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Degradation of recalcitrant compounds from the industrial effluents by Fenton-based approaches: A review

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The huge generation of industrial effluents and their inefficient treatments make the environment and public health in danger. The variety of pollutants present in the effluents depending upon the type of industry from which they are coming out, which are highly toxic and recalcitrant. Biological (conventional) treatment methods fail for their effective degradation and mineralization. Wastewaters characterize by such compounds need cutting-edge and innovative technologies for their effective degradation and removal. In this review, we have highlighted some of the most preferable treatment methods with their mechanisms and applications in the context of wastewater containing recalcitrant compounds. It has been reported in the literature that Fenton-based approaches are one of the most efficient and versatile processes for degradation/mineralization of recalcitrant compounds. However, despite several advantages, some disadvantages are associated with these processeswhich make complications for their full-scale applications. Hence, we have to appropriately select the treatment options, which could be efficient enough and serve the overall purpose.

Keywords: Advanced oxidation processes, electro-Fenton, Fenton process, photo-Fenton, recalcitrant compounds.

Introduction

The increasing problems associated with recalcitrant compounds removal from the effluents and their strict discharge standards required advanced and effective technologies[1,2]. The cost-effective andenvironmental-friendly approach would be suitable to serve the purpose. From the literature survey, the versatile applications of the advanced oxidation processes (AOPs) among physicochemical processes are one of the most suitable and widely adopted choices[2,3]. The hydroxyl radicals (•OH) are the main reactive species in the AOPs. These radicals effectively degrade the variety of recalcitrant compounds[3–5]. The Fenton-based processes are the most effective and widely recognized AOPs for the treatment of a wide variety of pollutants[2–4].

Applications of the Fenton-based approaches

Although, the applications of the Fenton process are wide and versatile due to its fast degradation rate and simplicity in operation[6,7]. However, the conventional Fenton process has some limitations, and to overcome those drawbacks various advanced Fenton-based approaches are developed and further improvements are underway to obtain sustainable solutions. Some of the Fenton-based approaches are summarized here as follows:

Fenton process

H. J. H. Fenton has first discovered the Fenton process in 1894[8], and its main development was proposed by Haber and Weiss[9,10]. The reagents utilized in the reaction are Fe^{2+} and H_2O_2, which produce the highly reactive hydroxyl radicals (•OH) under acidic conditions. The generated radicals rapidly and non-selectively degrade the variety of pollutants, which are non-biodegradable and recalcitrant[11]. The best treatment efficacy of the Fenton process was observed at the pH range of 2–4[12]. The hydroxyl radicals formed by the reaction of Fe^{2+} and H_2O_2 as shown in reaction (1)[11,13]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (1)$$

The other reactive species like $HO^{\bullet}_2$ also formed and Fe^{2+}

regenerated by the Fenton-like reaction as shown in reaction (2)[9,10]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{\bullet}_2 + H^+ \quad (2)$$

Among the generated species the hydroxyl radicals (•OH) are considered efficient for the degradation of organics[14]. The various operational parameters are involved viz. pH, reaction time, reagents ratio, and dosage of chemicals. However, pH and reagents ratio are the main influencing factors[15]. Despite the complexity of its mechanism and limitations, still, the process widely applied for numerous applications[2–4,11,12].

Photo-Fenton process (PFP)

The conventional Fenton process (CFP) is having some drawbacks, one of them is large sludge production. So, by the addition of ultraviolet or visible light in the CFP, iron sludge production was reduced, which also increases the degradation efficiency of the pollutants. The photo-assisted Fenton process effectively generates more •OH radicals and speed up the conversion of Fe^{3+} into Fe^{2+}, as per the reaction (3)[16,17]:

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

The destruction rate of contaminants largely depends upon the intensity and wavelength of UV radiation[18]. Despite several advantages of the photo-Fenton process over CFP still it holds some barriers, which limits the full-scale applications and required further improvement[7].

A variety of pollutants such as pesticides[2,19], antibiotics[20], dyes[21], chlorophenols, and other chlorinated compounds[22] in water have been degraded and mineralized by the applications of PFP, well stated in the literature. Also, the process is extensively utilized for other highly contaminated wastewater and landfill leachate treatment[23,24].

Electro-Fenton process (EFP)

Another promising Fenton-based approach that has been successfully adopted for a variety of recalcitrant compounds degradation and removal is EFP[15]. The drawbacks associated with the CFP like high reagents cost involvement and the large sludge production can be notably improved by the involvement of electrochemistry[15]. Several advantages of EFP such as versatility, high energy efficiency, amenability of automation, and environmental compatibility have been reported in the literature. Furthermore, the continuous regeneration of Fe^{2+} at the cathode (reaction 4) minimizes sludge production[15,25–28]. This makes the process more efficient and environmentally friendly[29].

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (4)$$

Sono-Fenton process (SFP)

The sonochemical oxidation techniques involve the use of sonic or ultrasonic waves to produce an oxidative environment via cavitation that yields localized microbubbles and supercritical regions in the aqueous phase[30–32]. During the reactions, the highly reactive radicals/species (•OH/•OOH/H•) were generated, which further degrade and mineralized the variety of compounds.

The intermediate complex ($[Fe^{III}(OOH)]^{2+}$) is produced by the general Fenton mechanism further dissociates into Fe^{2+} and •OOH under ultrasonic irradiation (reaction 5). Also, the remaining Fe^{2+} further reacts with H_2O_2 and generates more hydroxyl radicals[30].

$$Fe^{III}\,(OOH)^{2+} +))) \rightarrow Fe^{2+} + {}^{\bullet}OOH \quad (5)$$

The favorable effect of ultrasonic irradiation in combination with the Fenton system has been reported in several studies for wastewater treatment but the major problem for wide application is the high energy consumption of ultrasound systems[30,33–38].

The relevance of the review

This review is a brief outline of some of the Fenton-based approaches for wastewater treatment particularly focusing the recalcitrant degradation and mineralization. A variety of single and integrated AOPs have been adopted due to their versatile nature for complex wastewaters treatment. Still, the full-scale applications of these methods are limited. Hence, required more extensive research to overcome the associated limitations during the full-scale applications.

Conclusion

From the literature survey, it has been observed that several research efforts have been made toward Fenton-based approaches for highly contaminated wastewaters treatment, particularly for recalcitrant degradation and mineralization. The problems associated with the classical Fenton process like pH modulation, large sludge production are reduced in the photochemical AOPs. The utilization of sunlight in the replacement of UV lamps in the photo-Fenton process appears to be the most efficient technology without compromising the efficiency of the process. In the EFP, the generation of H_2O_2 and iron avoids the drawbacks of the CFP, such as reagents cost, and sludge production. The hybrid methods enhanced the hydroxyl radicals' concentration and reduced the associated limitations in the CFP. However, the full-scale applications of these approaches are limited and still required more studies. The integrated processes are considered to be more efficient and cost-effective.

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