative increase in dye removal with smaller particle sizes of charcoal may be due that they possess larger surfaces which increase the dye’s contact with charcoal surface (Liu et al. 2014).

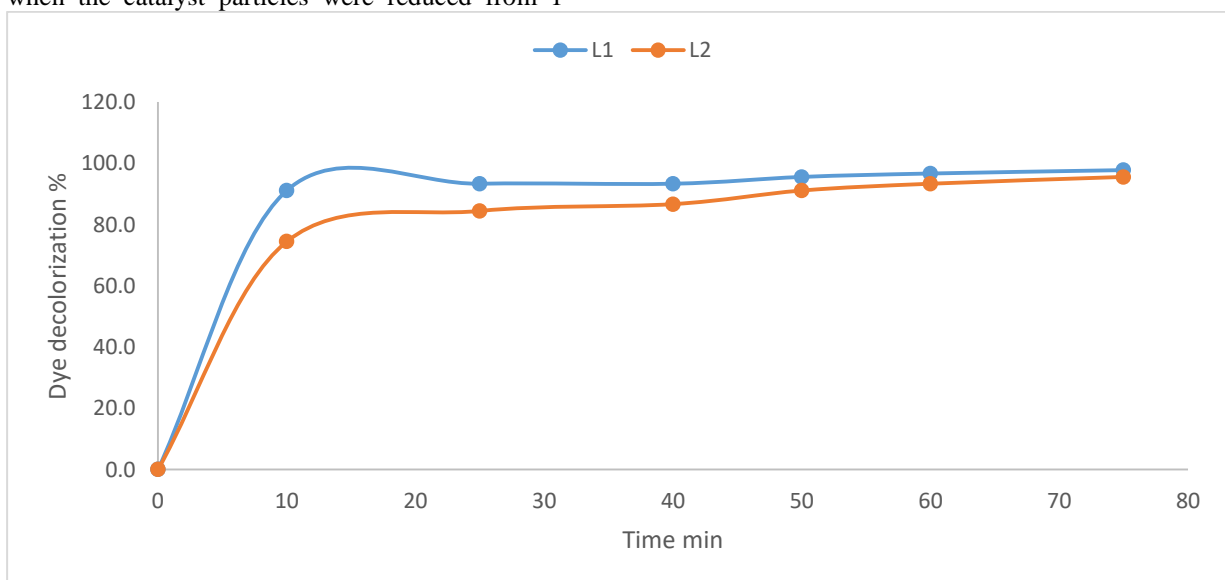


Fig. 8. Effect of Charcoal size on removal rate of RB 194 where L1=0.2mm, L2=1mm.

3.7. Effect of water quality on removal rate of RB194

The quality of the water used in the dyeing process and the level of salts in it may have an effect on the rates of dye removal by the Fenton reaction. What prompts the necessity of conducting this experiment is that the dye houses targeted in the study are all of low technology and do not take into account the quality of the water used, and some of

them use groundwater without treatment. The results obtained from this experiment (fig. 9) showed that the rate of dye removal decreased slightly when using tap water instead of distilled water from 98 % to 94.5 % after 90 min.

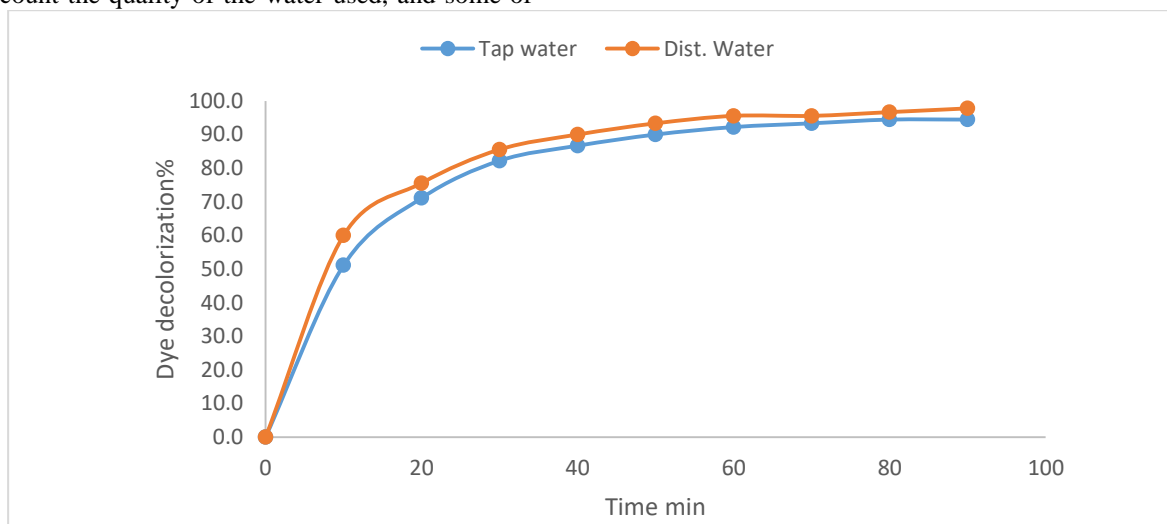


Fig. 9. Effect of water quality on removal rate of RB 194 using FIC catalyst.

