Decolorization of C.I. Acid blue 9 Solution by UV/Nano-TiO2, Fenton, Electro-Fenton and Electrocoagulation Processes: A Comparative Study

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Decolorization of C.I. Acid Blue 9 solution by UV/Nano-TiO2, Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: A comparative study

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A B S T R A C T

This study makes a comparison between UV/Nano-TiO2, Fenton, Fenton-like, electro-Fenton (EF) and electrocoagulation (EC) treatment methods to investigate the removal of C.I. Acid Blue 9 (AB9), which was chosen as the model organic contaminant. Results indicated that the decolorization efficiency was in order of Fenton > EC > UV/Nano-TiO2 > Fenton-like > EF. Desired concentrations of Fe2+ and H2O2 for the abatement of AB9 in the Fenton-based processes were found to be 10−4 M and 2 × 10−3 M, respectively. In the case of UV/Nano-TiO2 process, we have studied the influence of the basic photocatalytic parameters such as the irradiation time, pH of the solution and amount of TiO2 nanoparticles on the photocatalytic decolorization efficiency of AB9. Accordingly, it could be stated that the complete removal of color, after selecting desired operational parameters could be achieved in a relatively short time, about 25 min. Our results also revealed that the most effective decomposition of AB9 was observed with 150 mg/l of TiO2 nanoparticles in acidic condition. The effect of operational parameters including current density, initial pH and time of electrolysis were studied in electrocoagulation process. The results indicated that for a solution of 20 mg/l AB9, almost 98% color were removed, when the pH was about 6, the time of electrolysis was 8 min and the current density was approximately 25 A/m2 in electrocoagulation process.

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1. Introduction

Presence of color and its causative compounds has always been undesirable in water used for either industrial or domestic needs. Different coloring agents like dyes, inorganic pigments, tannins, lignins, etc. usually impart color. Among complex industrial wastewater with various types of coloring agents, dye wastes are predominant [1,2]. Dyes present in wastewater are of particular environmental concern since they not only give an undesirable color to the waters but also in some cases are themselves harmful compounds and can originate dangerous by-products through oxidation, hydrolysis, or other chemical reactions taking place in the waste phase [3]. Thus, there is an urgent need for textile industries to develop effective methods of water processing.

Commonly applied treatment methods for color removal from dye-contaminated effluents consist of various processes involving biological, physical and chemical decolorization methods [4]. Conventional treatments of dye effluents include biological oxidation and adsorption. Although less expensive than other approaches, biological treatment is ineffective for decolorization because the dyes are toxic. Adsorption onto activated carbon transfers most of the contaminant from the wastewater to the solid phase. This method therefore requires further disposal of the sludge.

In recent years, advanced oxidation processes (AOPs) and electrochemical methods have been developed to treat the contaminants of drinking water and industrial effluents. Advanced oxidation processes almost all are based on the generation of reactive species such as hydroxyl radicals (*OH) which degrade a broad range of organic pollutants quickly and non-selectively. Although it is claimed that there are other species involved, the active species responsible for the destruction of contaminants in most cases seems to be the hydroxyl radical (*OH) which is unstable and quite reactive. Due to the instability of *OH radical, it must be generated continuously “in situ” through chemical or photochemical reactions [5]. The organic matters (OMs) in the solution are attacked by hydroxyl radical as soon as *OH is generated, as described in the following equation:

\[ \text{•OH + OM} \rightarrow \text{intermediates} \]
\[ \rightarrow \text{harmless species (CO2, H2O, etc.)} \] (1)

The important advanced oxidation processes are H2O2/Fe2+ (Fenton’s reagent) [6], H2O2/Fe3+ (Fenton-like reagent) [7], electro-Fenton [8] and H2O2/O3 [9] as chemical procedures, UV/H2O2/Fe2+.
UV/H2O2/Fe3+ [10,11], UV/H2O2 [12], UV/O3 [13] and photoelectro-Fenton [14] as photoelectrochemical treatment, and UV/TiO2 [15,16], UV/TiO2O3 [17] and UV/ZnO [18,19] as photocatalytic methods. The versatility of AOP is also enhanced by the fact that they offer different possible ways for hydroxyl radical’s production thus allowing a better compliance with the specific treatment requirements.

