THE EFFECT OF PHOTO-FENTON OXIDATION PROCESS IN THE ENVIRONMENTAL TECHNOLOGY APPLICATIONS

ÇEVRESEL TEKNOLOJİ UYGULAMALARINDA FOTO-FENTON OKSİDASYON PROSESİNİN ETKİSİ

Assist. Prof. Dr. Murat KIRANŞAN

Gümüşhane University, Gümüşhane Vocational School, Department of Chemistry and Chemical Processing Technologies, 29100 Gümüşhane, Turkey

ABSTRACT

External factors affecting living beings constitute in the environment. After the industrial revolution, as a result of the economic growth race which affected the whole world, clean water crisis and other environmental problems emerged. Today, industrialization has the increased and environmental pollution has started to the increase significantly. The wastes that are released to the air, soil and water environment from various industries negatively affect in the living creatures and the ecosystem that live on the it by disrupting the natural equilibrium. As a result of industrial development in the last century and developments in the medicine the life quality and life of the people have increased and the world population has increased. However, the removal and disposal of the solid and liquid wastes which have increased rapidly have begin to pose an important problem especially in the big cities.

Treatment of wastewater is the most important cause of environmental problems. The main reason for water pollution comes from the uncontrolled discharge of the used water into the receiving environment. The physical, biological and chemical treatment techniques known to date have been in the most preferred classical treatment methods. Advanced oxidation processes are methods to ensure the formation of the hydroxyl radicals ($OH^{\bullet}$) whose oxidizing power is quite high and effective. It is used to oxidize organic substances and pollutants that are difficult to decompose biologically. Hydroxyl radicals ($OH^{\bullet}$) reaction with organic matter allowing the organic substance that contaminates in the water to mineralize under favorable conditions and as a result, CO_2 and H_2O final products are the formed. Advanced oxidation processes; fenton includes techniques such as fenton-like, UV, photolysis and sonolysis. In some cases, a single oxidation process may be insufficient and multiple oxidation processes can be applied simultaneously.

The photo-fenton process is an effective and important advanced oxidation process. Classical fenton oxidation applied in the light radiation environment is the generally called photo-fenton oxidation processes. The oxidation potential of the photo-fenton process can be increased by UV radiation.

Keywords: Photo-Fenton Processes, Hydroxyl Radical, Hydrogen Peroxide, UV Radiation, Fe^{2+} and Fe^{3+} Ions.

ÖZET

Çevreyi canlıları etkileyen dış faktörler oluşturmaktadır. Sanayi devriminden sonra, tüm dünyayı etkileyen ekonomik büyüme yarışı sonucunda temiz su krizi ve diğer çevre sorunları ortaya çıktı. Günümüzde sanayileşme artmış ve çevre kirliliği önemli ölçüde sorun olmaya başlamıştır. Çeşitli endüstri kaynaklarından hava, toprak ve su ortamına salınan atıklar, doğal dengeyi bozarak canlıları ve üzerinde yaşadığımız ekosistemi olumsuz etkilemektedir. Geçen yüzyıldaki endüstriyel gelişme ve tıptaki gelişmeler sonucunda insanların yaşam kalitesi artmış

ve dünya nüfusu artmıştır. Bununla birlikte, hızla artan katı ve sıvı atıkların uzaklaştırılması ve bertarafı, özellikle büyük şehirlerde önemli bir sorun oluşturmaya başlamıştır.

