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HENRY JOHN HORSTMAN FENTON - SHORT BIOGRAPHY AND BRIEF HISTORY OF FENTON REAGENT DISCOVERY

HENRY JOHN HORSTMAN FENTON - KRÓTKA BIOGRAFIA I HISTORIA ODKRYCIA ODCZYNNIKA FENTONA

Abstract: The short biography of H.J.H. Fenton, an outstanding chemist, and brief history of Fenton reagent discovery were presented. Fenton reagent is defined, as a mixture of hydrogen peroxide and iron(II) ion ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}$). This is one of the most effective oxidizing agents for destroying organic compounds. The extraordinariness of Fenton chemistry results from the fact that it is very common in chemical, biological, and natural environmental systems. Nowadays, Fenton reagent plays a very important role in free radical biology and medicine. A very important role it also plays in natural environmental systems, and environment protection engineering (for example in wastewater treatment and remediation of groundwater). Therefore, it can be assumed, that the Fenton's discovery has played a very important role in all aspects of our life.

Keywords: Fenton's biography, Fenton reaction, Fenton reagent, Fenton chemistry, hydroxyl radical, ferryl ion, advanced oxidation

Abstrakt: W artykule przedstawiono krótką biografię H.J.H. Fentona, wybitnego chemika, a także opisano zwięźle historię odkrycia tzw. odczynnika Fentona, definiowanego jako mieszanina nadtlenu wodoru i soli żelaza(II). Odczynnik Fentona jest jednym z najbardziej efektywnych czynników zdolnych do utleniania i degradacji substancji organicznych. Niezwykłość odczynnika Fentona (oraz reakcji Fentona) wynika z faktu, że powszechnie występuje w systemach chemicznych, biologicznych oraz w środowisku naturalnym. Obecnie odczynnik Fentona odgrywa bardzo ważną rolę w biologii rodnikowej oraz w medycynie. Również bardzo ważną rolę spełnia w środowisku naturalnym oraz inżynierii ochrony środowiska jako czynnik degradujący zanieczyszczenia. Dlatego można stwierdzić, że odkrycie dokonane przez Fentona ma bardzo duże znaczenie we wszystkich aspektach naszego życia.

Słowa kluczowe: biografia Fentona, reakcja Fentona, odczynnik Fentona, chemia Fentona, rodnik hydroksylowy, jon ferrylowy, pogłębione utlenianie

Short biography of H.J.H. Fenton

Henry John Horstman Fenton was born on 18 February 1854 at Ealing, London. He received his earlier education at Magdalen College School, Oxford, and afterwards went to King's College, London, where he studied chemistry under professor C.L. Bloxam, and at the end of his course acted as demonstrator. As joint first holder of a scholarship established by the Clothworkers' Company for noncollegiate students of the physical sciences, he entered the University of Cambridge in 1875. After some 8 month at Cambridge, Fenton gained an entrance scholarship at Christ's College, which he entered in May of 1876. He was then 22 and thus older than the majority of undergraduates. His chemical knowledge and experience were also greatly in advance of those of men of the same university standing. By the time he

took his first-class B.A. in 1877, he was already an assistant demonstrator by Professor G.D. Liveing, who persuaded the University in 1878 to formalize Fenton's position by establishing for him the post of "Additional Demonstrator in Chemistry" [1-3].

Fenton was naturally a shy man, but he had a very independent spirit, and it was therefore perhaps not unnatural that he chafed at the discipline then imposed on members of the University *in statu pupillari* and not infrequently came into conflict with University and College authorities. On the other hand, Fenton's lectures were for many years an outstanding feature in the instruction given in the University Laboratory. They were meticulously prepared, stimulating, devoid of dogma, and usually presented in the form of

a debate. The value of his lectures was greatly enhanced by the informal discussions which he encouraged - at the close of every lecture a number of eager young men would come down to the lecture table and discuss with him, often for half an hour or more, the questions in which he had aroused their interest [4]. Moreover, Fenton was gifted with keen powers of observation and acuteness of interpretation and the whole of his experimental work were marked by its elegance.

