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Essay

Trends in Research on Electrochemical Oxidation

Hongna Li,[a,*] Zhiwei Shi,[b] and Changxiong Zhu[a,*]

[a]*Agricultural Clear Watershed Group, Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences, Beijing, 100081, China*
[b]*Beijing China Sciences GUOYI Environmental Protection Co., Ltd, Beijing 100080, China*

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Abstract. This paper presented a detailed chronological survey of scientific output related to electrochemical oxidation in SCI categories of "environmental sciences, environmental engineering and water resources" from 1975 to 2012. Publications were analyzed by distribution of the number of publications and times cited, source categories, source journals, author keywords, *KeyWords Plus*, and the most cited publications in these years. It was concluded that Pt, boron-doped diamond, TiO_2 were currently and would continue to be the predominant focused electrode materials at least over the next decade. And the foci of studied pollutants in the electrochemical oxidation were mainly concentrated in dyes and phenols popularly existing in the practical wastewaters. What's more, electrochemical degradation, wastewater treatment, electrochemical determination and fuel cell would be the key research topics currently and recently. Fenton, photocatalysis and coagulation were the most-frequent combination technology with electrochemical oxidation based on the bibliometric results. Contribution of Croatian chemists to the field is mentioned.

Keywords: electrochemical oxidation, bibliometric, research trends, electrode materials

INTRODUCTION

Electrochemical oxidation is one of the popular advanced oxidation processes (AOPs) in recent research.[1–4] It offers advantages including the environmental compatibility, versatility, energy efficiency and amenability to automation.[5,6] Electrochemical oxidation of organic compounds in aqueous solutions is an anodic process occurring in the potential region to produce oxygen from discharge of water. And the first step in the oxygen evolution is the anodic discharge of water to produce hydroxyl radicals (•OH), the powerful oxidizing agents.[5,6]

By means of electrochemical oxidation, pollutants can be completely mineralized by the hydroxyl radicals and other active substances generated in the electrolysis system.[7] With the electron transferred in the electrochemical cell, toxic substances would be transformed and polluted water would be purified. Furthermore, gas chromatography-mass spectrometry analysis indicated that this technique could be employed to eliminate biorefractory and toxic compounds such as azo dyes, phthalates, bisphenol-A, phenanthrene, indole, quinoline and pyrimidine in wastewater.[1,5] As a result, electrochemical oxidation related-research had attracted more and more attention in many fields, such as wastewater treatment, drinking water purification, disinfection, electrochemical determination and so on.[3,8–11] The limiting factor in implementing electrochemical technology for the effective degradation of organic pollutant is often the electrode material. Electrodes with higher oxygen evolution potential owned much stronger oxidation ability.[12–14] Besides, aqueous conditions and pollutant parameters were also included in the affecting factors in an electrochemical oxidation system.[3,7]

Despite the high increase of the publication amount related to electrochemical oxidation, there have been few reports aiming at gathering and analysis of the systematic data on the global scientific research in this field. Bibliometric method is a common research tool to analyze the trends and assess the patterns in a certain field. The Science Citation Index Expanded (SCI-EXPANDED) from Web of Science databases is the most important and frequently used source for a wide and thorough review of scientific achievement in all research scopes.[15,16]

In this paper, a traditional bibliometric method (analysis of the number of publications and times cited, subject categories, and the most-cited papers) was used to describe the latest advances in scientific research

* Authors to whom correspondence should be addressed. (lihongna@gmail.com; zhucx120@163.com)

related to electrochemical oxidation in SCI categories of "environmental sciences, environmental engineering and water resources". Besides, an innovative method – word cluster analysis of selected topics in the combination of paper titles, author keywords, *KeyWords Plus*, and abstracts[16] – was applied to evaluate the global research trends during the period 1993−2012. Results and discussions can help researchers to realize the distribution of electrochemical oxidation related-research and to clarify future research directions.

METHODOLOGY

The methodology used in this paper was similar to other bibliometric research. The data were based on the online version of the database SCI-EXPANDED. The 2012 edition of Web of Knowledge's Journal Citation Reports indexed 8471 major journals in 176 categories with citation references across the scientific disciplines. Of these, the 281 journals in the field of "environmental sciences", "engineering, environmental" or "water resources", were analyzed in this study. Since there is a limitation that most abstracts before 1991 are not included in SCI-EXPANDED,[15] "electrochemical oxid* or electrooxid* or electro-chemical oxid* or electro-oxid*" was used as the keywords to search titles, abstracts, and keywords from 1993 to 2012 only. And the categories were limited in "environmental sciences", "engineering, environment" and "water resources". The citations related to "electrochemical oxidation", "electrochemical oxidative", "electrooxidation", "electrooxidative", "electro-chemical oxidation", "electro-chemical oxidative", "electro-oxidation", and "electro-oxidative" in the three categories related to environment and water resources, were downloaded. In total, 2017 publications met the selection criteria and were used for further analysis. Downloaded publications included names of authors, contact addresses, titles, years of publication, author keywords, *KeyWords Plus*, abstracts, Web of Science categories, and journals names. Then analysis was carried out based on this information.

