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Electrochemical Methods for wastewater treatment

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ABSTRACT With a rapidly growing economy and burgeoning populations, the world's scarce water resources are seriously affected by pollution. This pollution is due to vast discharges of industrial and domestic wastewater, indiscriminate solid waste disposal and runoff from an agricultural sector. The wastewaters are also characterized by excessive use of fertilizer and pesticides and large-scale livestock breeding. Therefore, these wastewaters must be treated before being discharged.

Important advances in electrochemical technology over the last three decades have fostered the development of alternative methods to alleviate and prevent the generation of pollutants. Among recently developed methods, the electrochemical (EC) methods and advanced oxidation processes are attractive alternatives for wastewater treatment because of its environmental respectability and ease of operation.

This paper introduces mainly the EC and advanced oxidation methods, various factors affecting process efficiency, process requirements along with industrial applications.

1. Introduction:

The environment is polluted day by day due to either natural or manmade activities [1]. One of the important natural resources water is polluted due to natural disaster, industrial use, and various human activities [1]. By measuring certain parameters it can be known that up to which extent water is polluted. They are COD (chemical oxygen demand), BOD (Biochemical oxygen demand), pH, TOC (Total organic carbon), TDS (Total dissolved solids), volatile matters, non-volatile matters, total hardness, colour, odour, etc [2].

Wastewaters can be classified by mainly three different ways. They are domestic, industrial and agriculture wastewater. Due to water crisis, reuse of water becomes very essential now a day. For that, efficient process for removal of pollutants from wastewater is required. The wastewater contains hazardous pollutants in various forms. Fig. 1 mainly classifies various pollutants.

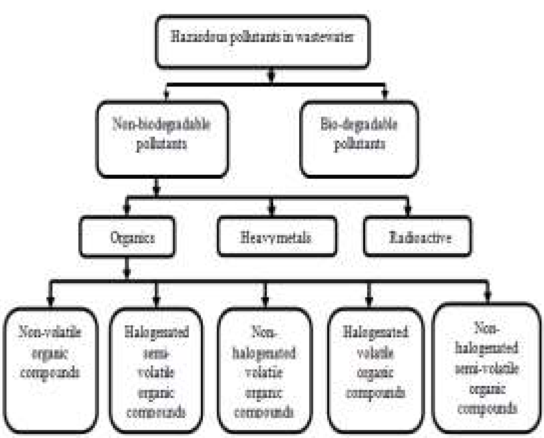

Fig. 1 Classification of pollutants in wastewater

The classifications of pollutants generally help to facilitate the selection of remediation technologies according to the treatability of each class in a specific contaminated media.Table 1 is the list of methods available for the treatment of wastewater.

2. Selection of Treatment Technology

The nature of the pollutants, the concentration of pollutants, and the media contaminated are the three most important determining factors when selecting the appropriate technology for treating a specific type of hazardous waste. Fig. 2 and Fig.3 shows effective remediation technology with respect to concentration of the pollutants in ppm. Fig. 4 is selection of technology according to COD content in wastes

Table 1 Methods for the treatment of wastewater

Sr. No.	Methods	Technology
1	Physicochemical methods	Adsorption, Coagulation Filtration, Ion exchange, Electrolysis, Membrane
2	Thermal degradation	Incineration
3	Chemical methods	Oxidation, Precipitation
	Advanced oxidation processes (AOPs)	Fenton's reagent using oxidants like O_3, TiO_2, O_2, H_2O, H_2O_2 and Catalyst as Fe^{+2}, Fe, Pt, Fe_2O_3, Photons, Ultra-sound Combination of AOPs
4	Microbiological treatments	Activated sludge process, Mixed cultures and Pure cultures
5	Enzymatic décompositions	
6	Electro-chemical process	Electro coagulation, Electro flocculation, Electro deposition, Electrochemical direct oxidation, Indirect oxidation, Electrochemical advanced oxidation methods

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Fig. 2 Treatment technologies according to concentration [2]

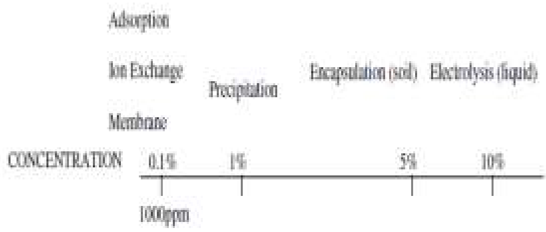

Fig. 3 Treatment technologies of heavy metals with respect to concentration [2]

