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Contamination of Water Resources by Food Dyes and Its Removal Technologies

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and Hammad Khan*

Abstract

Food dyes comprise different groups which impart color to a wide range of food products. Food products are mainly purchased and consumed by people because they are nutritive and flavorsome and have an attractive color. Food color stimulates appetite and enhances its esthetic appeal of food on table for customer. With sky rocketing industrialization and modernization, the worldwide production of dyes in 2010 was forecasted to be 2.1 metric tons. It has been estimated that 15% of total dyes produced worldwide are discharged to water bodies which adversely affect aquatic ecosystem. Dyes in water reduces its transparency, thereby declining light penetration in the water, hence influencing photosynthesis which consequently reduces dissolved oxygen which is an alarming situation for both aquatic flora and fauna. Dyes wastewater discharged from huge number of industries like textile, leathers, paint, food, pharmaceutical etc. and deteriorating the aquatic environment and pose threat to living organism. The presence of dye molecules in water channels is an emerging alarm to an environmental scientist. An environmental friendly and self-sustainable treatment method should be explored to address this problem. Therefore, this work elaborates the various methods used for removal and degradation of dyes in water, although some processes have a common shortcoming like production of secondary pollution to the environment. This chapter have tried to highlight the important application of food dyes, their contamination and their toxic effect. Herein we also focus on remediation techniques like separation (adsorption, filtration, etc.) and degradation (chemical, biological and electrochemical oxidation) of dyes in aqueous solution. The mechanism and pros and cons of different methods are explored and discussed briefly.

Keywords: food dyes, degradation, wastewater, contamination

1. Introduction

1.1 Pollution caused by dyes and their harmful effects on aquatic environment

Food dyes are promising colorants globally used to color a broad spectrum of food products. Food dyes not only impart color to food but also boost up appetite and promote attractiveness and esthetic appeal of food for consumer. According

to recent financial reports, 7×10^5 tons of 10,000 different dyes and pigments are produced worldwide, and its market is skyrocketing each year and has exceeded over US \$11 billion by 2008 [1]. Approximately 1-2% of dyes stuffs are lost during production and about 10-15% of dyes are discharge as effluent during dye applications [2]. From an environmental perspective, the discharge of dye effluents from dye manufacturing or consuming units into the water bodies poses potential threats to the quality of water and induces serious health problems to human, plants and animal life in particular and aquatic biota in general. The presence of dyes in wastewater even in trace amounts (less than 1 mg/dm^3 for few dyes) is remarkably objectionable and undesirable [3]. Most of the organic dyes used to color food products, for example, azo dyes, have aromatic centres in their molecular structures, and their metabolic and degradation products like aromatic amines (anilines), benzidines and benzene sulphonic acids are well-established carcinogens, mutagens and DNA adducts and hence induces subsequent deadly effects on cells [4]. Moreover dyes can make water colored, thereby reducing the transparency (sunlight penetration) and aeration of water body, which badly affects the efficacy of crucially important photosynthesis, consequently reducing significantly the dissolved oxygen (DO) levels in water. The discharge of dye effluents in water bodies poses direct and indirect consequences to aquatic ecosystem. The direct effects includes depletion of dissolved oxygen levels, decreased reoxygenation potential, leaching of dyestuff from soil into groundwater, reduced light penetration into water which hinders photosynthesis (which gives red signal to aquatic flora and fauna) and esthetic issue of water downstream [5, 6]. The bird's eye view of indirect effects caused by dye effluents includes death of aquatic organisms, genotoxicity and microtoxicity imposed by colored allergens, depression of human immune system, allergic reactions, hyperactivity in kids (ADHD), bladder cancer in humans and deadly process of water eutrophication [7].

1.2 Application of dyes

Both natural and synthetic dyes have indeed revolutionized the modern world both at domestic and industrial sectors. More recent and independent reviews have reported that over 100,000 different dyes and pigments are in practice, and their annual production has exceeded over 7×10^7 tons. Nowadays the use of dyes is indispensable because dyes are widely used in electronics; textile; rubber; food; leather; cosmetics; paper and pulp; photography; solar cells/solar panel, i.e. dye-sensitized solar cells; pharmaceuticals; pigment; agriculture research; paints; printing inks; cosmetics; coloring of plastics products; and many other fields of domestic and industrial interest [8, 9]. Similarly dyes are also used to assess the efficacy of sewage and wastewater treatment plants as well as agriculture research. Textile industries consume more than 70% of total dyes produced worldwide [10]. Dyes in textile, food or in any other industries are used in minute quantities; for instance, it has been reported that one ton of textile dye is more than enough to color 42,000 clothes/suits [11].

