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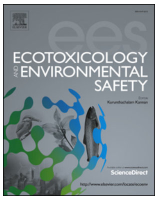

Comparison of photo-Fenton, $O_3/H_2O_2/UV$ and photocatalytic processes for the treatment of gray water

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ABSTRACT

This research was carried out to compare and optimize the gray water treatment performance by the photo-Fenton, photocatalysis and ozone/H_2O_2/UV processes. Experimental design and optimization were carried out using Central Composite Design of Response Surface Methodology. The results of experiments showed that the most effective and influencing factors in photo-Fenton process were H_2O_2/Fe^{2+} ratio, in ozone/H_2O_2/UV experiment were O_3 concentration, H_2O_2 concentration, reaction time and pH and in photocatalytic process were TiO_2 concentration, pH and reaction time. The highest COD removal in photo-Fenton, ozone/H_2O_2/UV and photocatalytic process were 90%, 92% and 55%, respectively. The results were analyzed by design expert software and for all three processes second-order models were proposed to simulate the COD removal efficiency. In conclusion the ozone/H_2O_2/UV process is recommended for the treatment of gray water, since it was able to remove both COD and turbidity by 92% and 93%, respectively.

1. Introduction

Climate change and recent droughts have led to water shortage as a serious threat to life (Brissaud et al., 2008). In addition, increasing world population and rising living standards have also led to further consumption of fresh and available water (Chin, 2009). In recent years, new methods based on sustainability and preservation of environmental principles have been applied to solve the problem of reducing water resources (Metcalf et al., 2007). One of these methods, which is now widely considered by the countries of the world, is the reuse of gray water for various purposes (Sanchez et al., 2010). The use of this method, especially in the Middle East countries and North Africa, where water resources are more limited, is an important issue (Albalawneh and Chang, 2015; Bani-Melhem et al., 2015; Nautiyal et al., 2017). Accordingly, the reuse of gray water can be a safe alternative to fresh water sources for the landscape irrigation and also for carwashes, fire engines and toilet siphons. (Albalawneh and Chang, 2015; Lu and Leung, 2003; Nautiyal et al., 2017).

Gray water is defined as the wastewater produced from kitchens, laundries, baths and any non-toilet household sewage (Bani-Melhem et al., 2015; Schäfer et al., 2006). This kind of wastewater includes 80–85% of household wastewater (Bani-Melhem et al., 2015; Li et al., 2009; Nautiyal et al., 2017) and qualitatively contains chemicals such as surfactants found in detergents (Eriksson et al., 2002; Sanchez et al., 2010; Zhou et al., 2018a) and pathogenic bacteria (Bani-Melhem et al., 2015). Therefore, the treatment of these wastewaters not only develops water resources, but due to the low contamination of gray water compared to municipal wastewater, the cost of their treatment is lower.

There are various methods for treatment of gray water (Albalawneh and Chang, 2015), including biological (MBR) (Bani-Melhem et al., 2015; Merz et al., 2007), chemical (Nautiyal et al., 2017; Sanchez et al., 2010; Uliana et al., 2017) and physical (Kim et al., 2007; Ramona et al., 2004) methods. As the organic load of gray water is low, biological treatment methods do not have high efficiency. Also, physical treatment methods alone cannot reduce contamination to an environmental standard level (Metcalf and Eddy, 2003).

So far, several studies have been carried out on the use of chemical treatment and advanced oxidation process in gray water treatment. In 2010, Sanchez et al. used titanium dioxide nanoparticles as photocatalyst to treat gray water from hotels, and eliminated 65% of the DOC in 150 min (Sanchez et al., 2010). Tony et al. used Fenton process for treatment of gray water, and the maximum removal of COD occurred (95%) at a concentration of $Fe^{3+} = 40$ mg/L, $H_2O_2 = 200$ mg/L, and pH = 3 (Tony et al., 2016). In another research, a photocatalytic oxidation with titanium dioxide and UV radiation lowered the COD of laundry gray water from 139 mg/L to 26 mg/L (Pidou et al., 2007).