Author keywords and *KeyWords Plus* were used to analyze the overall variations of research trends comprehensively and precisely. All keywords (1993−2012), both those reported by authors and those attributed by SCI-EXPANDED, were identified and separated into 4 five-year spans (1993−1997, 1998−2002, 2003−2007, 2008−2012), and then their ranks and frequencies were calculated. Different words with an identical meaning and misspelled keywords were grouped and considered as a single keyword. For example, the word "electrochemical oxidation*" represented "electrochemical oxidation", "electrochemical-oxidation", "electrooxidation", "electrochemical oxidation process" and "electrochemical advanced oxidation process"; the word "boron-doped diamond*" represented "boron-doped diamond electrode(s)", "BDD electrode(s)", "BDD anode(s)", "boron-doped diamond (BDD)", and "BDD". A word cluster analysis combination of the words in titles, author keywords, *KeyWords Plus*, and words in abstracts was used in the analysis.[15,17]

RESULTS AND DISCUSSION

Characteristics of Publication Outputs

Research related to electrochemical oxidation increased rapidly over the last few decades in the categories of "environmental sciences", "engineering, environment" and "water resources" (Figure 1), from one publication in 1975 to 321 publications in 2012 with "electrochemical oxid* or electrooxid* or electro-chemical oxid* or electro-oxid*" as the search key-words in topics. There is a need to explain that the statistical result might have some imperfection, considering the limitation that most abstracts before 1991 are not included in SCI-EXPANDED.[15] However, the analysis of author keywords, *KeyWords* Plus and research trends were not affected by this limitation, due to the used data were in the scope of 1993 to 2012. The only one paper published by Fiegna in 1975 illustrated some interesting findings in the electrochemical study of titanium-oxide electrolyte system and put forward the possibility that TiO_2 might be used as the electrode to improve the characteristics of the electrochemical oxidation system.[18] An obvious increase of annual research papers appeared since 1991 based on the current used methodology. The number of times cited per publication showed five peaks in 1993, 1995, 2000, 2003 and 2005 with 152 for Loft *et al.*,[19] 230 for Powell *et al.*,[20] 238 for Brillas *et al.*,[21] 288 for Zhou *et al.*[22] and 235 for Quan *et al.*[23] Loft *et al.* investigated the analysis methods of 8-hydroxydeoxyguanosine with electrochemical detection as a urinary biomarker of oxidative DNA damage and offered a valuable tool for testing risk cancer or other degenerative diseases in humans.[19] Brillas *et al.* investigated the treatment of 2,4-dichlorophenoxyacetic acid (2,4-D) by both electro-Fenton and photoelectro-Fenton processes and a notable mineralization efficiency was attributed to the large production of oxidizing hydroxyl radicals by the reaction between electrogenerated H_2O_2 and Fe^{2+} added to the solution.[21] Zhou *et al.* had carried out research on several Pt-based anode catalysts supported on carbon for direct ethanol fuel cells.[22] Quan *et al.* prepared titanium oxide nanotubes and investigated their potentials in the degradation of pentachlorophenol as electrodes.[23]

Of the 281 journals covering the three studied categories, 116 different journals published articles relating to electrochemical oxidation during 1975−2012 ac-

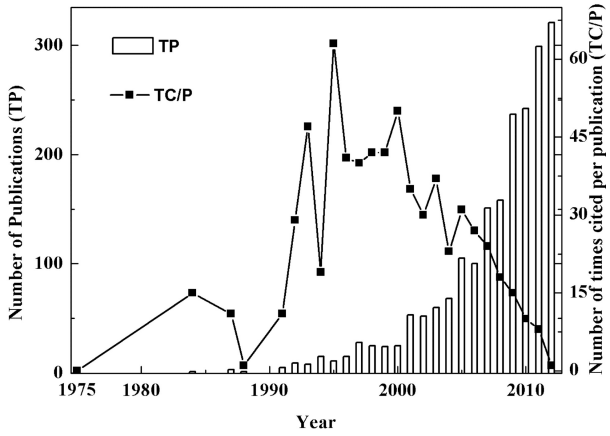

Figure 1. SCI-EXPANDED journal publications with electrochemical oxidation in topics and the number of times cited per publication during 1975−2012.

cording to the analysis results. Among these, 42 journals (36.2 %) contained only one article, and 7 journals (6.0 %) contained more than 100 articles. In this particular research field, *Journal of Hazardous Materials* published the most articles (279, 13.8 %). *Applied Catalysis B-Environmental* ranked second with 214 (10.6 %), and *Environmental Science & Technology* (170, 8.4 %) and *Energy & Environmental Science* (155, 7.7 %) ranked third and fourth, respectively. *Chemical Engineering Journal* (152, 7.5 %), *Water Research* (142, 7.0 %) and *Chemosphere* (114, 5.7 %) were close on its heels.