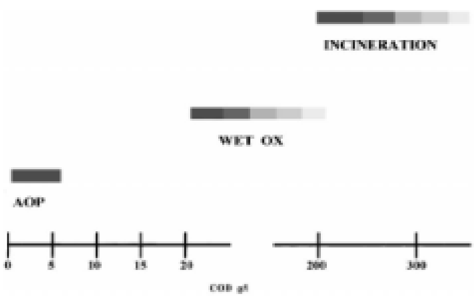

Fig. 4 Suitability of water treatment technologies according to COD contents [3]

3. Electrochemical technology:
As can be seen from Fig. 3, electrolysis is one of the ways for the treatment of wastewater containing higher concentration of metals. The method is also proved efficient for the elimination of various refractory organics. Numbers of electrochemical technologies are available for effective wastewater treatment. Different electrochemical processes; its major application and its working principals are listed in Table 2.

4. Electrochemical process requirements: To use electrochemical process as remedial technology either as batch or continuous process, basic requirements are: (a) electrochemical reactor (b) electrodes © D.C. power supply

5. Electrochemical process mechanism: Mechanism of the process is divided mainly in to two types: (1) direct electrolysis and (2) indirect electrolysis.

(1) Direct electrolysis: It involves direct reaction of species at electrode surfaces. An electron transfer to or from the undesired pollutant occurs at the surface of an electrode in the process. Oxidation or reduction processes occur directly on inert electrodes without the involvement of other substances (e.g., electron mediators, biocidal species). The direct process is again sub divided into the oxidation and reduction of organic and inorganic pollutants

(2) In-direct electrolysis: electrolysis involves production of active species at the electrode and further reaction with the targeted pollutants or processes. The redox reagent acts as an intermediary for shuttling electrons between the pollutant substrate and the electrode. These redox reagents can be electrochemically generated either in a reversible or irreversible manner Indirect processes include processes of electro coagulation, Electro flotation and electro flocculation and advanced oxidation processes. An electrolysis can be done both with reversibly (b) and irreversibly (c) electro generated reagents.

6. Brief description of different electrochemical processes:
A. In- direct electrolysis
(1) Electro flotation: involves the electrolytic production of gases [3, 4] (e.g., O a, H2) that can be used to attach pollutants (e.g., fats and oils) to the gas bubbles and carry them up to the top of the solution where they can be more easily collected and removed. The FF-flocculation-flotation process

Table 2 Electrochemical processes

Sr. No.	EC process	Major application	Working principals
A	Indirect oxidation	Toxic and bio refractory pollutants	Oxidation in electrolyte by producing active species in it
1	Electro-coagulation	Effluents containing suspended solids, oil, grease, organic and inorganic pollutants	Electrochemical production of destabilization reagent to neutralize pollutants
2	Electro-flotation	Mining industries, waste water treatment	Electrolytic production of gases used to attach pollutants
3	Electro flocculation	Effluents containing suspended solids, oil, grease, organic and inorganic pollutants	Uses sacrificial electrodes to add coagulating metal cations to the water and then uses the hydrogen gas generated at the cathode to float these coagulated pollutants to the surface.
B	Direct anodic oxidation	Organic pollutant removal and wastewater treatment	Oxidation at electrode surface
1	Electrochemical deposition	Metal recovery or heavy metal –effluent treatment	Oxidation/ reduction of a solid metal and its dissolved ion
C	Advanced electrochemical process	Refractory organic pollutant removal	In-direct oxidation, mainly by producing OH radical
1	Electro-Fenton	Wastewater treatment, organic pollutant removal	Generation of Fenton's reagent H_2O_2 using cathode

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2	Photo assisted electrochemical method	Wastewater treatment,	Photochemical and photo catalytic action of UV irradiation
3	Photo electro Fenton method	Dyes removal , WWT	Electro generated H2O2 with Fe+2 & UV

Factors affecting electro flotation: The performance of an electro flotation system is affected [3,4] by the power and/or chemical consumptions. Addition to it, pollutant removal efficiency is largely dependent on the size of the bubbles formed. Similarly power consumption relates to the cell design, electrode materials, electrode arrangement, as well as the operating conditions such as current density, water conductivity and pH.