2. Techniques incorporated for dye removal from wastewater

Purification of water from dyes tuff is of tremendous importance from both perspectives, i.e. water purification and its reusability. Pollution caused by dyes has attracted the attention of environmental chemists worldwide more specifically in developed countries like the USA, United Kingdom, Germany, China, Japan, Scandinavian countries, etc., which have incorporated rapid

industrializations and are more vulnerable to dye pollution. Nevertheless dyes cause severe water pollution; hence these dyes need to be eventually removed to minimize or eliminate their dreadful impacts. Consequently the worldwide environmental standards so far have turned more stringent, seeking more precise technological tools to cope with this global environmental issue, and that is why it has attracted the attention of environmental scientists worldwide from past two decades. Various techniques like physicochemical methods, enzymatic degradation, microbiological treatment, chemical methods and advanced oxidation techniques have been developed so far [12–14]. But unfortunately most of the organic dyes are non-biodegradable, thermally stable and refractory with respect to biochemical oxidation due to their large/complex sizes and inert nature. These characteristics have rendered organic dyes reluctant with respect to decolourization by using conventional methods of wastewater treatment like filtration, coagulation, biochemical and physicochemical techniques. Thus from the last two decades, research for more efficient and sophisticated techniques for removal of these dyes from wastewater to minimize or eliminate the water pollution has been turned the core interest to environmental scientists worldwide [15]. The dye abatement techniques in water are broadly classified into two principal types.

2.1 Segregation techniques

Segregation techniques involve separation of dyes pollutants via multiple physical techniques like adsorption, filtration/nanofiltration or coagulation processes. These traditional water purification methods like filtration, ion exchange, coagulation by lime or by using salts of iron/aluminium, adsorption over activated carbon and other low-cost adsorbents have been proven to be very effective decolourization methods. Among techniques decontamination of dyes by adsorption offer the most promising, simple and efficient technique. Similarly the use of low-cost adsorbents such as vegetable matter, saw dust, fruits peels, hen feathers, other carbonaceous materials, etc. make the dye removal process more economical and feasible [16, 17], but their utility is limited by production of associated hazardous sludge which poses an another issue of their disposal at suitable safe site. Similarly the use of adsorption and coagulations techniques for decolourization of wastewater is limited by regular regeneration of adsorbent and coagulant materials after dye adsorption and coagulation, respectively, which is much needed (to make the process economical and efficient), so this in turn gives rise to other issues [18, 19].

2.2 Degradation techniques

2.2.1 Chemical techniques

Over the past two decades, chemical techniques are also withdrawing the attention of environmental chemists; these techniques include chemical oxidation by using hypochlorite (OCl^{-1}), chlorine dioxide or ozone which has always shown high efficiency and reproducibility. But this technique has a major disadvantage with respect to relatively high prices and production of secondary pollutants like chlorinated hydrocarbons which are known carcinogens; similarly the difficulty in storage and transportation of reactants causes a substantial inconvenience for safe operation [20]; thus environmental scientists are looking for more, convenient, advanced, safe, efficient and sophisticated techniques which must be incorporated for removal of dyes from wastewater [12] .

2.2.2 Advanced oxidation processes (AOPs)

The term advanced oxidation processes is actually coined to address the process of oxidation of organic pollutants primarily via in situ generations of highly reactive hydroxyl free radicals ($\cdot\text{OH}$) from H_2O_2 . These hydroxyl free radicals are strong oxidizing species by virtue of powerful oxidation potential of (2.80 V) vs. SHE. Different advanced oxidation processes are ozonation; photocatalytic methods using O_3/UV , TiO_2/UV and $\text{H}_2\text{O}_2/\text{UV}$; and Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{+2}$). Fenton's reagent offers a novel dye degradation technique [21]. The phenomenal Fenton's reagent was named after Fenton who introduced it for the first time almost 100 years ago in 1884. Fenton's reagent is a precursor of hydroxyl free radicals; these madly reactive hydroxyl free radicals attack dye substrate molecules at the sites of multiple bonds and carry out either excessive hydroxylation of dye contaminants or causes dehydrogenation of dye molecules, hence producing stable inorganic materials directly or indirectly converting the dye pollutant into biodegradable and safe materials. Fenton's processes offer a remarkable efficiency and can be extended to much broader spectrum of dyes due to its fabulous non-selectivity [22]. Recently photo-Fenton's process, i.e. Fenton's coupled with light (UV or visible), electro-Fenton, sono-Fenton and sono-electro-Fenton are emerging water treatment techniques.