During 1975−2012, Brillas Enric from University of Barcelona (Spain) published the most papers (43, 2.1 %) in the studied fields. Rodrigo Manuel A. from University of Castilla La Mancha (Spain) ranked second with 25 (1.2 %). Oturan Mehmet A. from University of Paris Est (France) (24, 1.2 %) was in the third place, followed by Arias Conchita (23, 1.1 %) from University of Barcelona (Spain). Canizares Pablo (22, 1.1 %) from University of Castilla La Mancha (Spain) was in the fifth position. There were 4082 authors, who only published one paper related to electrochemical oxidation in the period, taking a ratio of 48.4 % in the all authors. A bias in analysis of authorship might occur when different authors had the same name or one author used different names (*e.g.*, maiden names) in their articles.[24]

Distribution of Author Keywords Analysis

Analysis of author keywords provides information about research trends as concerned by researchers. In 1997 publications from 1993 to 2012, 1570 (78.6 %) had author keywords. Author keywords were counted and ranked in four 5-year periods (Table 1); they included "boron-doped diamond*", "electro-fenton*", "decolorization*", "wastewater treatment", "electro-coagulation", "hydroxyl radical*" and "phenol*". Words with "*" included their single and plural forms.

"Boron-doped diamond" didn't appear in the first two 5-year period, and corresponded research to electrochemical oxidation with this kind of electrode material had attracted more and more attention these years (#2, 10.0 % during 2008−2012). They showed extremely wide potential window, corrosion stability, and possessed technologically important characteristics such as an inert surface, high O_2-overpotential, and strong oxidation capacity.[6,7,20] As a result, they had greater advantages in electrochemical oxidation experiments compared with other electrodes.[5] It had already been proved by research on phenolic compounds mineralization, endocrine disruptors degradation, color removal of dyes wastewater, disinfection of drinking water and so on. [2,5,7] Hydroxyl radical had a high redox potential (E_0 = 2.7 V) and was a main component in electrochemical chloride-free oxidation. The rank and percentage of publications went up to #6 (4.6 %) during 2008−2012. Cong *et al.* proved the existence of •OH in the electrochemical chloride-free system.[25] Jeong *et al.* determined different kinds of reactive oxygen species produced in 0.2 M KH_2PO_4 and pointed out that •OH played a major role in microorganism inactivation and organic degradation.[12] What's more, the role of electrode material on the generation of oxidants was determined with BDD, Ti/RuO_2, Ti/IrO_2, Ti/Pt-IrO_2, and Pt as anode materials in KH_2PO_4 electrolyte and BDD produced the most amount of •OH.[12]

Electro-fenton, electro-coagulation, and photocatalysis were typical technology conducted meantime in electrochemical oxidation system. These combined technologies could bring about much more outstanding treatment efficiency.[1,2,5,6] As a result, their rank and percentage of publications went up from N/A, #20 (2.0 %), N/A during 1993−1997 to #3 (7.2 %), #5 (5.1 %) and #24 (1.9 %) during 2008−2012, respectively. The analysis of author keywords demonstrated that the most common pollutants treated by electrochemical oxidation were "phenol*" and "dye*". Other research topics can be identified from Table 1, such as "fenton", "photocatalysis" and "cyclic voltammetry*". Thereinto cyclic voltammetry could be used to investigate the adsorption phases and reduction mechanisms in the electrochemical cell.[11,26]

Distribution of *KeyWords Plus* Analysis

In the SCI-EXPANDED database, *KeyWords Plus* offers additional search terms extracted from the titles of articles cited by authors in their bibliographies and footnotes, and as a result title-word and author-keyword indexing can be substantially augmented.[27] In 1997 publications from 1993 to 2012, 1936 (97.0 %) had *KeyWords Plus*. Other than the search keywords, the top

Table 1. Top 30 most frequent author keywords used during 1993−2012 in four 5-year periods