Among them, heterogeneous photocatalysis using TiO2 or ZnO nanoparticles is regarded as a promising method for the transformation of toxic and bioreistant compounds into harmless species (CO2, H2O, etc.). With the advent of nanotechnology the nanostructured TiO2 has found a great deal of applications. Nanotechnology is a growing and cutting edge technology with applications in many fields of research and development areas including biology, chemistry, material science, medicine and physics. With the inception of nanoscience and nanotechnology nanoscale materials, in general, and nanostructured TiO2 materials, in particular, have received significant attention. With a typical dimension of less than 100 nm, nanostructured TiO2 materials have become attractive for numerous applications in different fields. It is known to have golden properties, which include non-toxicity, abundance, and potentially least costly compared to other nanomaterials [20,21]. Briefly, TiO2 is a semiconductor and when it is illuminated with the light of λ < 390 nm, electrons are promoted from the valence band to the conduction band of the semiconducting oxide to give electron–hole pairs [15,22,23]:

\[
\text{TiO}_2 + h\nu (\lambda < 390 \text{ nm}) \rightarrow e^- + h^+ \tag{2}
\]

The valence band (h+) potential is positive enough to generate hydroxyl radicals at the surface of TiO2 and the conduction band (e-) potential is negative enough to reduce molecular oxygen as shown in the following equations:

\[
e^- + O_2(\text{ads}) \rightarrow 2O_2(\text{ads}) \tag{3}
\]

\[
e^- + H(\text{ads}) \rightarrow H^+ + H(\text{ads}) \tag{4}
\]

\[h_{\text{VB}}^+ + OH(\text{ads}) \rightarrow OH(\text{ads}) \text{ (in alkaline solutions)} \tag{5}
\]

\[h_{\text{VB}}^+ + H_2O(\text{ads}) \rightarrow H^+ + OH(\text{ads}) \text{ (in neutral solutions)} \tag{6}
\]

The hydroxyl radical is a powerful oxidizing agent and attacks organic matters present at or near the surface of TiO2. It causes, ultimately, complete decomposition of toxic and bioreistant compounds into harmless species (CO2, H2O, etc.) [22,24].

The other advanced oxidation processes are Fenton-based processes. Fenton’s reagent is a mixture of ferrous ion (Fe2+) and hydrogen peroxide (H2O2) generating hydroxyl radical (•OH) in situ according to the following equation:

\[\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot \text{OH} \tag{7}\]

Fe(III) can also catalyze the decomposition of H2O2. The reaction of H2O2 with Fe(III) (so called the Fenton’s-like reagent) goes through the formation of hydroperoxyl radical HO2• [25]:

\[\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^{•} + \cdot \text{H} \tag{8}\]

In electro-Fenton method, •OH radicals are produced in the bulk of the solution from the reaction of electrogernated H2O2 and Fe2+ (Eq. (7)). Hydrogen peroxide is produced electrochemically upon two electron reduction of oxygen on several electrodes (mercury pool, graphite, carbon polytetrafluoroethylene O2-fed cathodes) [26,27] according to the following equation:

\[O_2 + 2e^- + 2H^+ \rightarrow 2\text{H}_2\text{O} \tag{9}\]

In this system, catalytic reaction can be propagated via Fe2+ regeneration which mainly takes place by the reduction of Fe3+ species with electrogernated \(\text{H}_2\text{O}_2\) (Eq. (8)) and reduction of it in cathode surface (Eq. (10)):

\[\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \tag{10}\]

This system has been used successfully for the decolorization of disfectroorganic dyes [28,29].