Fenton obtained his M.A. in 1881. He married in 1892, Edith, daughter of George Fergusson of Richmond. They left no children. In 1899 Fenton was elected into the Royal Society (FRS), and served on the Council of that body from 1913 until 1916. FRS (*Fellow of the Royal Society*) is an

honour accorded to distinguished scientists and a category of membership of the Royal Society. Fellows are entitled to put the letters FRS after their names. The Certificate of a Candidate for Election [5] (Fig. 1) mentions his most important work with hydrogen peroxide and iron(II):

“Has made the remarkable discovery that hydrogen peroxide, although inactive alone, in presence of an iron salt, at once oxidises tartaric and other similar acids, carbohydrates, &c, giving rise to very characteristic products - a discovery of special importance in connection with plant metabolism, which he has elaborated with particular skill and thoroughness (...).”

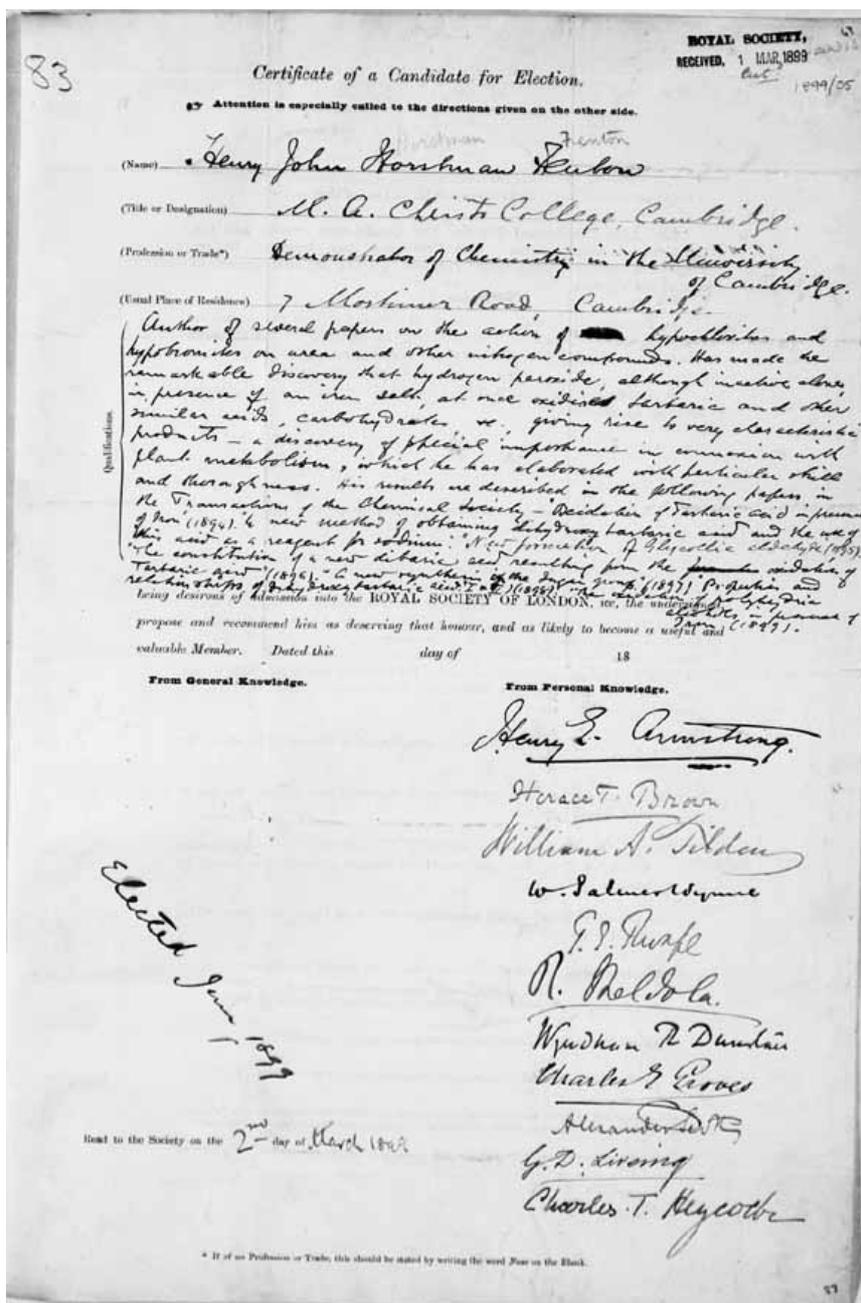


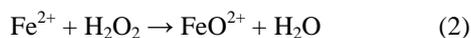
Fig. 1. The Fenton's certificate as a candidate for election to the Royal Society [5]