	TP	93−12R(%)	93−97R(%)	98−02R(%)	03−07R(%)	08−12R(%)
electrochemical oxidation*	296	1(19)	1(16)	1(13)	1(16)	1(17)
boron-doped diamond*	115	2(7.3)	N/A	N/A	9(3.9)	2(10)
electro-fenton*	92	3(5.9)	N/A	7(4.8)	5(6)	3(7.2)
decolorization*	89	4(5.7)	20(2)	15(3.2)	4(6.3)	4(5.8)
wastewater treatment	80	5(5.1)	7(4.1)	5(7.1)	2(7.9)	7(3.8)
electrolysis	65	6(4.1)	5(6.1)	3(7.9)	3(6.5)	15(2.7)
electrocoagulation	64	7(4.1)	20(2)	N/A	17(2.9)	5(5.1)
hydroxyl radical*	64	7(4.1)	7(4.1)	20(2.4)	7(4.2)	6(4.6)
phenol*	59	9(3.8)	3(8.2)	20(2.4)	12(3.4)	7(3.8)
electrochemical treatment	56	10(3.6)	3(8.2)	7(4.8)	6(5.2)	16(2.6)
wastewater	54	11(3.4)	N/A	2(8.7)	11(3.7)	14(2.9)
anodic oxidation	51	12(3.2)	N/A	6(6.3)	24(2.1)	10(3.5)
electrochemical degradation	47	13(3)	N/A	78(0.79)	24(2.1)	9(3.8)
platinum*	47	13(3)	2(12)	7(4.8)	12(3.4)	20(2.1)
oxidation	45	15(2.9)	5(6.1)	3(7.9)	14(3.1)	22(2)
fuel cell*	44	16(2.8)	7(4.1)	78(0.79)	22(2.6)	11(3.1)
advanced oxidation process*	43	17(2.7)	20(2)	78(0.79)	17(2.9)	13(3)
water treatment	42	18(2.7)	N/A	20(2.4)	9(3.9)	18(2.4)
fenton*	41	19(2.6)	N/A	11(4)	17(2.9)	11(3.1)
degradation	37	20(2.4)	N/A	N/A	7(4.2)	20(2.1)
mineralization	35	21(2.2)	N/A	34(1.6)	24(2.1)	17(2.5)
electrocatalysis	33	22(2.1)	N/A	20(2.4)	29(1.6)	18(2.4)
COD	31	23(2)	20(2)	N/A	14(3.1)	25(1.8)
COD removal	31	23(2)	20(2)	15(3.2)	24(2.1)	25(1.8)
electrochemical	31	23(2)	20(2)	34(1.6)	17(2.9)	28(1.7)
dye*	31	23(2)	N/A	20(2.4)	14(3.1)	25(1.8)
electrochemistry	28	27(1.8)	7(4.1)	7(4.8)	38(1.3)	30(1.5)
photocatalysis	27	28(1.7)	N/A	15(3.2)	46(1)	24(1.9)
TiO_2*	27	28(1.7)	20(2)	34(1.6)	17(2.9)	22(2)
cyclic voltammetry*	25	30(1.6)	20(2)	78(0.79)	29(1.6)	28(1.7)

TP, total number of publications; R (%), rank and percentage of author keywords in total publications. Words with "*" included their single and plural forms.

five most frequent *Keywords Plus* were "degradation", "wastewater*", "waste-water treatment", "electrode*", and "removal". Words with "*" included their single and plural forms. Other research topics can be identified from Table 2.

"Wastewater", "organic pollutants", "decolorization*" and "advanced oxidation process*" didn't appear in the first 5-year period and their rank and percentage of publications reached #3 (17.6 %), #13 (6.9 %), #16 (5.8 %) and #18 (5.3 %) during 2008−2012, respectively. This indicated that the organic pollutants in the wastewaters had gradually become the hot target of electrochemical oxidation, especially dye pollutants. Besides, "phenol*", "hydrogen peroxide*", "adsorption", "nanoparticles" and "dye*" were also contained as the most frequently used *KeyWords Plus* as shown in

Table 2. Top 30 most frequently used *Keywords Plus* during 1993−2012 in four 5-year periods

	TP	93−12R(%)	93−97R(%)	98−02R(%)	03−07R(%)	08−12R(%)
oxidation	451	1(23.3)	1(23)	1(23)	1(27.5)	1(21.8)
degradation	325	2(16.8)	7(4.9)	2(13.3)	2(18.4)	4(17.2)
electrochemical oxidation*	313	3(16.2)	18(3.3)	13(6.1)	5(13.7)	2(19.1)
wastewater*	286	4(14.8)	N/A	13(6.1)	8(11.9)	3(17.6)
waste-water treatment	268	5(13.8)	7(4.9)	2(13.3)	3(15)	6(13.9)
electrode*	261	6(13.5)	2(13.1)	7(10.3)	4(14.3)	7(13.6)
removal	258	7(13.3)	5(6.6)	7(10.3)	8(11.9)	5(14.6)
anodic-oxidation	201	8(10.4)	7(4.9)	2(13.3)	7(12.1)	9(9.6)
phenol*	181	9(9.3)	3(11.5)	6(12.1)	6(13.4)	11(7.4)
aqueous-solution*	176	10(9.1)	N/A	20(3.6)	11(9.3)	8(10.2)
hydrogen-peroxide*	160	11(8.3)	18(3.3)	7(10.3)	10(10.2)	10(7.5)
water	147	12(7.6)	7(4.9)	5(12.7)	12(8.7)	15(6.6)
organic pollutants	128	13(6.6)	N/A	53(1.8)	13(8.5)	13(6.9)
acid	113	14(5.8)	5(6.6)	148(0.6)	18(5.2)	14(6.7)
performance	109	15(5.6)	N/A	36(2.4)	27(3.5)	12(7.1)
decolorization*	108	16(5.6)	N/A	36(2.4)	15(6.1)	16(5.8)
reduction	97	17(5)	18(3.3)	12(7.3)	24(3.9)	19(5.2)
adsorption	88	18(4.5)	7(4.9)	11(8.5)	30(3.3)	21(4.5)
kinetics	88	18(4.5)	34(1.6)	15(5.5)	14(6.3)	28(3.9)
platinum*	87	20(4.5)	7(4.9)	28(3)	18(5.2)	23(4.4)
TiO_2*	86	21(4.4)	7(4.9)	16(4.8)	18(5.2)	24(4.2)
advanced oxidation process*	77	22(4)	N/A	77(1.2)	55(2)	18(5.3)
mineralization	75	23(3.9)	N/A	53(1.8)	22(4.3)	25(4.2)
photocatalytic degradation	75	23(3.9)	N/A	28(3)	17(5.4)	32(3.6)
effluents	75	23(3.9)	N/A	53(1.8)	21(4.6)	26(4.1)
boron-doped diamond*	74	26(3.8)	N/A	N/A	N/A	16(5.8)
fenton*	74	26(3.8)	N/A	18(4.2)	24(3.9)	31(3.8)
nanoparticles	70	28(3.6)	N/A	N/A	47(2.2)	20(4.8)
reactor	70	28(3.6)	N/A	53(1.8)	16(5.6)	33(3.5)
dye*	68	30(3.5)	N/A	N/A	23(4.1)	29(3.8)