Electrocoagulation (EC) is an alternative approach which was widely used in wastewater treatment loaded from textile industries [30,31]. This process includes the generation of coagulants in situ by dissolving electrically either aluminium or iron ions in aluminium or iron electrodes, respectively. The metal ions generation takes place at the anode and the hydrogen gas is released from the cathode. The hydrogen gas would also help float the flocculated particles out of water. When a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction of water [32]. Electrocoagulation of wastewater using iron electrodes takes place according to the following reactions:

anodic reactions : \[4\text{Fe(s)} \rightarrow 4\text{Fe(aq)}^{2+} + 8e^- \tag{11}\]

\[4\text{Fe(aq)}^{2+} + 10\text{H}_2\text{O}(1) + \text{O}_2(\text{g})(1) \rightarrow 4\text{Fe(OH)}_3(s) + 8\text{H}^{+}(\text{aq}) \tag{12}\]

cathodic reaction : \[8\text{H}^{+}(\text{aq}) + 8e^- \rightarrow 4\text{H}_2(\text{g}) \tag{13}\]

overall reaction : \[4\text{Fe(s)} + 10\text{H}_2\text{O}(1) + \text{O}_2(\text{g}) \rightarrow 4\text{Fe(OH)}_3(s) + 4\text{H}_2(\text{g}) \tag{14}\]

The generated \(\text{Fe(aq)}^{3+}\) ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. These hydroxides/polyhydroxides/polyhydroxymetallic compounds have strong affinity with dispersed/dissolved as well as the counter ions to cause coagulation/adsorption [33–35].

C.I. Acid Blue 9 (AB9) which belongs to acidic dyes group is soluble in cold water and methanol. It can be found in thousands of textile (as a dye for wool and silk), foodstuff and pharmaceutical wastewaters. In addition, C.I. Acid Blue 9 is one of the components Aquashade which can be used as an aquatic algaecide/herbicide, in natural or manmade ponds, lakes, fountains, fish farms, and fish hatcheries, and may be applied by both professional applicators and homeowners. It is hazardous in case of ingestion, of skin contact (irritant), of eye contact (irritant), of inhalation [36].

In the present research work various advanced oxidation processes and electrochemical methods including UV/Nano-TiO2, Fenton, Fenton-like, electro-Fenton and electrocoagulation processes were applied to decolorization of the solution containing C.I. Acid Blue 9. In each process the most effective operational parameters were investigated. Moreover, the performance of these processes in terms of decolorization efficiency, kinetic rate constant and electrical energy consumption was compared.

2. Materials and methods

2.1. Chemicals

TiO2 Degussa P-25 nanoparticles (having 80% anatase and 20% rutile, specific surface area (BET) 50 m2/g and particle size 21 nm) were kindly supplied by Degussa Co., Germany. To determine the crystal phase composition of TiO2 nanoparticles, X-ray diffraction (XRD) measurements were carried out at room temperature by using Siemens X-ray diffraction D5000 with Cu Kα radiation (λ = 0.15478 nm). The accelerating voltage of 40 kV and emission
current of 30 mA were used. The average crystallite size of the samples was calculated according to Debye–Scherrer formula:

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (15)$$

where $D$ is the average crystallite size (Å), $\lambda$ is the wavelength of the X-ray radiation (Cu Kα = 1.54178 Å), $\beta$ is the full width at half maximum (fwhm) intensity of the peak and $\theta$ is the diffraction angle. The mean particle size of Degussa P-25 sample was calculated using the parameters of width and intensity of the peak and the equation above. The $\lambda_{\text{max}}$ value used in the calculation was 625 nm (fwhm).

### 2.4. Fenton and Fenton-like processes

Fenton and Fenton-like batch experiments were performed in beakers with a reaction mixture of dye, Fe$^{2+}$ or Fe$^{3+}$ and H$_2$O$_2$. The required amounts of iron ions were added and the pH was adjusted in optimum amount of 3.0 with sulphuric acid. With addition of H$_2$O$_2$, Fenton reaction is initiated. Continuous mixing was provided by a magnetic stirrer.

### 2.5. Electrocoagulation process

All electrocoagulation experiments were performed in batch electrolyte cell. The volume of cell was 500 ml. Iron (ST 37-2) plates were used as anode, and steel (grade 304) plates were used as cathode. Dimensions of electrodes were 40 mm × 50 mm × 1 mm and the distance between two electrodes was 15 mm in all experiments. The electrodes were connected to a dc power supply (ADAK PS808, Iran) with galvanostatic operational options for controlling the current density (CD). In each run, 200 ml of AB9 solution was placed into the electrolytic cell. The conductivity measurement was carried out using a Philips conductivity meter (PW 9509, England). The operation started when the current density was adjusted to a desired value. During process, the solution was agitated at 200 rpm to form and float the flocs. At the end of EC, the solution was filtered through 0.2 μm membrane filter (Schleicher & Schuell, Germany) and then the samples were analyzed.

