

Advantages and Disadvantages of Fenton Process

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The Fenton reaction is primarily based on the idea of the formation of oxidizing radicals, which are created by the catalytic action of Fe^{2+} on the decomposition of H_2O_2 , added in a certain amount and ratio to water, which also contains various organic substances. Oxidative radicals oxidize the present organic substances to varying degrees during the momentary period of their existence. This Fenton reaction is homogeneous because the catalyst (Fe^{2+} ion) is dissolved in water. However, the catalyst can also be heterogeneous.

Fenton

processes

AOPs

1. Advantages of the Fenton Process and Its Historical Role

The Fenton process is based on inexpensive reagents and the reactor arrangement is simple. Compared to other oxidation systems, e.g., gas–liquid (chlorination, ozonation), the reaction is not negatively affected by mass transfer. Concurrently, the system of Fenton components can also be bubbled with air or oxygen, similar to the heterogeneous Fenton reaction, where dissolved oxygen in water accelerates the formation of Fe^{2+} in the case of using solid Fe particles as their source. The reaction can be easily controlled, and the Fenton process is indispensable if simple and affordable chemicals together with a simple reactor equipment (essentially a stirred tank) are used.

Fenton's discovery of oxidizing radicals enabled the development of other new processes based on this phenomenon, in which various oxidizing radicals, e.g., singlet oxygen, are also generated by physicochemical processes, preferably by the action of UV radiation of various wavelengths, including solar radiation, ultrasound, cold plasma, and streams of electrons, from which dozens can be assembled by combination. This created a huge space for further theoretical and experimental studies of advanced oxidation processes and the verification of their effectiveness and the quality of products for the destruction of hundreds of different organic substances. It should be emphasized that the classic Fenton reaction is an excellent basis for the development of such advanced AOP modifications.

Essentially, AOPs are considered to be reactions where the formation of radicals is initiated by another application of energy intervention, such as ultraviolet radiation. Due to the more powerful generation of hydroxyl radicals, in most cases, AOPs also show a higher efficiency of decomposition of organic substances than the classical Fenton reaction, which is their greatest benefit. Some strongly recalcitrant substances (chloro and nitro derivatives of phenol, phthalates, polyaromatics, polychlorinated aromatics such as PCBs, dioxins and furans, pharmaceuticals,

chlorinated fungicides and pesticides, alkyl benzyl sulfonates, etc.) can be significantly disrupted only by these new AOPs. However, they are also more energy intensive, more expensive, and their strong oxidizing power, in such situations where the mineralization of organic substances does not occur, can lead to the formation of oxidation byproducts, which appear more hazardous than the original organic substances. With the classical Fenton reaction, such danger is less serious.

Nevertheless, the simple version of the Fenton reaction is irreplaceable when the concentration of the target pollutant to be removed reaches the values given by regulations or standards due to its simplicity, incomparably lower costs, and the reduction in the risk of creating hazardous side- and endproducts, which happens frequently. This trend is evident not only from the great interest in studying the application of the Fenton reaction in developing countries, where this simple technology is experiencing a great renaissance, but also in economically developed ones, where it seems to be an ideal decontamination technique for the decontamination of water from various smaller brownfields.

Why Are These Promising Methods Not Applied in Industry More Commonly?

AOP is currently receiving extreme attention in literature. AOPs can be made both in the homogeneous variant ($\text{O}_3/\text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ a $\text{H}_2\text{O}_2/\text{UV}$) and the heterogeneous one, e.g., $\text{H}_2\text{O}_2/\text{TiO}_2/\text{UV}$. However, the main drawback of the homogeneous system is the inhibition of radical propagation due to the presence of radical scavengers that are commonly present in water, such as carbonates, bicarbonates, and NOM. This is the main reason why homogeneous variants, including the classical Fenton method, are not implemented for the treatment of contaminated waters on an industrial scale, although the application of the Fenton method to various wastewaters is being addressed in laboratories. There have been a large number of similar contributions in the last decade, especially from developing countries, where methods of wastewater treatment from various local sources are beginning to be considered, e.g., from wastewater refineries, the textile industry, especially from dyeworks, tanneries, etc. [1][2][3]. However, Vega and Valdés [4] documented that the aforementioned limiting factor could be reduced by a heterogeneous arrangement.

