APPLICATIONS OF FENTON AND FENTON-LİKE PROCESSES IN THE REMOVAL OF ORGANIC POLLUTANTS IN WASTEWATER

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ABSTRACT

Water pollution, which is an important form of the environmental pollution, is the mainly caused by organic materials that cause excessive biological development using dissolved oxygen and heavy metals and organic pollutants that the have a toxic effect on aquatic organisms if their concentration exceeds a certain value. Wastewater occurs in groundwater, streams, lakes and seas. Factors that the cause pollution in the wastewater and accordingly, cause environmental pollution; organic substances (proteins, carbohydrates, fats, surfactants, phenols, pesticides, chlorinated compounds etc.), heavy metal compounds (antimony, arsenic, boron, copper, barium, zinc, nickel, chrome, tin, cobalt, silver, mercury etc.), cyanide, polychlorobiphenyl (PCB), aromatic and aliphatic hydrocarbons, asbestos, substances formed during refining and distillation processes, pharmaceutical drug wastes, textile organic dyes.

It is produced in the hazardous wastewater as a by-product during the production of the chemicals and when these wastewater is the discharged into the environment it is creates important problems. The first of these problems is the toxic effect of various organic pollutants (phenol, benzene, chlorinated compounds, pesticides etc.) in the wastewater on microorganisms. Therefore, wastewater containing hazardous organic pollutants must be given to the main treatment system after being treated in a pre-treatment system. The pollutant type should then be converted to less harmful by appropriate treatment.

Fenton reactions are the widely accepted for their ability to the break down most organic compounds. It is also provides an important way for the oxidation in the environment through hydroxyl radical ($OH^•$). The reaction known as fenton reaction is the oxidation of Fe^{2+} ion with hydrogen peroxide (H_2O_2) to form hydroxyl radical ($OH^•$). Fenton oxidation is an advanced oxidation technology in which a mixture of H_2O_2 and Fe^{2+} salts is the added directly to wastewater. This mixture leads to the emergence of the hydroxyl radicals ($OH^•$) through catalytic decomposition of the hydrogen peroxide (H_2O_2) and this process is the significantly increased by method efficiency. In addition, Fe^{3+} salts formed in the oxidation step provide removal of other pollutants by coagulation and sedimentation. Oxidation systems based on the fenton methods can treatment organic and inorganic pollutants. Hydrogen peroxide (H_2O_2) and iron salts are used in the fenton methods chemistry. Hydrogen peroxide (H_2O_2) activity increases with the addition of the iron salt to form hydroxyl radicals ($OH^•$).

Keywords: Fenton Processes, Organic Pollutant, Hydroxyl Radicals, Oxidation Potential, Hydrogen Peroxide.

1. INTRODUCTION

The increasing population in the world and in our country brings more needs and consumption with each passing day. In order to meet these needs, there is an improvement in existing activities or alternative solutions (Ataş, 2012). With the economic growth, environmental pollution becomes a big problem as a result of the technological and industrial developments worldwide. The significant reduction of toxic and harmful organic pollution of these wastes by breaking down has been of great interest lately (Oturan et al., 2011).

Pollution in water sources is divided into two parts as direct pollution and indirect sources of pollution. Direct sources of pollution; Industrial institution waste, refineries and processed plant waste are examples. Pollutants contained in indirect sources of pollution mix with the water and affect the atmosphere by mixing the soil with groundwater systems and rainwater (Aytepe, 2015). Pollutants are generally examined in two parts. These are organic and inorganic pollutants. Some of the organic water pollutants include pollutants such as industrial solvents, volatile organic compounds, insecticides, pesticides, dyes (Vijayaraghavan and Yun, 2008). Inorganic water pollutants, on the other hand, contain acidic pollutants such as metal and fertilizers. For the treatment of these pollutants, various wastes are treated before the industrial wastewater is discharged to the receiving environment by various physicochemical and biological methods (Hai et al., 2007). Waste water known as contaminated or partially or completely altered waters as a result of domestic, industrial, agricultural and other uses and water from mines and ore processing plants are known as wastewater (Üçpınar, 2003). Industrial wastewater can be considered as wastewater from food, textile, paper and cellulose, chemistry, petroleum, coal mines, metal, synthetic rubber/plastic and other enterprises (Uzal et al., 2005). Textile industry is considered as the most polluting industry in terms of discharge volume and leaving water content compared to other industrial sectors (Şen and Demirer, 2003).