Ozonation is also reliable, safe and effective wastewater treatment tool which utilizes ozone gas as a strong oxidant usually used to disinfect water in swimming pools. In aqueous medium the mode of action of ozone is quite complicated. Molecular ozone can also oxidize the dyestuff in water by virtue of selective, direct or by indirect decomposition through a chain reaction mechanism by generating in situ free hydroxyl radicals (OH^\cdot) [23]. AOPs show a tremendously high degree of decolourization efficiency with associated photocatalytic degradation of dyestuff [24]. But their sky kissing prices and operational difficulties put a question mark and limit the use of these photocatalytic techniques for decolourization of wastewater.

2.2.3 Microbiological and enzymatic degradation techniques

On the contrary to AOPs microbiological methods like activated sludge process, aerobic and anaerobic decomposition of pure and mixed cultures using fungi and bacteria and enzymatic degradation techniques have so far shown excellent decolourization and degradation efficiencies of dyes in wastewater; furthermore these methods are gaining popularity by virtue of their simplicity, ease of operation and applicability [25]. Biodegradation processes may be aerobic and anaerobic, and sometimes the combinations of both aerobic and anaerobic biological treatments are used for dye removal from water [26]. The main mechanism of dye removal in biological treatment is the adsorption of dyestuff on to biomass, but at saturation point, the adsorption potential of dyes by biomass drops [27]. Unfortunately the utility of these microbiological methods is quite inadequate because most of the dyes are stable and resistant towards biodegradation due to their huge sizes, complicated and conjugated benzenoid structures with extensive electron delocalization and high degree of stability. Similarly due to high degree of specificity and sensitivity of the enzymes of the microorganisms, these techniques cannot be extended over a broader spectrum of dyes and needs an extensive study and homework of enzymes, their nature, selection and applicability. Thus biological abatement of dyes in wastewater has become difficult owing to the bio-refractory nature and stability of dyes. That is why environmental chemists were chewing their nails to explore more advanced, effective and non-selective

techniques to achieve dye abatement goals. Thanks to electrochemical techniques which have taken the bull of organic pollutants by horns and have controlled the aquatic pollution to a great extent [22].

2.2.4 Catalytic degradations

Catalytic degradations assisted by suitable promoter and coupled techniques like photocatalytic, sonocatalytic and photoelectrocatalytic degradations of dyes have so far shown excellent efficiencies. But here again catalytic poisoning and recovery of catalyst materials causes issues.

2.2.5 Electrochemical techniques

The term electrochemical techniques refers to application of DC current from a suitable source and carrying out an entire degradation of pollutants by electro-oxidation or reduction processes to inorganic materials. The main pollutants for electrochemical methods are not only dyes, but also other pollutants like pharmaceuticals, pesticides, herbicides, detergents and many other harmful contaminants are the subjects of investigation. Electrochemical techniques usually incorporated for wastewater abatements are electrochemical reduction, electrochemical oxidation, electrocoagulation methods, photoelectrocatalytic and photo-assisted Fenton's oxidation techniques. Electrochemical oxidation techniques are further subdivided into two types which include direct and indirect oxidation techniques [28]. Over the past 10 years, the electrochemical methods have received a remarkable attention. This is because these methods have promising water decontamination potentials, have shown great novelty due to their versatility and potential cost-effectiveness and offer the most promising, clean, safe, efficient and green technologies for the decolourization of wastewater. Wastewater abatement using electrochemical methods has a fantastic advantage of environmental compatibility because its sole reagent, i.e. the electron, is a safe, clean and green reagent produced in situ and works most efficiently. Furthermore these methods are gaining attention of environmental chemists due to their excellent efficiencies, flexibility of automation and safe applicability over a broad spectrum of organic dyes [28]. These techniques need mild conditions for their operation, no heating of the samples are required and work under ambient conditions of both parameters, i.e. temperature and pressure. Nowadays a vast variety of electrochemical techniques are in practice such as electrochemical oxidation (EO), electrocoagulation (EC) using a variety of anodes, active chlorine indirect oxidation, etc. Recently emerging techniques which utilize twin technologies of both electrochemical cells and suitable light like UV light or sono-electrochemical degradations of dyes in wastewater are gaining much attention and appreciation [29, 30]. These photo- and sono-assisted electrochemical setups have been categorized as electrochemical advanced oxidation processes (EAOPs) [21]. The use of electrochemical methods for abatement of contaminants in wastewater was pioneered by Nilsson et al. 1973 [31] by electrochemical oxidation of phenolic-based wastes; later in the early 1980s, these studies were proceeded in collaboration with Chettier and Watkinson [32].