TP, total number of publications; R (%), rank and percentage of *Keywords Plus* in total publications. Words with "*" included their single and plural forms.

Table 2. Phenolic organics and dyes commonly existed in industrial wastewaters.[28] Most of them were toxic and recalcitrant to biodegradation, causing decay in the efficiency of biological plants currently used for the treatment of wastewaters containing such coumponds. As a result, electrochemical oxidation, with strong oxidizing ability, was carried out. Hydrogen peroxide (#10, 7.5 % in the period of 2008−2012) is a strong oxidant generated on the cathode fed with O_2. Organic pollutants can be oxidized by H_2O_2 directly or by the hydroxyl radicals produced from the electronic transfer reaction of H_2O_2.[29] Electrosorption technique, was popularly studied during the desalination process. It had many advantages such as low energy intensive, relatively inexpensive process, simple to regenerate and low fouling of electrodes.[30,31] Nanostructure-related research

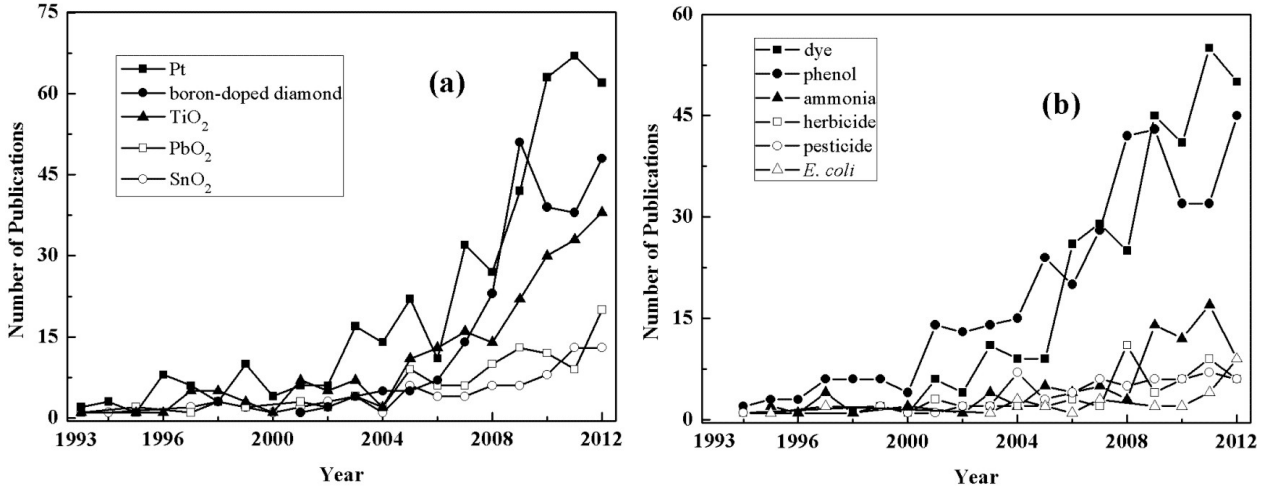

Figure 2. Comparison of the trends of (a) electrodes (b) pollutants during 1993−2012.

didn't appear until the third period 2002−2007 and the publication number kept increasing these days (#20, 4.8 %). Nano-materials were widely used to fabricate new and excellent electrodes for different purposes. Carbon, alpha-MnO_2, ultra-thin V_2O_5 and ultrafine SnO_x particles were all recently used to fabricate the nano-materials and related research were underway in this area.[9] What's more, "Pt*" "TiO_2" and "BDD" were common electrode materials in the studied categories (Table 2). "BDD" appeared since the third 5-year stage and obtained high interests from that time on (#16, 5.8 % in the period of 2008−2012).

Hot Issues

Hot issues were analyzed through the combination of paper titles, author keywords, *KeyWords Plus*, and abstracts. Synonymic single words and congeneric phrases were summed and grouped into categories, in order to depict the development history of the research and, more importantly, to explore new directions and new magnets in the scientific research. The words listed in Figures 2 and 3 all included their plural forms, abbreviations, and other transformations, as well as words with similar meanings.