Atık su arıtımı çevre kirliliği sorunlarının en önemli nedenidir. Su kirliliğinin temel nedeni, kullanılan suyun kontrolsüz bir şekilde alıcı ortama deşarjından kaynaklanmaktadır. Bugüne kadar bilinen fiziksel, biyolojik ve kimyasal arıtım teknikleri en çok tercih edilen klasik arıtma yöntemlerinden olmuştur. İleri oksidasyon prosesleri, oksitleme gücü oldukça yüksek ve etkili olan hidroksil radikallerinin ($OH^{\bullet}$) oluşumunu sağlamak için kullanılan etkili yöntemlerdir. Hidroksil radikalleri ($OH^{\bullet}$) biyolojik olarak ayrıştırılması ve giderimi zor olan organik maddeleri ve kirleticileri oksitlemek için kullanılır. Hidroksil radikalleri ($OH^{\bullet}$) organik madde ile reaksiyona girerek suyu kirleten organik maddenin uygun koşullar altında mineralleşmesine izin verir ve sonuç olarak CO_2 ve H_2O son ürünleri oluşur. İleri oksidasyon prosesleri; fenton, fenton benzeri, UV, fotoliz ve sonoliz gibi teknikleri içerir. Bazı durumlarda, tek bir oksidasyon prosesi yetersiz olabilir ve aynı anda çoklu oksidasyon prosesleri uygulanabilir.

Foto-fenton prosesi etkili ve önemli bir ileri oksidasyon prosesidir. Işık radyasyonu ortamında uygulanan klasik fenton oksidasyonu genel olarak foto-fenton oksidasyon prosesleri olarak adlandırılır. Foto-fenton prosesinin oksidasyon potansiyeli UV radyasyonu ile arttırılabilir.

Anahtar Kelimeler: Foto-Fenton Prosesleri, Hidroksil Radikali, Hidrojen Peroksit, UV Radyasyonu, Fe^{2+} ve Fe^{3+} İyonları.

1. INTRODUCTION

Organic waste materials (proteins, carbohydrates, surfactants, phenols, pesticides, chlorinated compounds etc.), inorganic waste materials (chromium, zinc, lead, nickel, copper, arsenic, mercury, antimony, cadmium etc.) cause environmental pollution. Pollution caused by the industrial wastewater threatens human health and environmental poise too much and the causes environmental problems (Papic et al., 2004). Water that is the contaminated as a result of domestic, industrial, agricultural and other uses or whose properties are partially or completely changed, and water originating from mines and mineral processing facilities are defined as waste water (Üçpınar, 2003; Aytepe, 2015). Industrial wastewater can also be considered as water from food, textile, paper and cellulose, chemical petroleum, coal mines, metal, synthetic rubber/plastic and other establisment. Compared to other industrial sectors, the textile industry is the characterized as the industry that pollutes and affects the environment the most considering the discharge volume and effluent composition (Uzal et al., 2005; Şen and Demirer, 2003).

In the urban and industrial wastewater, natural and synthetic substances coming to wastewater treatment plants are exposed to various improvement processes. These applications are various activities and in the some cases these substances can be released into the surface waters without being changed (Daneshvar et al., 2003). In addition, less active conjugated forms can be deconjugated during wastewater treatment and in the environment and it can be form the more effective and stable compounds (Fernandes et al., 2004). Although these compounds are effectively removed in the treatment plants, they can also be transported to surface waters by using the sludge released after wastewater application in the agriculture. These potentially hazardous substances enter the aquatic environment and cause some negative physiological effects in the natural life and the human body through the food chain allowing the formation of the unhealthy environments in the human organism (Aytepe, 2015). In textile applications, paper and plastic wastes, additives used in the food industries, organic dyes and pharmaceutical wastes that pollution the nature and adversely affect health are considered as the important causes of environmental pollution (Sanghi et al., 2002). Biological and chemical treatment, electrochemical methods, coagulation, filtration, flocculation, adsorption, chemical oxidation

methods of the can be used to prevent the negative effect industrial wastes in the water environment (Walker et al., 2003). As an alternative to these processes, advanced oxidation processes (AOPs) that provide higher efficiency and support low energy consumption are preferred. Advanced oxidation processes (AOPs) is an oxidation method based on the reaction of the highly reactive species such as hydroxyl radicals (•OH) and organic pollutants (Akdağ Anıt, 2016). Nowadays, photo-fenton oxidation processes can be given as the most remarkable method of advanced oxidation processes that convert organic pollutants into harmless substances such as CO_2, H_2O and minerals.