Textile industry wastewater can show different amounts and properties depending on the raw material processed, the product produced, the technologies and chemicals used (Sreeja and Sosamony, 2016). Wastewater generally contains high organic compounds, strong color, high temperature, turbidity and total dissolved solid matter (Elango et al., 2017). The textile industry has colored wastewater that contains various dyestuffs in different concentrations. Physical, chemical and biological treatment methods are used to treat industrial wastewater (Suryawan et al., 2017). Biological treatment is a more preferred method considering the economic and environmental factors compared to physical and chemical treatment methods (Türkeş, 2019). However, as the sensitivity to environmental pollution increases day by day and especially wastewater discharge standards are tightened in this context, the application of a single treatment method is not sufficient to achieve the desired treatment efficiency. For this reason, it is recommended to use different treatment technologies together (Suryawan et al., 2017; Khamparia and Jaspal, 2017).

Along with advanced oxidation processes, biologically difficult or non-degradable organics in wastewater or drinking water can be broken down by oxidation method. During the oxidation process, oxidation up to CO_2 is generally not observed, but after oxidation, the biodegradability of wastewater increases (Akbulut, 2020). Advanced oxidation processes (AOP) show higher micro-contaminant removal performance than traditional oxidation methods based on longer contact times because of stronger oxidant doses, higher free radical compounds, hydrogen peroxide (H_2O_2) and hydroxyl molecule (OH) (Lee et al., 2009). Fenton and photo-fenton processes, which are advanced oxidation processes, have many advantages such as being simpler and more economical than other oxidation processes and short reaction time. Fenton and photo-fenton processes can be applied in many different areas (Akbulut, 2020). The Fenton process, an advanced oxidation process, was discovered nearly 100 years ago. The use of the Fenton process as an oxidation process started after the 1960s. The Fenton reaction was first discovered in 1894 by H.J. Fenton. Removal of organic pollutants is a very important stage of modern industrial chemical production, agriculture and municipal water cycle (Akbal et al., 2002).

2. MATERIALS AND METHODS

2.1 Mechanisms of Fenton and Fenton-Like Process

The Fenton reaction was discovered during the research of Henry John Horstman Fenton in 1894 (Ebrahiem et al., 2017). In 1934, it was discovered by Haber and Weis that the active oxidizer in the fenton reaction was hydroxyl ($OH^{\bullet}$) radicals (Haber and Weiss, 1934). Fenton reaction is based on the formation of hydroxyl radicals ($OH^{\bullet}$) with high oxidation potential (E^0 = 2.8 eV) as a result of reaction of H_2O_2 and Fe^{2+} ions in acidic aqueous medium (Blanco et al., 2014; GilPavas et al., 2017). The classical Fenton mechanism occurs mainly in the absence of organic compounds by the following reactions (Deng and Englehardt, 2006) (Eq. (2.1-2.7)).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad (2.1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (2.2)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (2.3)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (2.4)$$

$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + O_2H^{+} \quad (2.5)$$

$$Fe^{2+} + HO_2 + H^{+} \rightarrow Fe^{3+} + H_2O_2 \quad (2.6)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \quad (2.7)$$

In the above reactions, iron undergoes ion exchange between Fe^{2+} and Fe^{3+} and plays the role of catalyst. Reaction of the hydroxyl radical ($OH^{\bullet}$) with organic compounds causes the formation of carbon-centered radicals. The hydroxyl radical reacts with organic compounds, essentially H is removed from C-H, N-H or O-H bonds, added to C=C bonds or reacts with aromatic rings (Pignatello et al., 2006).

3. RESULTS AND DISCUSSION

3.1 Parameters Effecting of the Efficiency of Fenton Process

3.1.1 Effect of pH

It has been stated that pH is an important factor for the efficient removal of pollutants in wastewater in Fenton process. Acidic conditions are more appropriate in terms of redox reactions, especially in the removing color and organic pollutants from wastewater of textile industry (Pouran et al., 2015). The most optimum pH range is specified as 2-4. When the pH falls below the 2-4 range, $H_3O_2^{+}$ is formed as can be seen in reactions 1.8 and 1.9. As a result, the formation of hydroxyl radical ($OH^{\bullet}$) is greatly reduced (Torrades and Montano, 2014; Pouran et al., 2015; Abedinzadeh et al., 2018; Azak, 2012).

$$H_2O_2 + H^{+} \rightarrow H_3O_2^{+} \quad (2.8)$$

$$OH^{\bullet} + H^{+} + e^{-} \rightarrow H_2O \quad (2.9)$$

When the pH rises above the 2-4 range, hydroxyl radical ($OH^{\bullet}$) formation becomes difficult as the H_2O_2 degrades and loses it’s oxidation properties as seen in Reaction 1.10 (Azak, 2012).

$$2H_2O_2 \rightarrow O_2 + 2H_2O \quad (2.10)$$

3.1.2 Effect of Fe^{2+} Ion Concentration

As can be seen in the fenton reaction given in reaction 1.1, Fe^{2+} ion reacts with H_2O_2 to form the hydroxyl radical ($OH^{\bullet}$). When the concentration of Fe^{2+} ion increases according to the reaction, the hydroxyl radicals formed ($OH^{\bullet}$) will also increase and accordingly in the removal efficiency of organic pollutants will increase (Matavos-Aramyan and Moussavi, 2017).