The analysis described above suggested that Pt, boron-doped diamond, iron, TiO_2, activated carbon, PbO_2 and SnO_2 were the electrode materials of highest concern in the studied fields (Figure 2a). The important position of the anode material was obvious in an anodic oxidation process. Pt, BDD, PbO_2, TiO_2, and SnO_2 had been the objects of recent investigations, due to the reason that they had shown better characteristics in the electrochemical oxidation system.[22,29,32] High activity and stability of Pt made it a suitable electrode material and electrocatalyst for electro-oxidation. The top cited publication related to Pt electrode was in 2009. It reviewed the electrochemical decontamination of dyes wastewaters and indicated that Pt led to high decolorization efficiency.[2,29] As an electrocatalyst, the most cited publication related to Pt was about the synthesis of Pt based anode catalysts for direct ethanol fuel cells in 2003.[22] Boron-doped diamond was presently the subject of considerable interests as an electrode material. The first paper related to boron-doped diamond in the studied categories of environment and water resources was published in 2001. In this paper, boron-doped diamond was compared with $Ti/SnO_2/PbO_2$ in para-chlorophenol degradation and a new parameter not influenced by mass-transfer limitation was introduced.[32] After the review by Panizza and Cerisola[6] about the application of boron-doped diamond electrodes in 2005, BDD began to attract more and more attention. PbO_2, TiO_2, SnO_2 were all dimensional stable anodes (DSA) -type electrode materials, showing high surface area, with excellent mechanical and chemical resistance even at high current density and in strongly acid media. PbO_2 and SnO_2 were both of high O_2-overvoltage and their excellent performances had already been confirmed, especially in the study of phenol and reactive dyes.[2,6] TiO_2 could be doped with different metal oxides to fabricate different electrodes. For example, Mohan *et al.* evidenced that Ti coated anodes yielded a more rapid COD decay in the sequence Ti/TiO_2-RuO_2-PbO_2 < Ti/TiO_2-SnO_2 < Ti/TiO_2-RuO_2 for acid Brown 14 mineralization.[2,33] Besides, TiO_2 could also be used as a photocatalyst to improve the electrochemical characteristic of certain material.[34]

Dyes were important pollutants of highest concern (Figure 2b). The amount of synthetic organic dyes was increasing rapidly with a production over 7×10^5 tons worldwide in 2008, extensively used in the textile in-

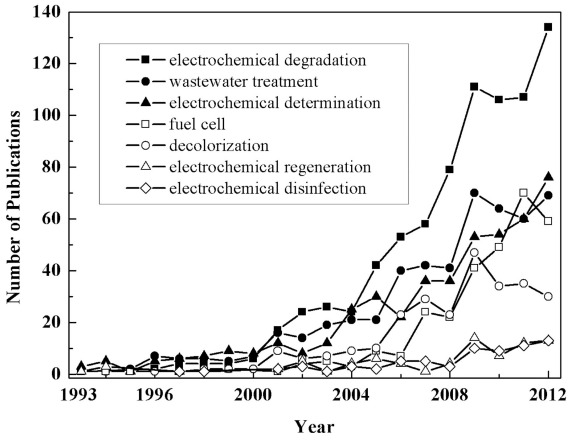

Figure 3. Comparison of the trends of research topics during 1993−2012.

dustry, leather tanning industry, paper production, food technology and agricultural research.[2] Their release caused both environmental pollution and great public concern, so effective methods were underway to treat these substances.[35] The top cited paper related to dyes was published in 2009 and a general review of efficient electrochemical technologies to treat dyeing effluents was concretely presented.[3] Phenolic compounds were common in pesticides, dyes, pharmaceuticals and petrochemical industries.[36] Most of these compounds were known by their high toxicity level and their persistence, and thus their recovery or elimination was required prior to discharge or reuse. Moreover, ammonia, herbicide, pesticide, *E. coli* were also important pollutants commonly studied with electrochemical oxidation processes. High levels of NH_4^+-N removal (95.0 %) was achieved along with moderate mineralization (60.0−80.0 %) with Ti/RuO_2-IrO_2 electrodes as anodes in the advanced treatment of biologically pretreated coking wastewater.[1] BDD showed high current efficiency and low energy consumption in ammonia removal, attributed to its high oxygen evolution overvoltage and low chloride evolution overvoltage (1.5V vs. SCE).[37] Exposures to herbicides/pesticides were associated with an increased Parkinson's disease risk in a dose-response relationship in the univariate analysis.[38] Unfortunately, these substances were relatively stable in the natural environment and couldn't be degraded effectively by microbial or ordinary chemical processes. The top cited publication in this field was reported in 1999 and it put forward the degradation mechanism of 2,4-D with electro-Fenton and photoelectro-Fenton processes.[21] Besides, publications related to *E. coli* kept increasing these years, indicating an increasing and urgent demand for a safe and sanitary environment and water.[7]