Over the past two decades, much of the research regarding decolourization of wastewater by electrochemical oxidation has been focused on the use of different anodic materials, their relative efficiencies, exploration of various factors affecting process efficiency (like pH, temperature, nature and concentration of electrolytes, etc.), kinetics and mechanism of oxidation of a variety of pollutants in water. The electrochemical oxidation is of two types, the first type is direct oxidation also called anodic oxidation by using suitable anode material. Direct oxidation is carried

out by physically adsorbed hydroxyl free radical ($\cdot\text{OH}$) or chemisorbed active oxygen in oxide lattice. The second type of electrochemical oxidation is indirect oxidation using appropriate oxidant material such as hypochlorite (OCl^{-1}) which is formed anodically [33, 34]. The main degradation products of electrochemical oxidation of organic pollutants are CO_2 and water; thus during electrochemical oxidation of dyes, neither sludge formation occurs nor further treatment of degradation product is required; moreover no harmful by-products are formed; this is one of the greatest superiorities of electrochemical oxidation over other methods used for decolourization of wastewater [35]. A flow sheet representation of various techniques utilized for dyes abatement is shown below (**Figure 1**).

2.2.6 Electrochemical oxidation and its types

Environmental chemists took a long comfortable breath when they incorporated electrochemistry for removal of organics from wastewater. Electrochemical oxidation effectively degrades organics in wastewater. Electrochemical oxidation may be either indirect or direct oxidation processes. Indirect electro-oxidation also called mediated oxidation involves electro-generations of oxidizing species (EOS) in water at electrodes (anode) like active chlorine species, physisorbed hydroxyl free radicals or chemisorbed active oxygen atoms (in metal oxide anode lattice) which are very efficient, and oxidation mediated by these EOS gives rise to partial or complete decontamination of organics. Indirect oxidation processes can be elaborated by twin approaches:

1. Electrochemical transformation
2. Electrochemical combustion

During electrochemical transformation, the stable and refractory organic contaminants are converted into biodegradable materials (most often in to carboxylic acids) by chemisorbed active oxygen atoms. Then during electrochemical combustion which is also called electrochemical incineration, the organic contaminants are entirely mineralized to CO_2 , water and inorganic ions by virtue of physisorbed hydroxyl free radicals ($\cdot\text{OH}$). These hydroxyl free radicals are potentially strong oxidants with a powerful oxidation potential of ($E_o = 2.80 \text{ V}$) vs. SHE; that is why this radical has been ranked as second most powerful oxidizing agent after fluorine in electrochemical series. The ($\cdot\text{OH}$) radicals induce excessive dehydrogenation and hydroxylation of organic contaminants which ultimately oxidizes to yield CO_2 . The mechanism of indirect oxidation of a dye pollutant at a metal oxide (MO_x) anode can be summarized as follows [36, 37]:

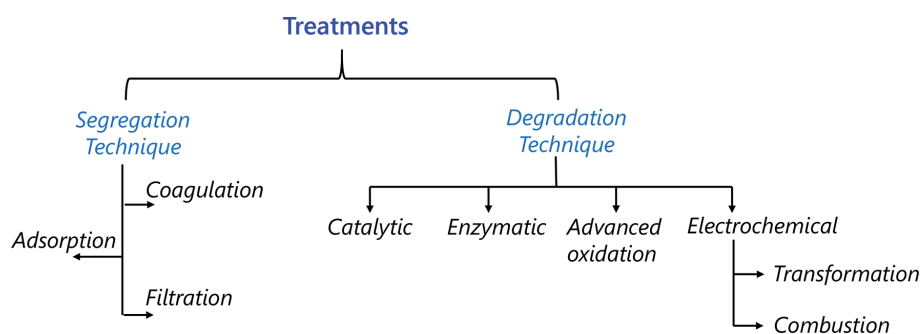


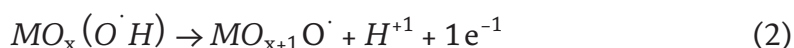
Figure 1.
Different methods used to remove dyes from wastewater.

