The closing of the circle "EMER": one waste catalyzes the treatment of another

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Summary

The category "industrial waste" is a very broad set of wastes, most of them marked by a high degree of hazardousness and impact on the environment.
Iride Acque SB srl, with the aim of promoting a culture of sustainability, has focused on two types:
- Spent batteries, containing, in all versions, metals (particularly Fe, Mn, Zn) that are highly harmful to the environment
- Industrial wastes, particularly those with a high "biorefractory" organic load (non-biodegradable, toxic or microorganism-inhibiting compounds). Their treatment is critical: traditional biological oxidation systems are generally ineffective, while "advanced" chemical-physical systems still involve high profiles of complexity and inefficiency.
Starting from the insight that some metals present in spent batteries are the ones capable of catalyzing the formation of hydroxyl radicals, a highly reactive chemical species at the basis of one of the most effective processes used in the industrial purification field (the "Fenton" process), Iride Acque has developed and patented the "EMER- (Enhanced Magnetic Heterogeneous Reactor) technology."
At the heart of this technology is the innovative catalyst used: a secondary product patented by Iride to help realize the concept of circular economy in industry. Obtained from suitably treated battery waste, and immersed in the reaction bath adhered to high-potential magnetic rods, this material allows the development of advanced oxidation reactions of complex compounds up to 25 percent more efficient than traditional Fenton, with a significant reduction in the amounts of reagents used and by-products generated.
The presentation will feature.
- The results of studies by leading University Institutes, relating to catalyst characterization, releases, operational optimization and process kinetics
- The effectiveness of the technology, tested on a variety of wastewater types, reactor models developed by the Company, and a summary of operational data collected in the field.

Riassunto

La categoria "rifiuti industriali" è un insieme molto ampio di scarti, per la maggior parte contraddistinti da elevato grado di pericolosità ed impatto sull'ambiente.
Iride Acque Società Benefit, con lo scopo di promuovere la cultura della sostenibilità, si è focalizzata su due tipologie:
- Le batterie esauste, contenenti, in tutte le versioni, metalli (in particolare Fe, Mn, Zn) altamente dannosi per l'ambiente
- I reflui industriali, in particolare quelli ad alto tenore di carico organico "biorefrattario" (composti non biodegradabili, tossici o inibenti i microrganismi). Il loro trattamento è critico: i tradi-

zionali sistemi ad ossidazione biologica sono generalmente inefficaci, mentre quelli chimico-fisici "avanzati" comportano profili di complessità ed inefficienza ancora elevati.
Partendo dall'intuizione che alcuni metalli presenti nelle batterie esauste sono quelli in grado di catalizzare la formazione dei radicali ossidrili, specie chimica altamente reattiva alla base di uno dei più efficaci processi utilizzati in campo depurativo industriale (il processo "Fenton"), Iride Acque ha sviluppato e brevettato la "tecnologia EMER- (Enhanced Magnetic Heterogeneous Reactor)". Il cuore di questa tecnologia è l'innovativo catalizzatore impiegato: un prodotto secondario brevettato da Iride per contribuire a realizzare il concetto di economia circolare in ambito industriale. Ottenuto dai rifiuti di batterie opportunamente trattati, ed immerso nel bagno di reazione adeso a barre magnetiche ad alto potenziale, questo materiale permette lo sviluppo di reazioni di ossidazione avanzata dei composti complessi fino al 25% più efficaci del Fenton tradizionale, con una sensibile riduzione delle quantità di reagenti utilizzati e dei sottoprodotti generati.
Nella presentazione saranno illustrati
- I risultati degli studi di primari Istituti Universitari, relativi alla caratterizzazione del catalizzatore, ai rilasci, all'ottimizzazione operativa e alle cinetiche del processo
- L'efficacia della tecnologia, testata su svariate tipologie di reflui, i modelli di reattori sviluppati dalla Società e la sintesi dei dati operativi raccolti sul campo.