Based on our keyword analysis, the hottest research topics were electrochemical degradation, wastewater treatment, electrochemical determination, fuel cell, decolorization, electrochemical regeneration and disinfection (Figure 3). The topic of "electrochemical degradation" had a distinctly higher incidence, being mentioned in 802 papers at a rate of over 134 papers in 2012. More attention was paid to the research on "electrochemical degradation" during all the period, due to a serious situation of water pollution and the corresponding countermeasures of "wastewater treatment". It was known that the conventional biochemical oxidative treatment of wastewaters often produced final effluent still exceeding standards, attributed to ineffective treatment of recalcitrant organic compounds.[14,39] Electrochemical oxidation, as one of advanced oxidation processes, could lead to a significant decrease in organic load and color and was thus a hot practice point. Electrochemical determination was attracting more and more interests based on the analysis results, due to the special sensitivity and convenience of this method. It had already been popularly investigated in the detection of surface-active substances, biomembrane interactions, dopamine, berberine and so on.[8,10,40] Božena Ćosović *et al.* even pointed out that electrochemical techniques offered the possibility of direct investigation of adsorption characteristics of complex natural organic matters at the electrode-electrolyte interface.[4] And surface active substances could also be analyzed by nondestructive electrochemical methods.[10] Moreover, electrochemical regeneration of adsorbents had constituted an excellent alternative way these years. A novel electrofenton-based method was used to promote the regeneration of granular activated carbon previously adsorbed with toluene and efficient cleaning and regeneration was approached.[41] Compared with indirect oxidation, electrochemical regeneration of phenol in the graphite adsorbents revealed that although there were some similarities, much lower concentrations of breakdown products could be achieved.[42] Fuel cells converted chemical energy directly into electrical energy with high efficiency. One great appeal of fuel cells was that they generated electricity with very little pollution – much of the hydrogen and oxygen used in generating electricity ultimately combined to form a harmless byproduct, namely water.[43] The top cited publication related to fuel cells was in 2003 and developed a novel catalyst for direct ethanol fuel cells.[22] Electrochemical process was showing great potential in disinfection treatment for both drinking water and wastewater. As public demand for safe and standard water was increasing, the disinfection process was to be conducted by technologies with stronger oxidizing ability and less harmful disinfection byproducts.[9,14]

Most-cited Publications

The impact of a paper can be traced and evaluated by the yearly variations in the number of citations.[15,24]

Table 3. Top 10 most frequently cited publications during 1927−2012

	TC-2012	Year	C/Y	Title/Journal	Country
1	288	2003	29	Pt based anode catalysts for direct ethanol fuel cells / Applied Catalysis B-Environmental	China, Greece
2	262	2009	66	Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review / Applied Catalysis B-Environmental	Italy, Spain
3	238	2000	18	Mineralization of 2,4-D by advanced electrochemical oxidation processes / Water Research	Spain
4	235	2005	29	Preparation of titania nanotubes and their environmental applications as electrode / Environmental Science & Technology	China
5	231	1998	15	Immobilisation of TiO_2 powder for the treatment of polluted water / Applied Catalysis B-Environmental	Ireland
6	230	1995	13	Coupled iron corrosion and chromate reduction – mechanisms for subsurface remediation / Environmental Science & Technology	USA
7	223	2004	25	Fundamentals, present and future perspectives of electrocoagulation / Journal of Hazardous Materials	USA, Bangladesh, Mexico
8	220	2005	28	Electrochemically assisted microbial production of hydrogen from acetate / Environmental Science & Technology	USA
9	210	1998	14	Aniline mineralization by AOP's: anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes / Applied Catalysis B-Environmental	Spain
10	199	2003	20	Synergism between rutile and anatase TiO_2 particles in photocatalytic oxidation of naphthalene / Applied Catalysis A-General	Japan

TC-2012: total citations of articles from publication to 2012; C/Y: number of citations/year.

Table 3 showed the top 10 most frequently cited publications related to electrochemical oxidation through 2012, in the categories of "environmental sciences", "engineering, environmental" and "water resources". Four were published in *Applied Catalysis B-Environmental* (impact factor, IF= 5.825 in 2012), and three were published in *Environmental Science & Technology* (impact factor, IF= 5.257 in 2012), and the other three were published in *Water Research* (IF=4.655 in 2012), *Journal of Hazardous Materials* (IF= 3.925 in 2012), and *Applied Catalysis A-General* (IF=3.41 in 2012), respectively. The top cited publication was "Pt based anode catalysts for direct ethanol fuel cells" published in *Applied Catalysis B-Environmental* and was cited 288 times through 2012.[22] This paper demonstrated a novel method to prepare nanometer-sized carbon supported Pt-based bimetallic and trimetallic catalysts for direct ethanol fuel cells. And the related research was still attracting more interests these days in the field of electricity generating due to its unique advantage of causing no pollution in the process. The second most frequently cited publication was also in *Applied Catalysis B-Environmental*, with 262 referee records through 2012.[2] This paper presented a general review of efficient electrochemical technologies developed to decolorize and/or degrade dyeing effluents for environmental protection, including technical processes of electrocoagulation, electrochemical reduction, electrochemical oxidation, indirect electro-oxidation with active chlorine species, photoelectro-fenton and photoelectrocatalysis. Finally it was proposed that application of these methods as pre-treatment stage for biological post-treatment should be focused in order to develop more economical coupled methods. And it was gradually recognized by more and more researchers in implementing sewage wastewater treatment more cheaply and effectively. The article life of the top 10 most frequently cited publications was shown in Figure 4.