### 3. Results and discussion

#### 3.1. Decolorization efficiency of UV/Nano-TiO$_2$ process

The efficiency of photocatalytic processes strongly depended upon the pH of the reaction solution. This is due to the amphoteric behavior of semiconducting titanium dioxide. The surface charge properties of TiO$_2$ change with the changes of pH values [36]. Fig. 1 demonstrates the photodegradation of AB9 at different pH from 2 to 12. As it is clear from the figure, the best results were obtained in acidic condition. According to the zero point of charge of TiO$_2$, its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution [38,39]. Since AB9 has a sulphuric group in its structure, which is negatively charged, the acidic solution favors adsorption of it onto photocatalyst surface, thus the photodegradation efficiency increases. There is also the photocatalytic degradation of AB9 in acidic solutions, which is probably due

### Table 1

Structure and characteristics of C.I. Acid Blue 9

<table>
<thead>
<tr>
<th>Chemical class</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenyl methane</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Color index number</th>
<th>42,090</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>625 (406)</td>
</tr>
<tr>
<td>$M_w$ (g mol$^{-1}$)</td>
<td>792.86</td>
</tr>
</tbody>
</table>

---

to the formation of $\cdot$OH as it can be inferred from the following reactions (Eqs. (3) and (16)–(18)) [15]:

\[ \text{O}_2^{(ads)} + \text{H}^+ \rightarrow \text{HO}_2^* \]  
(16)

\[ 2\text{HO}_2^- \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \]  
(17)

\[ \text{H}_2\text{O}_2 + \text{O}_2^{(ads)} \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2 \]  
(18)

Experiments performed with different concentrations of TiO$_2$ nanoparticles (Fig. 2) showed that the photodegradation efficiency increased with an increase in the amount of nanophotocatalyst but once it exceeded a certain level (150 mg/l), it was accompanied by a decrease in photodegradation efficiency. The most effective decomposition of AB9 was observed with 150 mg/l of TiO$_2$ nanoparticles. Increasing the concentration of the photocatalyst gave rise to a higher number and density of TiO$_2$ nanoparticles, which in turn caused photons absorbed and AB9 molecules adsorbed to increase. All of these processes went hand in hand to enhance the efficiency of photodegradation. Above a certain level (150 mg/l), the substrate molecules available were not sufficient for adsorption by the increased number of TiO$_2$ particles. Hence the additional catalyst powder was not involved in the catalyst’s activity and the photodegradation efficiency did not increase with an increase in the amount of catalyst beyond a certain limit. Another cause for this is supposedly an increased opacity of the suspension, brought about as a result of excess of TiO$_2$ particles [40,41].

Fig. 3 shows a typical time-dependent UV–vis spectrum of AB9 solution during photocatalytic process. The spectrum of AB9 in the visible region exhibits a main band with a maximum at 625 nm. As it is clear from this figure, the absorption peaks diminished and finally disappeared under reaction, which indicated that the AB9 had been degraded. No new absorption bands appear in either the visible or ultraviolet regions. Complete removal of AB9 was observed after 25 min in the desired conditions.

3.2. Decolorization efficiency of Fenton and Fenton-like processes

To determine the desired conditions of Fenton and Fenton-like processes for the decolorization of AB9 dye, important variables such as effect dosage of H$_2$O$_2$ and iron ion concentration on color removal efficiency was investigated. In order to investigate the effect of H$_2$O$_2$ concentration on the decolorization efficiency, experiments were conducted at different H$_2$O$_2$ concentrations with 10$^{-4}$ M Fe$^{2+}$ or Fe$^{3+}$ solutions. Fig. 4a and b shows the relationship between the decolorization of dye and the initial concentration of H$_2$O$_2$ in the Fenton and Fenton-like processes. To render the Fenton and Fenton-like processes competitive with other processes, it is essential that their applications represent a low cost operation, which basically implies a better control of H$_2$O$_2$ dosage. The objective of this evaluation is to select the effective operational concentration of H$_2$O$_2$ in Fenton and Fenton-like processes. For the Fenton process, the addition of H$_2$O$_2$ between 4 $\times$ 10$^{-3}$ M and 2 $\times$ 10$^{-2}$ M increases the decolorization of the dye from 86% to 96% at 10 min. The increase in the decolorization is due to the increase in hydroxyl radical concentration by addition of H$_2$O$_2$. Further increase from 2 $\times$ 10$^{-3}$ M to 3 $\times$ 10$^{-3}$ M causes little decrease in decolorization. This little increase is due to the fact that at a higher H$_2$O$_2$ concentration scavenging of hydroxyl radicals will occur, which can be expressed by the following equations [42]:

\[ \text{HO}^* + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \]  
(19)

\[ \text{HO}_2^* + \text{HO}^* \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  
(20)

In the Fenton-like process, the addition of H$_2$O$_2$ between 4 $\times$ 10$^{-4}$ M and 2 $\times$ 10$^{-3}$ M increases decolorization from 50% to 94%, respectively at 70 min. Further increase causes no significant change in decolorization for Fenton-like processes.

Fig. 5a and b shows the effect of iron ion concentration on the dye degradation in Fenton and Fenton-like reactions. The extent of degradation of the dye increased with increasing iron ion concentration. In the case of Fenton oxidation, an obvious increase of the decolorization efficiency was observed by raising initial Fe$^{2+}$ concentration from 5 $\times$ 10$^{-5}$ M to 10$^{-4}$ M. However, further increase
in the concentration of ferrous ions above $10^{-4}$ M did not bring about further improvement in the dye removal. This fact was probably due to the consumption of the percentage of $\cdot$OH by an excess of ferrous ions (Eq. (21)) [27]:

$$\text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (21)$$

For Fenton-like process, when the iron ion concentration was $5 \times 10^{-5}$ M, dye removal was only 71% after 70 min. By contrast, the extent of degradation was 91%, 93% and 97% after 70 min at Fe$^{3+}$ concentration of $10^{-4}$ M, $2 \times 10^{-4}$ M and $3 \times 10^{-4}$ M, respectively.

Fig. 6a and b shows the effect of ratio of [H$_2$O$_2$]/[Fe ion] on AB9 decolorization, in Fenton and Fenton-like reactions. In the case of Fenton oxidation, with increasing of ratio from 4 to 20 decolorization efficiency was increased. However, further increase did not cause to further removal. In the case of Fenton-like, with increasing of ratio from 20 removal did not reduce and decolorization efficiency did not considerably increase.

### 3.3. Decolorization efficiency of electro-Fenton process

The pH of solution in the electro-Fenton process has important influence in H$_2$O$_2$ electrogeneration and stability of iron ions. In this order, effect of pH on color removal efficiency of AB9 was investigated. Fig. 7 shows the comparative decolorization of 200 ml solutions containing 20 mg/l of AB9 at different pH under $-0.50$ V/SCE constant cathodic potential. As it can be seen, the best pH is 3.0. Decolorization efficiency decreased from 90% to 38% at 120 min with increasing pH from 3.0 to 5.0. Results show that below pH 3.0 color removal efficiency is decreased due to enhanced hydrogen evaluation on the cathode surface [43]. On the other hand, high concentration of H$^+$ ions inhibit the formation of Fe–OOH$^{2+}$ complex from reaction of Fe$^{3+}$ and H$_2$O$_2$ [7]. At pH above 3.0 due to insufficient protons concentration for H$_2$O$_2$ electrogeneration [43] and also precipitation of Fe(III) [44], decolorization efficiency is reduced.