1. Introduction

The global concern about industrial wastewaters containing non-biodegradable molecules grows bigger each year: in fact, the presence of those organic pollutants in the generated wastewater, poses serious threat to public health since most of them are toxic, endocrine disrupting, mutagenic or potentially carcinogenic to humans, animals, and aquatic life.
These compounds are known to be high in chemical oxygen demand (COD) and low in biological oxygen demand (BOD): traditional wastewater management methods (biodegradation and/or physico-chemical processes, followed by filtration and adsorption-based separations) are able to treat a majority of anthropogenically-polluted water sources, but no single method described above is efficient enough to produce water with legally- and practically-acceptable levels of refractory toxic chemicals.[1]
Advanced oxidation processes (AOPs) have recently emerged as an important class of technologies for the oxidation and destruction of a wide range of organic pollutants in water and wastewater; these treatment processes, involving the generation of extraordinarily reactive species (hydroxyl radicals) can either eliminate organic pollutants completely through mineralisation or convert them to the products that are less harmful to human health and the aquatic environment. [2]
Hydroxyl radical is the second strongest oxidant preceded by the fluorine, and it reacts 106-1012 times faster than ozone depending on the substrate to be degraded [3] [4], with rate constants usually in the order of 106-109M-1 s-1 [5]
Starting from the insight that some metals present in spent batteries are the ones capable of catalyzing the formation of hydroxyl radicals, Iride Acque has developed and patented the "EMER- (Enhanced Magnetic Heterogeneous Reactor) technology". Core of this technology is the innovative catalyst used: a secondary product patented by Iride to help realize the concept of circular economy in industry.
Obtained from suitably treated battery waste this material allows the development of advanced oxidation reactions of complex compounds up to 25 percent more efficient than traditional Fenton, with a significant reduction in the amounts of reagents used and by-products generated.

2. Report

2.1 Fenton process

One common feature of AOP systems is higher treatment costs. The only exception is Fenton process, where under acidic conditions, a Fe2+/H2O2 mixture produces hydroxide radicals in a very cost-effective manner. [6]

The general mechanism of the Fenton process can be represented as follows:

$$Fe(II)+H_2O_2 \rightarrow Fe(III)+{}^{\bullet}OH+OH^- \quad k = 40\text{–}80\ M^{-1}\ s^{-1} \tag{1}$$

$$Fe(III)+H_2O_2 \rightarrow Fe(II)+HO_2^{\bullet}+H^+ \quad k = 0{\cdot}001\text{–}0{\cdot}01\ M^{-1}\ s^{-1} \tag{2}$$

$$\text{Organic matter}+{}^{\bullet}OH \rightarrow \text{degradation products} \tag{3}$$

Even though the Fenton reaction was initially formulated for Fe(II) and H2O2 many redox-active metals such as Cu, Mn, and Ni also display Fenton-like reactions (Masarwa et al., 1988; Goldstein et al., 1993).

Fenton process has been applied to industrial wastewaters with the result of significant reductions of toxicity, improvement of biodegradability, colour and odour removal. [7]

Several successful applications have been reported in the treatment of diverse wastewaters from olive oil industries [8], textile industries [9], paper pulp factories [10], cork processing facilities [11] and winery industries [12], as well as effluents from refinery and fuel terminals [13], sludge waste [14], landfill leachate [15] ,[16] and contaminated soils [17][18].

The main reasons for the huge popularity and widespread applicability of Fenton oxidation processes are the high efficiency of mineralization (that enables the transformation of organic pollutants into non-toxic CO2), the shortest reaction time among all other AOPs, implementation at ambient pressure and temperature, the use of cheap, moderately reactive, and easy-to-handle reagents (iron and H_2O_2; easy implementation as a stand-alone or hybrid system and also facilitates easy integration in existing water treatment processes. [1] [19] [20]

2.2 Heterogeneous Fenton process

However, two main drawbacks were identified:

- wastage of oxidants due to the radical scavenging effect of hydrogen peroxide as in reaction and its self-decomposition as in reaction

-continuous loss of iron ions and the formation of solid sludge, with several economic and environmental drawbacks.

These limitations can be overcome to some extent by application of heterogeneous catalysts: solid materials where HO• production occurs on the surface, with exposure to substrates occurring after diffusion away from the surface but confined to within the boundary layer near the surface. [21]

Decomposition of aqueous H2O2 over some metals (Ag, Cu, Fe, Mn, Ni, Zn and Pt) and their oxides on supported silica, alumina, and zeolites has been a subject of research since the beginning of the previous century [22]. [23]. [24]

Numerous heterogeneous catalysts have been used in Fenton reactions: iron minerals (relatively less priced and can be separated magnetically from the reaction medium) [25], ferrites, clays, zeolite, alumina, fly ash based catalysts and other types of heterogeneous catalyst. [1]

Generally speaking, solid catalysts must satisfy a number of requirements for the use as Fenton reagents, as having high activity for contaminant removal, presenting no leaching of active cations, pH and temperature stability, and ability to promote a high H2O2 conversion with minimum decomposition. Also they should be reasonably priced. [20]

2.3 EMER – the IRIDE patented catalyst

The innovative catalyst, patented by Iride Acque Società Benefit, is obtained from the waste material of parts of batteries and/or batteries in common use, and has chemical-physical properties that can be used with high yields in advanced chemical oxidation processes.
This catalyst is composed of two main components:
- catalytic component A) consisting of a mixture of one or more of the following compounds: carbon black, lithium-iron phosphate, interstitial derivatives of graphite, oxides and/or hydroxides of iron, zinc, manganese, nickel, lithium;
- a catalytic component B) consisting of a mixture of one or more of the following metals: iron, zinc, manganese, nickel, lithium.