(2)Electro coagulation: In coagulation [5-7], coagulating agent (Alum i.e. Aluminum sulphate or ferric chloride) & other additives i.e. poly electrolytes are dosed to produce large aggregates which can be separated physically. The coagulant's role is to destabilize the colloidal suspension by reducing the attractive forces there by lowering the energy barrier & enabling particles to aggregate. Electro coagulation is the process in which coagulant is generated 'in situ' by dissolution of metal due to oxidation of the anode.

Three successive stages of the process are [8-10]:

1. Formation of coagulants by electrolytic oxidation of the sacrificial (consumable) electrode
2. Destabilization of the contaminants, particulate suspension and breaking emulsions
3. Aggregation of the destabilized phases to form floc and collection or separation of floc

Factors affecting Electrocoagulation: Parameters affecting the performance of the process are current AC or DC [11], pH, current density (A/m2) corrosion rate (mm/year), time for electrolysis (min), electrode distance (mm), initial concentration of pollutants (mg/l), concentration of NaCl (mg/l), temperature (K) ,stirring rate (rpm), retention time (min) and electrode material.

B. Advanced oxidation process: Any oxidation process in which hydroxyl radical is the dominant species is defined as an advanced oxidation process (AOP) [7, 12-14]. The various reagents generally used for the process are ozone, hydrogen peroxide, oxygen, and air, in precise, pre-programmed dosages, sequences, and combinations. These procedures may also be combined with UV irradiation and specific catalysts. This results in the development of hydroxyl radicals. The AOP (Table 3) procedure is particularly useful for cleaning biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in waste water. The contaminant materials are converted to a large extent into stable inorganic compounds such as water, carbon dioxide and salts, i.e. they undergo mineralization. The possible combination of advanced oxidation process with oxidants and catalysts are shown in Table 4.

Table 3 Various AOPs

Sr. No.	Types of AOPs	Process familier with
1	O_3	Ozone oxidation
2	UV	photolysis
3	H_2O_2/ O_3	Peroxone
4	H_2O_2 / Fe^{+2}	Fenton
5	H_2O_2 /Fe^{+3}	Fenton- like
6	H_2O_2/Fe^{+2} /Fe^{+3} (UV)	Photo assisted fenton / Sonolysis
6	H_2O_2 / Fe^{+3} - oxalate	Fenton oxalate
8	Mn^{+2} / oxalic acid/	ozone
9	TiO_2 / hv /O_2	Photo catalysis
11	O_3 /UV	UV -Ozone
12	H_2O_2 /UV	H_2O_2 photolysis
13	UV /O_3 /H_2O_2	Combined technology
14	UV /O_3 /H_2O_2 / Fe^{+2}	Combined technology
15	O_3 /Fe^{+2}	Ozone-fenton oxidation

Table 4 Possible AOPs with different combinations of oxidants and catalysts [13, 14]

Catalyst	Metals and Ions	Metal oxides	Oxidants	Photons	Ultrasound	Electron					
Oxidant	Fe^{+2}	Fe	Pt	TiO_2	Fe_2O_3	OH-	O_3	H_2O_2	UV	US	e-
O_3	X	X	X		X					X	
H_2O_2	X	X	X	X	X	X		X	X	X	
O_2	X	X	X	X			X		X	X	
H_2O				X						X	X
TiO_2									X		

Note: X represents a combination that can generate hydroxyl radicals.

C. Description of Electrochemical advanced oxidation methods:

(1)Electro-Fenton method: The electro- Fenton method corresponds to a coupling between the Fenton's reagent and electrochemistry in which H2O2 electro generated at the cathode reacts with Fe2+ present in the medium leading to the formation of hydroxyl radicals from Fenton's reaction [7]. A small quantity of Fe2+ or Fe3+ ions is then added to the solution to strongly increase the oxidation power of electro generated H2O2. An advantage of the electro-Fenton process is the catalytic behavior of the Fe3+/Fe2+ system where Fe2+ is oxidized by H2O2 from Fenton's reaction giving rise to hydroxyl radical and Fe3+, whereas Fe3+ thus obtained or initially added to the solution is continuously reduced to Fe2+ from reaction. Organic pollutants are then oxidized by the combined action of OH produced at the anode.