In order to investigate the effect of initial ferric concentration on the decolorization efficiency of AB9, several electrolyses of 200 ml containing 20 mg/l of AB9 with initial pH 3.0 were carried out at $-0.5$ V potential in the absence or in the presence of $5 \times 10^{-5}$ to $3 \times 10^{-4}$ M Fe$^{3+}$ using 9.5 cm$^2$ cathode surface area and 0.05 M NaClO$_4$ as supporting electrolyte. The change of AB9 decolorization with time is depicted in Fig. 8. It can be observed that in the absence of Fe$^{3+}$, about 23% of AB9 is destructed at 120 min. It can be attributed to direct reaction of dye with H$_2$O$_2$ or its reaction with $\cdot$OH formed from anodic oxidation process. Decolorization efficiency undergoes a fast acceleration when Fe$^{3+}$ is added. Fe$^{3+}$ react with H$_2$O$_2$ (Eq. (8)) and produce HO$_2^*$ and Fe$^{2+}$ from Fenton-like process. Regenerated Fe$^{2+}$ can react with H$_2$O$_2$ and produce strong hydroxyl radicals. In addition, Fe$^{2+}$ can be regenerated at cathode surface from reduction of Fe$^{3+}$ (Eq. (10)) [45]. By increasing Fe$^{3+}$ concentration to $10^{-4}$ M, AB9 decay increases. This effect can be related to both increasing HO$_2^*$ concentration (Eq. (8)) and also an increasing quantity of Fe$^{2+}$ regenerated (Eqs. (8) and (10)) which subsequently enhance the production of strong oxidant $\cdot$OH by Fenton’s reaction (Eq. (11)). However, at higher Fe$^{3+}$ concentr-
tration, effect of increasing ferric concentration on decolorization efficiency is negligible. In fact, before optimum concentration of Fe\(^{3+}\) (10\(^{-4}\) M), Fe\(^{3+}\) concentration is rate-determining and controls the overall reaction rate. However, after 10\(^{-4}\) M Fe\(^{3+}\), H\(_2\)O\(_2\) concentration is limiting parameter and therefore, although Fe\(^{3+}\) concentration increases, production of •OH is constant. These findings concludes that a small concentration of Fe\(^{3+}\) is effective for electro-Fenton systems.

Fig. 7. Decolorization of AB9 in different pH solutions by electro-Fenton application; \(C_0 = 20\) mg/l, [NaClO\(_4\)] = 0.05 M, \(A = 9.5\) cm\(^2\), \(E = -0.5\) V, and stirring speed = 200 rpm.

Fig. 8. Effect of Fe\(^{3+}\) concentration on decolorization of AB9 by electro-Fenton process; \(C_0 = 20\) mg/l, [NaClO\(_4\)] = 0.05 M, pH 3.0, \(A = 9.5\) cm\(^2\), \(E = -0.5\) V, and stirring speed = 200 rpm.

Fig. 9. UV–vis spectra changes of AB9 (20 mg/l) by electro-Fenton process; [NaClO\(_4\)] = 0.05 M, pH 3.0, \(A = 9.5\) cm\(^2\), \(E = -0.5\) V, and stirring speed = 200 rpm.

Fig. 10. Variation of color removal efficiency with time at different current densities; \(C_0 = 20\) mg/l, pH 6.08, \(\gamma = 15.9\) mS/cm, and stirring speed = 200 rpm.

Fig. 9 shows time-dependent UV–vis spectrum of AB9 solution during electro-Fenton process. As it is clear from this figure, the absorption peaks diminished and finally disappeared under reaction, which indicated that the AB9 had been degraded. No new absorption bands appear in either the visible or ultraviolet regions.
The changes in the absorption spectra of AB9 solution during the EC process at different electrolysis times are shown in Fig. 11. The spectrum of AB9 in the visible region exhibits a main band with a maximum at 625 nm. This figure shows the absorption peaks corresponding to dye molecules diminish and finally disappear with increase of the reaction time.

It is clear that a technically efficient process must also be feasible economically. The major operating cost of EC is associated with electrical energy consumption during process. Although increasing current density and electrolysis time enhances the efficiency of EC, it causes to raise the cell voltage, energy consumption and operating costs consequently. The electrical energy required to decolorization (R > 95%) of the solution containing 20 mg/l AB9 at various current densities was calculated in terms of kWh/m³ using the equation given as follows:

\[
E = \frac{UIt_{EC}}{V_s} \times 10^{-3}
\]

where \(E\) is the electrical energy required to decolorize (R > 95%) of solution containing 20 mg/l AB9 at various current densities was calculated in terms of kWh/m³ using the equation given as follows:

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\[
E = \frac{UIt_{EC}}{V_s} \times 10^{-3}
\]
not form. At the pH > 9 color removal efficiency decreased about 9%, because above this pH, Fe(OH)₄⁻ was the dominant species which was a dissolving species and it was unable to form flocs [32].