Advanced oxidation treatment of gray water can be affected by various factors such as reaction time, H_2O_2/Fe^{2+} ratio, pH, titanium dioxide concentration, ozone concentration, and UV intensity (Albalawneh and Chang, 2015; Sanchez et al., 2010). Therefore, it is

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necessary to find the optimal amount of parameters by conducting the least number of tests in order to save time and money. The application of Response Surface Methodology is a practical method used to optimize the parameters and evaluate the interactions between them (Azadi et al., 2018; Mohammadzadeh et al., 2016). It is a mathematical regression relationship between independent parameters and generates a response with the least number of tests, and provides the optimize value for the response parameter in the optimization stage (Azadi et al., 2017).

In this research, the advanced chemical oxidation process was used for the treatment of gray water, with the purpose of water reuse in irrigation of urban landscaping. To do this, photo-Fenton, photocatalysis and H_2O_2/UV/ozone processes were used. The effects of independent parameters such as reaction time, H_2O_2/Fe^{2+} ratio, pH, titanium dioxide concentration and ozonation rate on the removal of COD (as the response parameter) were evaluated through RSM method. To the best of our knowledge, no comparison has been made so far between these three processes simultaneously for the treatment of gray water using the RSM method.

2. Material and methods

2.1. Characteristics of gray water

The gray water tested in this study was collected from a student dormitory at Shiraz University, Shiraz, Iran. The COD and turbidity of this gray water varied from 80 to 90 mg/L and 65–80 NTU, respectively. Considering the fact that according to US EPA standards, the BOD and turbidity of treated gray water should be less than 10 mg/L and 2 NTU, respectively, for urban landscape irrigation (EPA guidelines, 2004), this wastewater needed to be treated. The pH of raw gray water was 8.5.

2.2. Advanced oxidation theory

The advanced oxidation process is a chemical oxidation process that can oxide the contaminants by producing active hydroxyl radicals. These hydroxyl radicals are produced through UV/H_2O_2, ozone/H_2O_2, UV/ozone, Fenton detector and TiO_2/UV processes (Sharma et al., 2011). In the photo-Fenton test, the iron ion reacts with H_2O_2 and produces radical hydroxyl. The produced radicals can decompose organic matters through this process and convert them into inorganic compounds. The reaction between iron and H_2O_2 was first described by Fenton (1894) and its equations are shown below (Kitis et al., 1999; Venkatadri and Peters, 1993).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O_2H^{\bullet} + H^{+} \tag{2}$$

This process is influenced by various factors such as pH, temperature, iron concentration, hydrogen peroxide concentration and molar proportion of hydrogen peroxide to iron. The detector used in this process (iron ion) is available and maintainable, and its management is easy. It is also safe and does not harm the environment.

The photo-Fenton process involves the use of hydrogen peroxide and ferrous iron with ultraviolet radiation that can decompose pollutants by producing radical hydroxyl. The combination of hydrogen peroxide and UV light with Fe^{2+} or Fe^{3+} ions produce more radical hydroxyls in comparison with the Fenton process, and consequently, increases the organic matter decomposition rate (Hoigne and Bader, 1976). According to Eqs. (3) and (4), the Fe^{3+} ion is decomposed under UV rays at a wavelength of 180–400 nm and produces $OH^{\bullet}$ (Chin, 2009).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \tag{3}$$

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + OH^{\bullet} + H^{+} \tag{4}$$

In photo-Fenton process inorganic anions have desire to reduce the decomposition rate by suppressing the hydroxyl radicals. For example, sulfate and chloride anion react with iron ions (Fe^{2+} and Fe^{3+}) in the solution and produce complicated products. This result in decreasing the concentration of iron ions, one of the main factors in photo-Fenton process, and reduction of COD removal efficiency occurs due to deficiency of iron ion. However, anions such as nitrate, carbonate and bicarbonate are reluctant to produce complicated products using iron ions of solution. They directly consume hydroxyl radicals and reduce its concentration in the solution as shown in Eqs. (5)–(7) (Devi et al., 2011).