3.8. Effect of chemical additives

The dyeing process often requires the addition of some chemicals that improve the process of attaching the dye to the fabric or, on the contrary, help remove excess from it. Such additions may have a positive or negative effect on the Fenton reaction. In this experiment, some chemicals commonly used in dyeing houses were investigated and their effect on the rates of dye removal were studied. These additives included three concentrations of acetic acid and two

concentrations of sulfonic acid. In general, it was noticed a decrease in removal rate in the presence of acetic acid or sulphonic acid and this decline was increased as the concentration of these additives increase especially in the first 60 min. while the effect of sulphonic acid was more detrimental to the removal efficiency fig (10). After 90 min the removal efficiency was decreased about 4% in the presence of 0.25% acetic acid while it was declined about 13% in the presence of 1g/L sulphonic acid compared with distilled water.

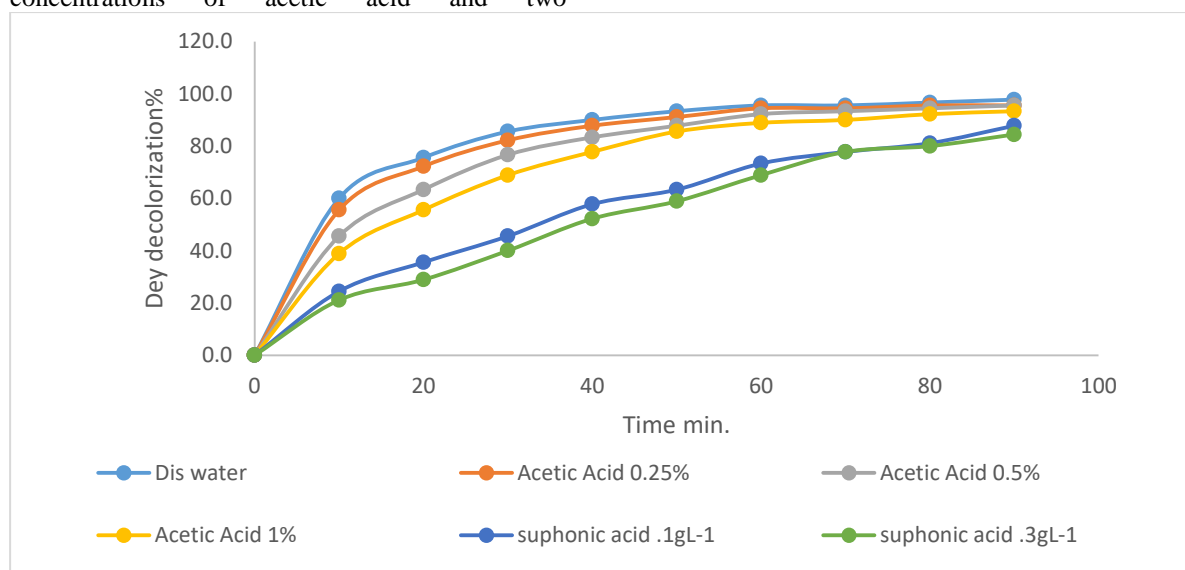


Fig. 10. Effect of chemical additives to the reaction mixture on removal rate of RB 194.

3.9. Activated sludge stage

The use of biological processes in treatment of effluents containing azo dyes are reported by many authors (Yu et al., 2023; Zhang et al., 2023). While the combination of this methods with other chemical or physical methods are preferable because it reduce the time required for degradation and aid in removal of harmful degradation products (Balci et al., 2023). The GC-MS spectrum showed multiple peaks demonstrating the partial mineralization of RB194 after the Fenton stage (Bahmani et al., 2013). studied the degradation of Reactive black 5 in sequential system composed of fenton reaction and activated sludge system and he stated that the position of peaks and suggested molecular weight indicated that RB5 was degraded into low molecular weight compounds after fenton process. Also, they suggested that decolorization is most likely related to the destruction of azo bonds ($-N=N-$) which represent an important part of chromophore. Although most of the color was removed in the Fenton reaction stage, the results of the chromatographic analysis indicated that the dye molecule was not completely degraded. Results showed, Fig (11), that the biological treatment stage using activated sludge has led to the completion of

the process of de-aromatization. The most dominant peaks were detected at retention time of 17 and 21.29 min in all samples (intermediate, at the end of fenton reaction and after biological treatment, these beaks are belonging to PHENOL, 2,6-BIS(1,1-DIMETHYLETHYL)-4 -METHYL and DECANE, 5,6-BIS(2,2-DIMETHYLPROPYLI DENE)-, (E,Z)-. The increase in peaks number at the end of fenton reaction and the emergence of new peaks at retention time 36.26, 37.7, 39.32, 40.36, 40.45, 41.38, 42.41 43.13, 43.37, 43.65, 43.88, 44.11, 44.45, 44.63, 44.71, 44.86, 45.04, 45.12 min relating to long chain aliphatic compounds indicating the presence of de-aromatization of cyclic compounds. After biological treatment, peak at 43.65 which represent a poly cyclic aromatic compounds, 43.88, 44.11, 44.45, 44.63, 44.71, 44.86, 45.04 and 45.12 were disappeared and a new peaks at 40.19, 40.54, 40.67, 40.77, 40.98, 41.08 and 41.20 which represent an aliphatic compounds were emerged indicating continuous of the de-aromatization process in biological treatment (Meerbergen et al. 2017) stated that, Pretreatment of reactive violet 5 with Fenton's reagent significantly enhanced its biological decolorization in activated sludge system.