First of all water is electrolyzed at metal oxide interface generating physically adsorbed (physisorbed) hydroxyl free radicals (O^\cdotH) as shown below;



Now the next step is a crucial one which entirely depends on selection of anode material; moreover this step exclusively differentiates between two limiting classes of electrode (anode) materials, i.e. active and non-active electrodes.

3. Active anodes like DSA types of anodes which carry out indirect oxidation of organics through formation of strong oxidants like hydroxyl free radicals, aqueous chlorine, i.e., $\text{Cl}_2(\text{aq})$, hypochlorous acid (HOCl) or hypochlorite ion (OCl^-), ClO_2^{-1} , ClO_3^{-1} , ClO_4^{-1} , etc. Now at active electrodes like DSA where higher oxidation states of metal electrode atoms (M) are available, the physically adsorbed hydroxyl free radicals undergoes transformation to chemically adsorbed (Chemisorbed) active oxygen with increase in oxidation state of metal atom (M) to form higher oxide (MO_{x+1}) accompanied by liberation of a proton and an electron as shown below:

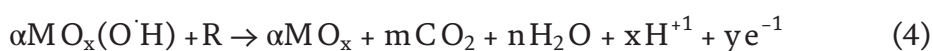


This surface redox couple $\text{MO}_x/\text{MO}_{x+1}\text{O}^\cdot$ also called chemisorbed active oxygen atoms, i.e. ($\text{MO}_{x+1}\text{O}^\cdot$), selectively attack dye molecule (R) and partially oxidize it to intermediate compounds (RO), while the metal oxide anode (MO_x) (MO_x) is regenerated as shown below:



As in active electrodes like DSA, the chemisorbed active oxygen atoms are chemically bonded to electrode surface; they do not have full freedom to attack dye molecules; that is why they carry out very poor oxidation of dyes in the presence of supporting electrolytes like Na_2SO_4 in the absence of chloride medium, but in the presence of NaCl as supporting electrolytes, the situation is entirely different. The second reason for decreased efficiency of DSA and likewise active electrodes have low oxygen evolution overpotentials (they start the unlikely Oxygen Evolution Reaction easily at low voltages).

4. At non-active anodes such as BDD and PbO_2 where the possibility of higher oxidation states for anode are entirely excluded (e.g. in PbO_2 electrode, the lead atom has oxidation state equal to +4, and it does not show oxidation state greater than +4), the physisorbed hydroxyl free radicals, i.e. $\text{MO}_x(\text{O}^\cdot\text{H})$, attack dye pollutant "R" non-selectively and completely mineralizes dye contaminants into organic species like CO_2 and H_2O , while the metal oxide anode (MO_x) is regenerated as shown below.



As these $^*\text{OH}$ radicals are physisorbed (i.e. not chemically bonded but are attached to electrode surface through weak Van der Waals forces which breaks easily) and $^*\text{OH}$ free radicals enjoy full freedom of attack on dye contaminants, these electrodes show greater degradation of dye contaminants. The second reason is that the non-active anodes have higher oxygen evolution over potentials (do not start OER easily).

Both physisorbed and chemisorbed active oxygen atoms undergo a simultaneous undesirable and unlikely competitive side reaction which is called oxygen evolution reaction (OER). This reaction substantially reduces the efficiency of electrodes for electrochemical oxidation of organics. Now as a general rule, the anode materials like active electrodes (DSA and others) have low oxygen evolution over potentials (i.e. they are excellent electro-catalysts for undesirable process of oxygen evolution reaction, i.e. OER; that is why they are active anodes) and hence carry out partial oxidation of organics. On the contrary the non-active anodes such as BDD and PbO_2 anodes have high oxygen evolution over potentials (i.e. they are poor electro-catalysts for OER; that is why they are termed as non-active anodes), and they carry out complete mineralization of organics to inorganic species like CO_2 and H_2O . The oxygen evolution potential of DSA (RuO_2) is 1.47 volts (Vs SHE in 0.5 M H_2SO_4), while that of BDD is 2.3 volts (Vs SHE in 0.5 M H_2SO_4). That is why non-active electrodes are most widely used anodes for elimination of organic contaminants during wastewater treatment in the absence of chloride medium [38–40].