2. MATERIALS AND METHODS

2.1 Mechanisms of Foto-fenton Oxidation Process

Classical fenton oxidation applied in the UV radiation environment is the generally to name as the photo-fenton oxidation processes. The oxidation potential can be increased by UV radiation. UV is in the wavelength range below the light wave visible to the human eye (λ = 100-390 nm range) (Bolton and Cater, 1997). In the photo-fenton process, hydrogen peroxide (H_2O_2) is consumed very quickly by direct fenton reaction, photo reduction of Fe^{3+} ions to Fe^{2+} ions and three simultaneous reactions called photolysis of H_2O_2 (Bolton and Cater, 1997).

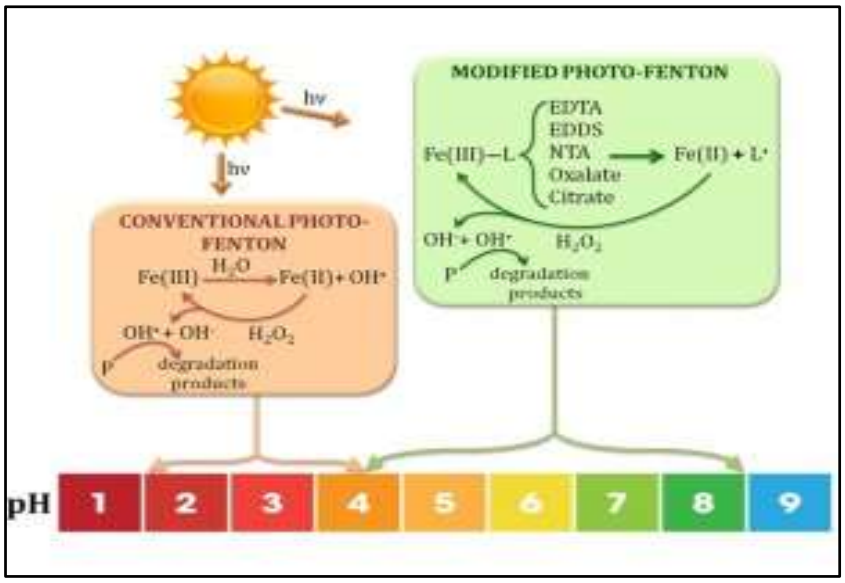

Figure 1. Foto-fenton Oxidation Process (Clarizia et al., 2017)

The combination of H_2O_2 and Fe^{2+} reaction as the follows by the give hydroxyl radicals (•OH) stoichiometrically as shown in the equation (Eq. (1.1-1.3)) (De Laat et al., 1999).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad (1.1)$$

$$Fe^{3+} + H_2O + UV \rightarrow Fe^{2+} + \bullet OH + H^+ \quad (1.2)$$

$$H_2O_2 + UV \rightarrow 2\ \bullet OH \ (\lambda < 400\ nm) \quad (1.3)$$

During the above reaction, Fe^{2+} ions reaction with H_2O_2 in the presence of the organic pollutants to form hydroxyl radicals (•OH) final products (De Laat et al., 1999). In the photo-fenton process, compounds that reaction slowly with the hydroxyl radical (•OH), as long as most of the light is the absorbed by H_2O_2, the power consumption for generating the hydroxyl radical (•OH) will be low, so that business costs will be low (Bolton and Cater, 1997). The need for less Fe^{2+}/Fe^{3+} in the presence of UV light makes the photo-fenton process more advantageous than other advanced oxidation processes (Bautitz et al., 2007).

3. RESULTS AND DISCUSSION

3.1 Factors Affecting Photo-Fenton Processes

3.1.1 Effect of Fe^{2+} Ion Concentration

It is known that Fe^{2+} concentration plays an complementary role in the speed and efficiency of fenton reactions (Bautitz et al., 2007). It is known that the excess or low concentration of the reagents in the reactions has negative effects on the reaction. For this reason, determining the correct concentration decreases the cost as well as increasing in the treatment efficiency (Bautitz et al., 2007).