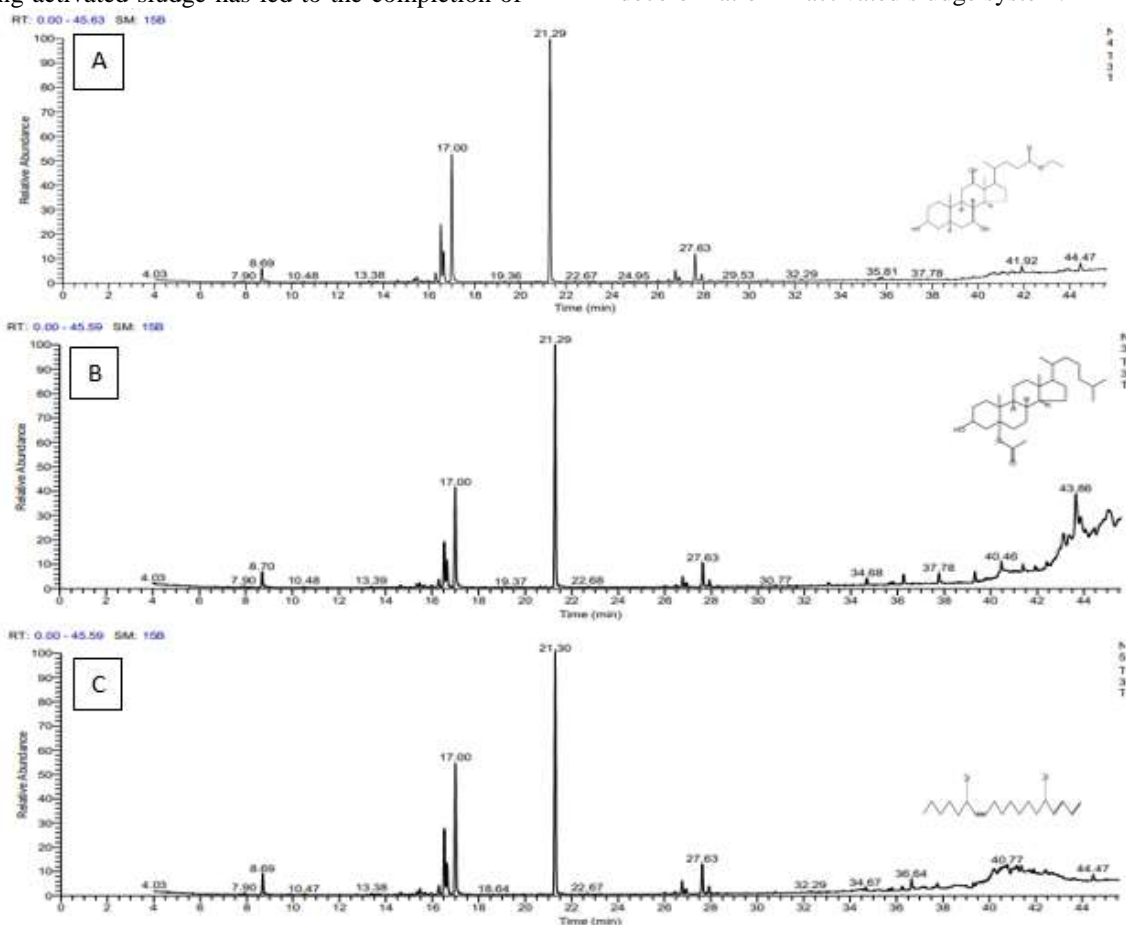


Fig. 11. GC chromatogram showing the sequence of RB194 degradation by fenton reaction followed by activated sludge treatment A: after 10 min. of fenton reaction (50% color removal), B: after 90 min (98% color removal), C: After Biological treatment using activated sludge.

4. Conclusion

We have shown that RB194 color removal was significantly higher when the conditions of Fenton-Like reaction were optimized while it was noticed that other factors as quality of water used in dyeing process and chemical additives which may differ from dyeing house to another may affect the rate of color removal or even the final removal percent. So such conditions should be taken in consideration when applying this technique. On the other hand the GC analysis revealed that the discharge of the fenton treated dyeing wastewater to activated sludge systems led to the completion of de-aromatization of degradation products and formation of shorter aliphatic chains. However, it should be noted that these findings were obtained for simple systems using one type of dyes so, further research is required with complexed textile effluents.

5. Conflicts of interest

“There are no conflicts to declare”.

6. Acknowledgment

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