Fenton was awarded his doctorate (ScD) in 1906. In 1911 he was made an honorary fellow of Christ's College. In 1924 he retired from the University of Cambridge, and after several years of illness he died in a nursing home in London on January 13, 1929, at the age of 74 [2, 3]. More details concern biography and career of H.J.H. Fenton are presented in Obituary Notices [3] and in "Studies of the British Chemical Community: the Principal Institutions, 1881-1972", by Dr. Gerrylynn K. Roberts and Dr. Robin Mackie of the Faculty of Arts, The Open University, UK [6].

What is the Fenton reaction?

In 1894, H.J.H. Fenton published a descriptive study describing how iron(II) ions in the presence of certain oxidizing agents yielded a solution with powerful and extraordinary oxidizing capabilities, and this mixture is typically referred as "Fenton reagent" [7].

Now, in literature, the Fenton reagent (or Fenton reaction) is defined as a mixture of hydrogen peroxide and iron(II) ion ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}$). The process is based on the formation of reactive oxidizing species, able to efficiently degrade the pollutants of the wastewater stream but the nature of these species is still under discussion and its formulation is a subject of controversy in the past and recent Fenton oxidation related literature [8-12]. Two reaction pathways for the first step of Fenton chemistry have been advanced: a radical pathway, which considers an OH radical production (reaction (1)) and a non-radical pathway considering ferryl ion (FeO^{2+} , an oxidizing Fe^{IV} species) production (reaction (2)) [13]:



Although the Fenton reagent has been known for more than a century, its application as an oxidizing process for destroying hazardous organics was not applied until the late 1960s [14, 15]. At present (independently from this controversy) we know that the Fenton reagent is one of the most effective methods of the oxidation of organic pollutants. The efficiency of the Fenton reaction depends mainly on H_2O_2 concentration, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio, pH and reaction time. Also, initial concentration of the pollutant and its character as well as temperature, have a substantial influence on final efficiency.

The main advantage of Fenton reagent is its simplicity: the components are commonly available and there is no need for special equipment like UV lamps, complex reaction vessels, TiO_2 particles, or ozone generators [16]. Because of its simplicity, Fenton reagent has the potential for widespread use in environmental protection technologies. Fenton reagent is an attractive oxidative tool for degradation of contaminants because of iron is very abundant and non-toxic element and hydrogen peroxide is easy to handle and environmentally safe [17].

The Fenton reagent destroys a wide variety of organic compounds without the formation of toxic by-products. Among the different technologies reported in literature for

the treatment of highly contaminated effluents, Fenton's reagent is characterized by its cost-effectiveness, simplicity and suitability to treat aqueous wastes showing a variable composition [18, 19]. This method offers a cost-effective source of highly oxidizing species, using easy-to-handle reagents. The important advantage of the Fenton process is that oxidation and coagulation take place simultaneously. The comprehensive investigations showed that Fenton reagent is effective in treating various industrial wastewater components including aromatic amines [20], a wide variety of dyes [21], pesticides [22], surfactants [23], explosives [24] as well as many other substances. Therefore, the Fenton reagent has been applied to treat a variety of wastes such as those associated with the textile industry, chemical manufactures, refinery and fuel terminals, engine and metal cleaning, etc. [18]. Also, the Fenton reagent can be effectively used for the destruction of toxic wastes and non-biodegradable effluents to render them more suitable for a secondary biological treatment [25].