$$NO_3^{-} + OH^{\bullet} \rightarrow NO_3^{\bullet} + OH^{-} \tag{5}$$

$$CO_3^{2-} + OH^{\bullet} \rightarrow OH^{-} + CO_3^{-\bullet} \tag{6}$$

$$HCO_3^{-} + OH^{\bullet} \rightarrow OH^{-} + HCO_3^{-\bullet} \tag{7}$$

In the photocatalytic oxidation method, the main components are a photocatalyst and a light source (Azadi et al., 2017; Poorkarimi et al., 2017; Zhou et al., 2018b), the interaction between these components leads to the production of active radicals and anionic superoxide radicals (Amiri et al., 2016; Azadi et al., 2017; Jiang et al., 2013). These active radicals can decompose refractory pollutants into biodegradable matters or inorganic ions such as carbon dioxide and water (Azadi et al., 2017; Jia et al., 2011; Poorkarimi et al., 2017). Various photocatalyst have been used for wastewater treatment (Maroufi et al., 2018). Titanium dioxide (TiO_2) is a photocatalyst that has been highly considered due to its unique properties such as non-toxicity, low cost, sustainability and availability (Azadi et al., 2017; Sanchez et al., 2010; Wang et al., 2017). Titanium dioxide nanoparticles include valence and conduction bands, and there is a large empty space between these two bands. When a titanium dioxide catalyst is exposed to a photon beam with equal or greater energy than the energy gap (eV 3.2), the electron is transferred from the valence band to the conduction band. In the conduction band, the electron reacts with the oxygen in the wastewater and produces $O_2^{-\bullet}$. In the valence band, a cavity is produced due to electron exit and produces hydroxyl radicals by contacting with water. These radicals are directly involved in the oxidation process for the decomposition of contaminants and bacteria (Bhadiyadra and Vaghani, 2015; Garcia-Martínez et al., 2005; Zhou et al., 2018a, 2018b). Eqs. (8)–(10) show the photocatalytic process with titanium dioxide (Garcia-Martínez et al., 2005).

$$TiO_2 + hv \rightarrow e^{-} \text{ (conduction band)} + h^{+} \text{ (valence band)} \tag{8}$$

$$H_2O + h^{+} \text{ (valence band)} \rightarrow OH^{\bullet} + H^{+}_{aq} \tag{9}$$

$$O_2 + e^{-} \text{ (conduction band)} \rightarrow O_2^{-\bullet} \tag{10}$$

$hv > $ gap energy

O_3/H_2O_2/UV process is one of the advanced oxidation processes which is more effective than other processes such as O_3 alone, O_3/H_2O_2 and O_3/UV. In this process O_3 decomposes to hydroxyl radicals. UV ray (254 nm) helps ozone molecules to active quickly and also presence of hydrogen peroxide increases the speed of reaction. (Al-Kdasi et al., 2004). These strong radicals attack organic matters and mineralize them into inorganic substance such as H_2O and CO_2. Eqs. (11)–(15) show the O_3/H_2O_2/UV process (Al-Kdasi et al., 2004; Arslan et al., 2017).

$$O_3 + H_2O_2 + hv \rightarrow OH^{\bullet} + O_2 + HO_2^{\bullet} \tag{11}$$

$$O_3 + OH^{\bullet} \rightarrow HO_2^{\bullet} + O_2 \tag{12}$$

$$O_3 + HO_2^{\bullet} \rightarrow OH^{\bullet} + 2O_2 \tag{13}$$

$$OH^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + O_2 \tag{14}$$

$$2OH^{\bullet} \rightarrow H_2O \tag{15}$$