Increasing the concentration of Fe^{2+} ions up to a certain point increases the rate of the hydroxyl radical production (Mirzaei et al., 2017). On the other hand, the presence of excess Fe^{2+} concentration start the formation of suspended Fe^{2+} sludge as well as reducing the reaction rate. In this case Fe^{2+} sludges are formed and require additional treatment cost (Deng et al., 2006).

As a result, iron concentration has an important effect on all fenton and photo-fenton oxidation processes and determining the optimum Fe^{2+} dosage is important in the removing organic pollutions (Kalkan, 2010).

3.1.2 Effect of pH

Studies show that the optimum pH value is 3 and in the acidic conditions below pH:3, hydroxyl radical (•OH) production of Fe^{+2} ions in the decreases (Neyens et al., 2003). The reason for this is that when Fe^{+2} ions increase above pH:5 they produce hydroxyl complexes instead of hydroxyl radicals (•OH), and H_2O_2 degrades under basic conditions and loses it is oxidation ability (Arslan-Alaton and Erdinç, 2006). For these reasons working at the most appropriate pH value will positively affect the process efficiency (Gagol et al., 2018).

The pH values of the solutions affect the oxidation of organic substances. Low pH (3-5 range) photo-fenton processes are known to be effective in the treatment of the industrial wastewater. For example, there are studies showing that it is effective in the removing color and toxic substances in the textile industry wastewater (Kang et al., 1999). As the rate of degradation of organic pollutants begins to decrease above pH:5 a decrease is observed in the photo-fenton yield. It is known that as the pH increases above 5, there is a decrease in the removal efficiency of organic pollutants (Bidga, 1995).

3.1.3 Effect of Oxidant (H_2O_2) Concentration

It is reported that the H_2O_2 concentration is not included in the reaction in the photo-fenton oxidation process studies and the removal efficiency is the very low in the treatment experiments performed under UV-C radiation (Behnajady et al., 2004). It has been stated that the negative effect of high doses of H_2O_2 on process efficiency is due to the hydroxyl scavenger (as can be seen in the following equation) effect of H_2O_2 (Eq. (1.4-1.6)) (Muruganandham and Swaminathan, 2004).

$$H_2O_2 + \bullet OH \rightarrow H_2O + HO_2\bullet \quad (1.4)$$

$$HO_2\bullet + \bullet OH \rightarrow H_2O + O_2 \quad (1.5)$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \quad (1.6)$$

3.1.4 Effect of Temperature

Temperature; it is one of the parameters affecting the photo-fenton reactions. Although it is known that it has a reaction slowing effect at temperatures under 20 ^{0}C, it is creates undesirable situations due to it is degrading effect on H_2O_2, especially when it increase above 40 ^{0}C (Aytaç, 2013).

3.1.5 Effect of Reaction Time

It is known that the reaction time has a positive effect on the oxidation potential in the studies conducted (Hwang et al., 2003). Although the reaction time varies according to the pollutant density and the preference of advanced oxidation processes, it is reported that the optimum reaction time for pollutant removal is in the range of 2-4 hours (Yılmaz, 2008).

3.1.6 Effect of UV Radiation

UV radiation light type is one of the important parameters affecting photo-fenton oxidation processes. Studies conducted with different types of light radiation in the literature show that the best removal efficiency occurs under UV-C (254 nm) (Xu et al., 2007).

4. CONCLUSION

It is seen in the studies that it is an effective process in the removing organic and inorganic pollutants by photo-fenton processes. Photo-fenton process is a process that improves and increases the formation of the hydroxyl radicals ($OH^{\bullet}$) by the effect of UV radiation. Hydroxyl radicals ($OH^{\bullet}$) are molecules that convert organic pollutants into harmless condition. Photo-fenton processes have many advantages over other advanced oxidation processes. The photo-fenton process is an economical process. It can be applied to many industrial wastewater. It is effective for organic and inorganic contaminants in the almost any concentration. Photo-fenton reactions occur quickly and in a very short time.

In recent years, it has been observed that the photo-fenton oxidation process has been applied in many areas. Waste water treatment, removal of chemicals in mineral wastes, odor and color removal, removal of textile dyes and pharmaceutical drug waste can be counted among it is application areas.

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