The references of the paper by Martínez-Huitle and Brillas[2] in *Applied Catalysis B-Environmental* were keeping a rapid growth once it was published. It was cited 110 times in 2012, the most in all the researched publications. This indicated that decontamination of wastewaters containing synthetic organic dyes by electrochemical methods had attracted more and more interests in the present time. The publication by Zhou *et al.*[22] in *Applied Catalysis B-Environmental*, the paper by Quan *et al.*[23] in *Environmental Science & Technology*, and the one by Mollah *et al.*[44] in *Journal of Hazardous Materials* also had shown quite vigorous article lives

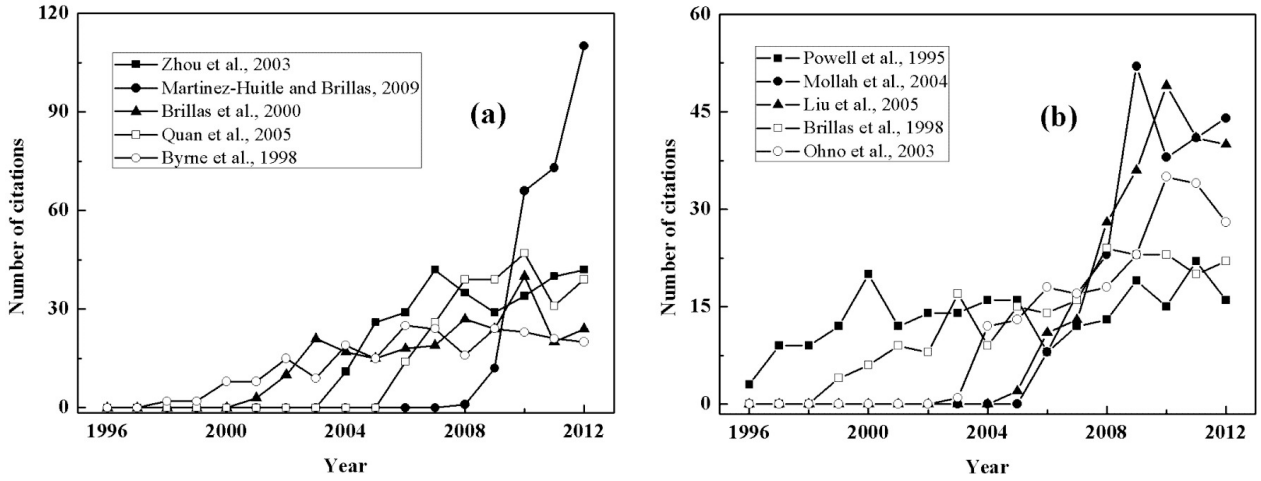

Figure 4. Citation history of the top 10 most frequently cited pulications from Table 3.

and were cited 42, 39 and 44 times in 2012, respectively. They indicated researchers' attention to outstanding anode catalysts for electrochemical oxidation, preparation and applications as electrode, and theory and practical study of electrocoagulation. On the other hand, the publications by Byrne *et al.*[45] had been cited less and less during the last four years. This was due to the reason that nano-TiO_2 had gradually become the foci of photocatalytic reaction and the related loading method kept improving and have already turned to be much more effective and up to date these days.[46,47]

CONCLUSIONS

The results contained considerable information concerning electrochemical oxidation in the three categories of "environmental sciences", "engineering, environmental" and "water resources". Based on the analysis of the annual publications, categories, journals, institutions, countries, research topics and tendencies, important findings were obtained on global scientific research fields from 1975 to 2012. Publications related to electrochemical oxidation increased sharply since 1991, indicating public attention was growing for advanced and efficient environmental technology. *Journal of Hazardous Materials* published the most articles. It was shown that the most frequently cited publications appeared in 2003 and 2009, which provided a detailed introduction to fabricate a novel catalyst for direct methanol fuel cell and a general review of efficient electrochemical technologies to deal with dyeing effluents for environmental protection. And then more deep investigation and more advanced treatment were carried out to improve the electrochemical efficacy. Synthetic analysis of author keywords, *KeyWords Plus*, and words in publication titles and abstracts, described the development of electrochemical oxidation related-research, and also predicted the future clues for hotspots in related fields. And it could be concluded that, Pt, boron-doped diamond, TiO_2 were currently and would continue to be the predominant focused electrode materials at least over the next decade, due to their excellent performance in electrochemical oxidation. And the foci of studied pollutants in the electrochemical oxidation were mainly concentrated in dyes and phenols, commonly existed in kinds of industrial wastewaters. What's more, electrochemical degradation, wastewater treatment, electrochemical determination and fuel cell would be the key research topics currently and recently. Finally, it was also concluded that fenton, photocatalysis and coagulation were the most-frequent combination technology with electrochemical oxidation to improve the total treatment efficacy based on the bibliometric results.

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