Parameters affecting the process: Electro- Fenton process is pH dependent process. Process also depends on the type of

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electrode.

(2)Photoelectron-Fenton method:

Photoelectron-Fenton method, where the treated solution is irradiated with UVA light of λmax = 360 nm that causes the photo-Fenton reaction of $Fe(OH)^{2+}$, the predominant species of Fe^{3+} in acid medium. Hydroxyl radicals can thus be produced at higher rate .In addition, complexes of Fe^{3+} with carboxylic acids generated from the initial pollutants, as oxalic acid, can be quickly photo decomposed into CO_2.

Parameters affecting the process: Intensity of the light and type of electrode affects the performance of the process.

(3) Electro-Fenton coupled to sonolysis (sono-electro-Fenton)

This new method corresponds to the coupling of electro-Fenton with the simultaneous irradiation of ultrasounds. Organic pollutants can then be destroyed by the combined action of OH generated by Fenton's reaction (2) and different processes caused by the ultrasounds such as pyrolysis in cavitation bubbles and oxidation by OH formed from water sonolysis:

$$H_2O + \text{ultrasounds} \quad H + OH$$

7. Conclusion:

The electrochemical process forms an attractive alternative and is successfully applied for industrial wastewater treatment. It does not produce any undesired reaction co-product nor use toxic or hazardous materials. Through this process metals or heavy metals can also be recovered. The method is also proved efficient for the elimination of various refractory organics. Basic goal of the waste water purification by means of different electrochemical procedures is the reduction of the chemical contaminants and the toxicity to such an extent that the cleaned waste water may be reintroduced into receiving streams or, at least, into a conventional sewage treatment

REFERENCE

[1] Mantell C L "Electrochemical Engineering" New york, McGraw-Hill Book Company, 4th Edition, (1960) | [2] Rajeshwar Krishnan & Ibanez G. Jorge, Environmental Electrochemistry -Fundamentals and Applications in Pollution, California, Academic press limited, (1997) | [3] Roberto Andreozzi, Vincenzo Caprio, Amedeo Insola, Raffaele Marotta, "Advanced oxidation processes (AOP) for water purification and recovery" Catalysis Today, 53 (1999):51–59 | [4] Peleka N Efrosyni, Matis A Kostasa "Application of flotation as a pretreatment process during desalination" Desalination, Volume 222, Issues 1-3, 1 (2008) :1-8, | [5] Huitle Martinez, Carlos A, Brillas Enri "Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review" Applied Catalysis B: Environmental, Volume 87, Issues 3-4, 7 (2009):105-145 | [6] Baklan, VY, Kolesnikova, IP "Influence of electrode material on the electro coagulation" Journal of Aersol Science, 27(1) S209-S210 (1996) | [7] Hector A. Moreno-Casilas, David L, Cocke, Jewel, Gomes A.G. "Electro-coagulation mechanism for cod removal" Separation and purification Tech.56 (2007):204-211 | [8] Yousuf M, Mollah A, Schennach Robert, Jose R. Parga, David L Cocke "Electro –coagulation (EC)-Science and applications" Journal of hazardous Materials B84 (2001):29-41. | [9] Pouet M.F, Grasmick A "Urban wastewater treatment by electro coagulation and flotation" Water Science and Technology 31 (3-4) (1995):275-283 | [10] Mollah M.Y.A, Morkovsky P, Gomes J.A.G, Kesmez M, Parga J, Cocke D.L. "Fundamentals- present and future perspectives of electro-coagulation" Hazard. Mater. 114 (2004):199–210. | [11] Modirshahla N, Behnajady M.A, Mohammadi-AghdamS, "Investigation of the effect of different electrodes and their connections on the removal efficiency of 4-NP from aqueous solution by elecrtocoagulation" Journal of Hazardous Material, 154(2008):778-786 | [12] Jüttner K, Galla U, Schmieder H. "Electrochemical approaches to environmental problems in the process industry" Electrochimica Acta, Volume 45, Issues 15-16, 3 (2000)2575-259 | [13] Carlos A, Martínez-Huitle, Brillas Enric "Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review" Applied Catalysis B: Environmental, 87(2009):105-145. | [14] Walter Z. Tang, "Physicochemical treatment of Hazardus waste, Chapter 4" CRC press LLC, 2004.