3.5. Comparison of the color removal efficiencies of different AOPs and EC methods

The comparison of different AOPs and electrochemical method is of interest to determine the best color removal performance and the most efficient process for the removal of target compound in the dye solution. The efficiency of decolorization of AB9 solution by different AOPs and electrochemical methods are illustrated in Fig. 13. It can be seen that the most effective AB9 decolorization rate was obtained by Fenton process and the ranking was in the order of Fenton > EC > UV/Nano-TiO₂ > Fenton-like > EF. In addition, the kinetic model, kinetic rate constant and electrical energy consumption have been compared in Table 3. According to these results, it is clear that the rate constant of Fenton process was higher than other processes (Table 3). However, selectivity of the suitable process for treatment of pollutants is related to various conditions such as economical aspects, required equipments, operational problems, secondary pollutions, energy consumption, etc. For example, although electrocoagulation is an effective method for removal of AB9 in the term of decolorization efficiency and electrical energy consumption (Table 3), it is not destructive and only transfers the contamination from one phase (aerous) to another phase (flocs). The advantages of photocatalysis are: destructive, no sludge production, potential of solar light utilization. But, light penetration limitation, fouling of the photocatalyst, and problem of fine TiO₂ separation from the treated liquid in slurry reactors are some of the disadvantages of this method. Fenton process is effective within narrow pH range of <3.5; and involves sludge generation. Electro-Fenton process requires further development for industrial acceptance. High cost of electricity is an impediment. It also comparatively required longer reaction time.

4. Conclusion

In this study, we assessed the possibility of different AOPs and electrocoagulation method for the AB9 decolorization. The following conclusions can be drawn from this work:

- The results indicated that the photocatalytic degradation of AB9 were obviously affected by the initial pH and the amount of TiO₂ nanoparticles. We learned that the desired amount of the photocatalyst was 150 ppm, with AB9 concentration of 20 ppm. It was also found that the best photocatalytic activity was obtained in acidic condition.
- The desired H₂O₂ dose and iron ion concentration for Fenton and for Fenton-like was found to be 2 × 10⁻³ M and 10⁻⁴ M, respectively.
- Decolorization was faster using Fenton oxidation process, whereas the electro-Fenton process was slower method. However, electro-Fenton process generated H₂O₂ in situ. • Electrocoagulation is an effective method for removal of AB9 in terms of decolorization efficiency, but it is not destructive and only transfers the contamination from aqueous phase to sludge. Decolorization of AB9 solution by electrocoagulation was affected by the current density, time of electrolysis and initial pH of the dye solution. It was found that for a solution with dye concentration of 20 mg/l, decolorization efficiency was of 98%, when the pH was about 6, time of electrolysis was 8 min and current density was approximately 25 A/m².
- It was found that the ranking of AB9 decolorization efficiency was in the order of Fenton > EC > UV/Nano-TiO₂ > Fenton-like > EF.

Acknowledgement

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References


Table 3

<table>
<thead>
<tr>
<th>Process</th>
<th>Kinetic model</th>
<th>Rate constant</th>
<th>R²</th>
<th>t₁/₂ (min)</th>
<th>Electrical energy consumption (kWh/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/Nano-TiO₂</td>
<td>First order</td>
<td>0.1141 min⁻¹</td>
<td>0.973</td>
<td>6.073</td>
<td>175.44</td>
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<tr>
<td>Fenton</td>
<td>Second order</td>
<td>0.615 min⁻¹ M⁻¹</td>
<td>0.934</td>
<td>0.267</td>
<td>–</td>
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<tr>
<td>Fenton-like</td>
<td>First order</td>
<td>0.0233 min⁻¹</td>
<td>0.984</td>
<td>29.74</td>
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</tr>
<tr>
<td>Electro-Fenton</td>
<td>First order</td>
<td>0.0108 min⁻¹</td>
<td>0.988</td>
<td>64.18</td>
<td>300</td>
</tr>
<tr>
<td>Electrocoagulation</td>
<td>First order</td>
<td>0.1206 min⁻¹</td>
<td>0.928</td>
<td>5.72</td>
<td>0.074</td>
</tr>
</tbody>
</table>