However, in the positive effect of this increase in Fe^{2+} ion concentration is not linear. Fe^{+2} ion concentration above a certain level decreases the reaction rate. At the same time, excess Fe^{+2} in the environment can increase the amount of solids, resulting in the excessive sludge formation at the process exit (Gürbüz, 2015; Nikravan, 2015).

3.1.3 Effect of H_2O_2 Concentration

In Fenton process, similar to Fe^{2+} ion, the amount of the hydrogen peroxide (H_2O_2) is the increased up to a certain value and the efficiency of the process increases. Because hydrogen peroxide (H_2O_2) is the source of hydroxyl radicals ($OH^{\bullet}$) formed by fenton reaction (Nikravan, 2015; Sönmez, 2015).

Increasing in the amount of H_2O_2 and getting away from its optimum level both increases in the process cost and reacts with excess H_2O_2 hydroxyl radical ($OH^{\bullet}$), leading to the formation of $HO_2^{\bullet}$ with much lower oxidation power (Nikravan, 2015; Sönmez, 2015).

3.1.4 Effect of Temperature

Ambient temperature is an important parameter in Fenton process. Fenton process applications performed in the low temperature environments require high Fe^{2+} and hydrogen peroxide (H_2O_2) concentrations. Added high Fe^{2+} and hydrogen peroxide (H_2O_2) concentrations cause excess sludge formation and increase in the process cost. The increase in the ambient temperature accelerates the formation of hydroxyl radical ($OH^{\bullet}$) in the fenton process and improves process performance (Aygun et al., 2012). However, in the relation ship between temperature increase and process efficiency increase is not linear. For this reason, temperatures between 20-40 ^{0}C are recommended (Ruiz, 2015).

3.2 Advantages of Fenton and Fenton-Like Processes

We can list the advantages of the fenton process as follows.

- The chemicals used can be easily obtained.
- It does not require any energy input.
- The initial investment cost is affordable and less.
- It is suitable for different processes.
- Hard decomposition and toxic compounds can be partially neutralized.
- Reducing toxicity for a biological treatment.
- Sudden start-up time is 1-2 hours.
- High efficiency.
- No longer leaving.
- Chemically inert sludge treatment.
- Stable in the treatment of a wide variety of pollutants.
- No need for additional equipment.
- Organic pollutants are easily destroyed (Öztürk, 2007; Özcan, 2010; Erdoğan, 2018).

3.3 Disadvantages of Fenton and fenton-like processes

We can list the disadvantages of the fenton process as follows.

- Concentrated solutions of H_2O_2 are dangerous and storage and transportation costs are high.
- The pH in the solution is lowered to 2-4 and eventually requires a large amount of the chemicals for the neutralization process.
- The need to remove the iron sediments that have formed when the process ends.
- The cost of the adding chemicals.
- Cost of the sludge disposal (Öztürk, 2007; Özcan, 2010; Erdoğan, 2018).

3.4 Application scope of Fenton process

Fenton process is used in the wastewater containing various toxic compounds, wastewater with a lot of color and in the removal of organic pollutants. The application scope of the Fenton process can be listed as follows.

- Reducing toxicity.
- To provide Biological Oxygen Demand and Chemical Oxygen Demand.
- To provide organic pollutant removal.
- It is used to remove color and odor in the wastewater.
- It is applied to increase biodegradation (Öztürk, 2007; Özcan, 2010; Erdoğan, 2018).

4. CONCLUSION

In this review, it is seen in studies that organic and inorganic pollutants are an effective process for removal with fenton processes. Fenton and fenton-like processes are processes that improve and increase the formation of hydroxyl radicals. Hydroxyl radicals ($OH^{\bullet}$) are molecules that convert organic pollutants into harmless ones. Fenton processes have many advantages over other advanced oxidation processes. Fenton processes are an economical process. It can be applied to many industrial wastewater. It is effective for organic and inorganic pollutants in almost every concentration (ng/L-µg/L). Fenton reactions take place quickly and in a very short time. Waste sludge formation is low. Fe^{2+} in the outlet water and $Fe(OH)_3$ in the form of sediment may create operational difficulties and costs.

In recent years, it has been observed that fenton reaction has been applied in many areas. Wastewater treatment, removal of chemicals in mineral wastes, odor and color removal, removal of textile dye and pharmaceutical drug waste can be counted among the application areas.

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