The process to obtain EMER catalyst from spent batteries is covered by international patent and constitutes an industrial secret. (Patent n. 102017000149010, 2017)

2.4 Effectiveness of the catalyst

A first study on the effectiveness of the Fenton process achievable with the use of the catalyst is presented in the patent application [(Brevetto n. 102017000149010, 2017)].
The test was performed on an industrial wastewater with an average COD of about 31,250 mg/l with a high presence of 4-Nitrophenol and trifluoroacetic acid (TFAA).
For comparison, on the same wastewater, a homogeneous “Fenton” treatment was conducted with the use of ferrous sulphate heptahydrate-as a catalyst.
The results are shown in table 1.

	Example 1	Example 2 (comparative)
COD reduction	83%	15%
Removal 4 nitrophenol	96%	35%

Tab. 1 – *Results of the effectiveness of the Fenton process*

From the values shown in the Table 1 you can see the considerable reduction of the COD, in absolute and compared to the classic Fenton.
A subsequent study was conducted by the team of Professor Di Palma of La Sapienza University of Rome. [26] from which it appears that in the oxidation tests with heterogeneous Fenton process, conducted on a reference compound (p-Benzoquinone) known to be recalcitrant to biological oxidation, the EMER catalyst process showed better performance than homogeneous Fenton (removal increase of about 25%), as reported in Fig. 1.

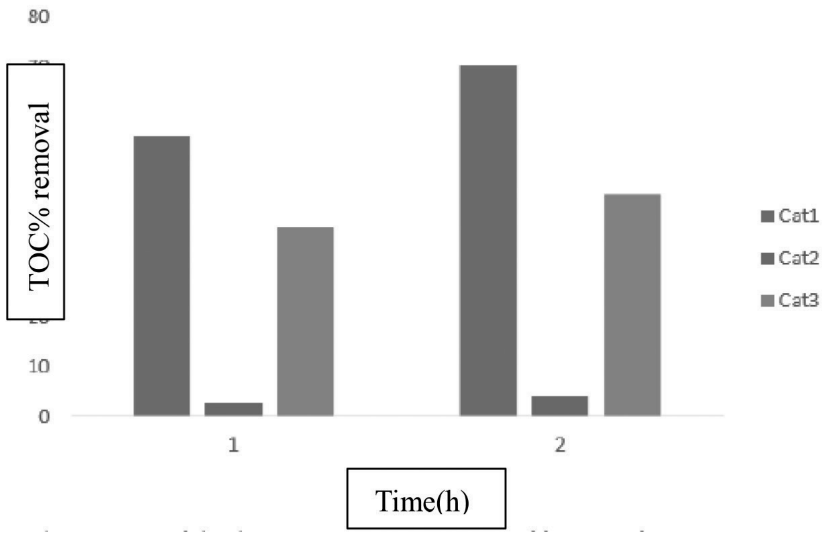

Fig. 1 – *Catalytic oxidation of b-benzoquinone: effect of EMER catalyst (cat1), iron-free catalyst(cat2) and homogeneous Fenton(cat3)*

Finally, Table 2 shows the performance results found during the activity of Iride Acque (in the laboratory and on an industrial scale) on real matrices, not synthetically generated in the laboratory.

	Abatement	Abatement	Abatement
Parameter	Min	Max	Medium
COD	24,7%	97%	69,5%
Non-ionic surfactants	21,2%	96,7%	73,9%
Anionic surfactants	92,4%	99,6%	96,8%
Cationic surfactants	52,9%	99,1%	85,2%
Total surfactants	80,3%	96,9%	89,9%

Tab. 2 – *Performace results of Iride Acque*

Investigations are still underway about the performance of the EMER process for nitrogen and phosphorus removal.

2.5 Release of cations from the catalyst

The verification that the catalyst did not change the composition of the wastewater making it incompatible with the current legislation for waste water was carried out by the University of Parma on a waste from the wine industry..All metals measured are below the limits of the wastewater legislation. Note the absence of harmful toxic metals such as chromium, lead, cadmium, mercury, arsenic and thallium. [27]

Further study was conducted by Prof. Di Palma of the University La Sapienza of Rome concluding that the use of catalyst, especially in the “flakes” configuration, allows not to alter the qualitative characteristics of the wastewater (in particular for the concentration of metals), maintain the effectiveness of the catalyst unchanged and significantly reduce the chemical sludge produced compared to the traditional Fenton process. [26]