Fenton reaction existed also in biological systems. The oxidative reactions of the Fenton chemistry show analogies with fundamental processes in biology, which are involved in the etiology of diseases [26]. Some reactive species, which arise in Fenton reaction, such as hydroxyl radical, are possible to damage different biological target molecules such as DNA, proteins, or lipids. Fenton chemistry plays an important role in these reactions [27]. Therefore, its occurrence plays a major role in the aging process and a variety of diseases.

Brief history of Fenton's discovery

Although Fenton's chief interest always seemed to lie in general and physical chemistry, the greater part of his original work was carried out in organic chemistry and his most important investigations centred round dihydroxymaleic acid [4]. He was led to the discovery of this compound in a curious way. The origin of the Fenton reagent appears to be a case of serendipity [1]. A fellow student was mixing reagents at random and obtained a solution with a violet colour that he showed to Fenton. The reagents were hydrogen peroxide, tartaric acid, a Fe(II) salt, and a base. On April 25th, 1876, Fenton (then an undergraduate at Christ's College, Cambridge, England) send a brief letter, titled "On a new reaction of tartaric acid", to the editor of *Chemical News* [28] reporting this experiment. This letter was published 10 days later, on May 5th. The purpose of the letter was to describe a test for tartaric acid [1, 29]. Under the heading of Correspondence, it reads in part:

"I have lately noticed the following reaction, which, besides presenting one or two rather interesting peculiarities, may, as far as I can judge at present, be proposed as a test for tartaric acid. To a very dilute solution of ferrous sulphate or chloride, a small quantity of a solution of tartaric acid or tartrate is added, followed by a few drops of chlorine water or hydric peroxide, and lastly, an excess of caustic potash or soda, when a fine violet colour is obtained (...)"

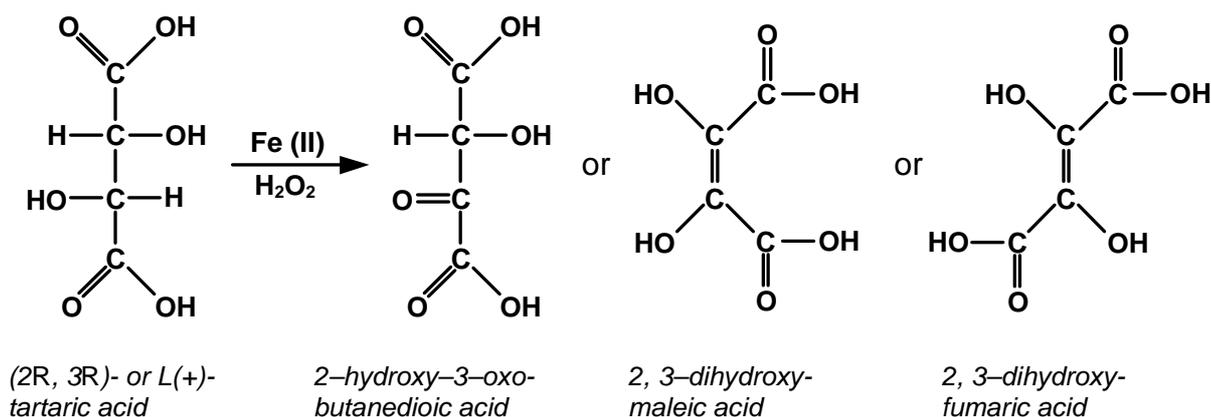


Fig. 2. Three possibilities for the structure of the oxidation product $\text{C}_4\text{H}_4\text{O}_6$ [1, 37]

Now it is known, that the violet colour was indeed formed by dihydroxymaleic acid. In a second letter to the editor of *Chemical News* [30] Fenton identified the colour as arising from a complex between iron and the oxidation product of tartaric acid [2]. Several years later Fenton succeeded in the difficult task of isolating this product, and showed that it was the previously unknown compound, dihydroxymaleic acid [4]. Fenton had established the molecular formula of this acid ($\text{C}_4\text{H}_4\text{O}_6$) by 1894 and deduced the structure (from three possibilities - Fig. 2) two years later [1, 29].

Thus, a new reagent (Fenton reagent) had been discovered. Hydrogen peroxide and a Fe(II) salt damage tartaric acid in a characteristic way, providing a valuable and new oxidizing agent for chemistry. In collaboration with scientists such as H. Jackson, M. Gosling, H.O. Jones, J.H. Ryffiel, and others Fenton went on to show that his oxidizing system could damage almost any organic molecule challenged with it [2].