2. Disadvantages of the Basic Fenton Process and Possible Solutions

The basic disadvantage of the Fenton reaction is the low pH value around pH 3, above which the radicals are not stable. Moreover, at a pH below 3, there is a strong reduction in radical formation [5], and at a pH above 3, specifically around pH 5, insoluble $\text{Fe}(\text{OH})_2$ is formed, and at a pH above 4, the low decomposition of peroxide, which preferentially decomposes into oxygen and water without the formation of radicals, appears. For these reasons, it is also necessary to focus on whether the target organic substances are soluble at all of the pH ranges suitable for the generation of radicals. In the case of heterogeneous catalysts, it is also essential to consider the isoelectric point and the surface charge of the catalyst as well as the target substance, i.e., whether the adsorption of the substance on the catalyst is favored at a given pH. It is one of the important control steps of radical oxidation

on the catalyst. Treated water also needs to be neutralized before being released into the environment, which increases the cost of chemicals.

It appears that it is possible to apply an additive that “wraps” the Fe ion and prevents the precipitation of iron hydroxide (e.g., by adding resorcinol, see Romero et al. [6]). This direction becomes interesting for further research related to the effort to realize pollutant oxidation at a neutral pH, which is highly urgent.

The application of the Fenton reaction under desired neutral conditions is currently possible only with its modified hybrid version, e.g., with the catalyst ferric-nitrilotriacetate complex (Fe^{3+} -NTA) and under the influence of UVA radiation (0.178 mM Fe^{3+} -NTA (1:1), 4.54 mM H_2O_2 , UVA intensity 4.05 mW/cm², hydraulic retention time (HRT) 2 h, influent pH 7.6 [7]). The application of various chelate complexes with Fe can also be considered as a variant of the homogeneous Fenton reaction, which is also possible in execution with UV. The generation of $\bullet\text{OH}$ radicals was also confirmed with the use of Fe^{3+} -ethylenediamine-N,N'-disuccinic acid (Fe^{3+} -EDDS), and regarding the degradation efficiency, it greatly surpassed other Fe^{3+} complexes, e.g., with citric, malic, oxalic, and wine acid.

Some authors solved the problem of reducing the high consumption of chemicals by treating effluents from treatment plants with extremely low values of iron and peroxide (from popular ratios such as $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ (in mmol/L) = 2/0.2 or 3/0.3. They choose the smallest one, perhaps 1.5/0.1), and the solution was doped with chelates (EDDS and citrate) when it was possible to work at an almost neutral pH, see Miralles-Cuevas et al. [8]. It was verified only for low values of drugs (carbamazepine, flumequine, ibuprofen, ofloxacin, and sulfa-methoxazole) around 15 $\mu\text{g/L}$ and very low values of COD (30–40 mg/L). However, the result of the Fenton reaction, e.g., in the simultaneous presence of complex substances, can be different from the classic Fenton reaction, see Kuznetsova et al. [9], and unlike the classic Fenton reaction, the reaction can also take place at a higher pH, which would be highly favorable. Nevertheless, a more acidic environment would be more favorable even in the presence of chelates and with a heterogeneous Fenton reaction (which is shown by the reduction in $\bullet\text{OH}$ oxidation potential formation at a neutral pH (2.8 V at pH 3 vs. 1.9 V at pH 7) [10]).

Additionally, another disadvantage of this reaction is the necessity to subsequently rid the treated water of Fe ions or complexes. Further disadvantages of the homogeneous Fenton process, such as the formation of a large amount of Fe^{3+} and the limited pH range in the very acidic region, prompted the testing of the Fenton process in a heterogeneous form. Additionally, the application in real wastewater encounters the presence of various chelating substances and phosphates, which can react with Fe ions and, thus, interfere with the generation of oxidative radicals, as already mentioned.

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