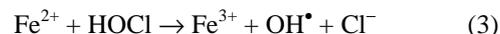
Fenton's first report [28] and his full paper [31] demonstrated three key features of what we now term "Fenton chemistry" [29]:

- (1) the oxidant may be not only hydrogen peroxide (eg chlorine water),
- (2) a reduced form of a heavy metal (in this case iron) is needed, but in low concentration,
- (3) a higher oxidation state of iron may be involved as an intermediate.

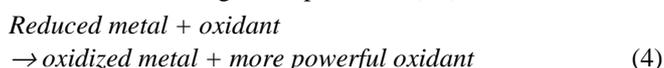
Although, Fenton described the oxidation of tartaric acid by iron(II) and hydrogen peroxide or chloric(I) (hypochlorous) acid, and found that iron acts catalytically (as a very small quantity of iron was required to bring about the reaction) [32] as well as determined the reaction product (dihydroxymaleic acid), he did not investigate the mechanism of the reaction that was later named after him; he used it as a synthetic tool to modify organic compounds [1, 33].

The term "Fenton reagent" [34] is often used to describe iron(II)/hydrogen peroxide system, and as this is the commonest choice of the metal/oxidant couple studied by Fenton, it seems a valid description. However, it is essential

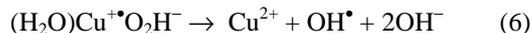
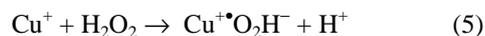
not to neglect the importance of other metals and oxidants, which participate in analogous reactions [29, 34]. Fenton himself, in his report [28], noted the use of chlorine water as an alternative to hydrogen peroxide. Chlorine water is a solution of chloric(I) (hypochlorous) acid (HOCl)/hypochlorite (OCl^-), depending on pH since $\text{p}K = 7.6$ [29]. The chloric(I) acid (as equivalent of H_2O_2 in classical Fenton reaction; equation (5)), is another potential source of hydroxyl radicals or similar powerful oxidant (reaction (3)):



The Fenton reaction can also involve several alternative reduced transition metals (such as Cu^+ , Cr^{3+} , Co^{2+} , V^{2+} , Ti^{3+} and Ni^{2+}), which catalyse similar reactions, and other oxidants as substitutes for hydrogen peroxide (eg CaO_2 [35]). It can be written in general pattern as [29]:



As an example, the reactions of Cu(I) with H_2O_2 , are presented below. The reaction of the copper(I) ion and hydrogen peroxide (reaction (5)) results in the formation of a copper complex, $(\text{H}_2\text{O})_m \text{Cu}^+\text{O}_2\text{H}^-$ that may react with organics present in solution. In acidic solution and in the absence of organics, the copper complex decomposes into free copper(I) ion and hydroxyl radical (reaction (6)) [36]:



Summary

The short biography of H.J.H. Fenton, a researcher who has demonstrated outstanding achievement in field of chemistry was presented. The brief history of Fenton reagent discovery was also described, because these data are very rarely published and contain little-known facts.

It can be assumed (after Koppenol) that if we look back at the history of the Fenton reaction, we see that it was first used as an analytical tool to detect tartaric acid, then it became a preparative tool to synthesize hydroxylated organic

compounds. Nowadays, this reaction plays a very important role in free radical biology and medicine [1]. A very important role Fenton reaction also plays in natural environmental systems, and environment protection engineering.

The extraordinariness of Fenton reagent (Fenton reaction and Fenton chemistry) results from the fact that it is very common in chemical, biological, and environmental systems. It is also a paradox that on the one hand Fenton reaction is successfully used in environment protection (for example in wastewater treatment and remediation of groundwater), and on the other hand, it is thought to be a factor, which causes damage to biomolecules (eg proteins, lipids, and DNA) and plays a major role in the aging process and a variety of diseases.

Therefore, it can be stated, that the Fenton's discovery has played a very important role in all aspects of our life.

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