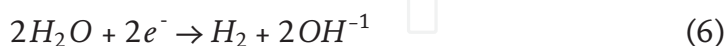
The well-known $^*\text{OH}$ free radical is a powerful oxidant ($E^\circ = 2.80 \text{ V vs. SHE}$), but it is unstable and has much shorter life than HClO ($E^\circ = 1.49 \text{ V vs. SHE}$); therefore in the dye decontamination from wastewater which is heavily loaded with inorganic salts like chlorides, the indirect electrochemical oxidation mediated by active chlorine species in situ provides an excellent tool for such wastewater abatement. The non-active electrodes like BDD, PbO_2 and SnO_2 are more active with respect to generation of physisorbed $^*\text{OH}$ free radicals for wastewater abatement; however they cannot be utilized for generation of active chlorine species because they preferably generate $^*\text{OH}$ free radical along with other mild oxidants like *peroxo-diphosphate*, *peroxodicarbonate*, *peroxodisulphate*, etc. On the contrary the active anode materials like platinum and DSA have remarkably high efficiency for oxidation of chloride ion, thereby generating active chlorine oxidants rather than generating physisorbed $^*\text{OH}$ free radicals at their surfaces [41].

When NaCl is used as supporting electrolyte with active electrodes like Ti-based DSA (which has been selected as model anode in this study), then chloride ions (Cl^-) undergo oxidation at anodes to produce a very strong dye killing oxidants in situ, i.e. aqueous chlorine (i.e. $\text{Cl}_2(\text{aq})$), HOCl , OCl^- , ClO_2^{-1} , ClO_3^{-1} and ClO_4^{-1} [30, 42, 43]. These species mediate the oxidation of organics as shown below.

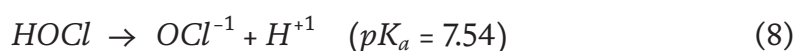
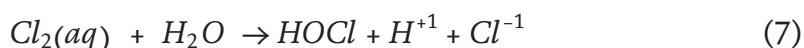
Reaction at anode:



Reaction at cathode:



Reaction at bulk:

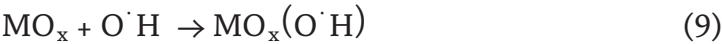


HOCl has greater oxidation potential (1.49 V) than OCl^{-1} (0.94 V). The type of active chlorine species in water depends upon pH solution, for example, at pH less than 03, dissolved chlorine (Cl_2) gas exists in water in the form of aqueous chlorine, i.e. $\text{Cl}_2(\text{aq})$. At pH range of 03–7.5, Cl_2 undergoes self-oxidation/self-reduction

reaction (disproportionation reaction) and forms HOCl, while at PH greater than 7.5, hypochlorite ions (OCl^-) exist in solution which is a much weaker oxidizing agent than HOCl [44].

Bonfatti has presented an alternative approach to electrochemical oxidation of organics; the schematic sketch of electrochemical oxidation at non-active oxide electrode (MO_x) and with associated CER is shown in **Figure 2**. Here “R” represents a dye pollutant molecule [45].

Figure 2 shows that in the first step, the hydroxide from solution adsorbs on metal oxide to form $\text{MO}_x(\cdot\text{OH})$ (see reaction 05 given below), and then it reacts with chloride ions (Cl^-) to yield adsorbed hypochlorous acid radical, i.e. $\text{MO}_x(\text{HO}\cdot\text{Cl})$ (see reaction 10); this adsorbed hypochlorous radical attacks organic pollutant (R) and degrades it to CO_2 and H_2O , and chloride ions are regenerated (see reaction 11). This degradation reaction proceeds simultaneously with chlorine evolution reaction (CER) to produce Cl_2 , some of which Cl_2 gas evolves (if applied current density is very high), while some chlorine gas dissolve in water in the form of aqueous chlorine $\text{Cl}_2(\text{aq})$. This aqueous chlorine reacts with hydroxide ions to generate HOCl, OCl^- , ClO_3^- , ClO_2^- , etc. (depending on pH of solution), which are active chlorine species and oxidize organic pollutants in situ.



The oxidation of organic compounds via active chlorine species had a serious concern about the formation of chlorinated organic compounds in water which are known as carcinogens, but Panizza and Bonfatti successfully demonstrated that by selecting optimal experimental conditions, the generations of toxic chlorinated compounds can be totally avoided in aqueous medium [46, 47]. For example,

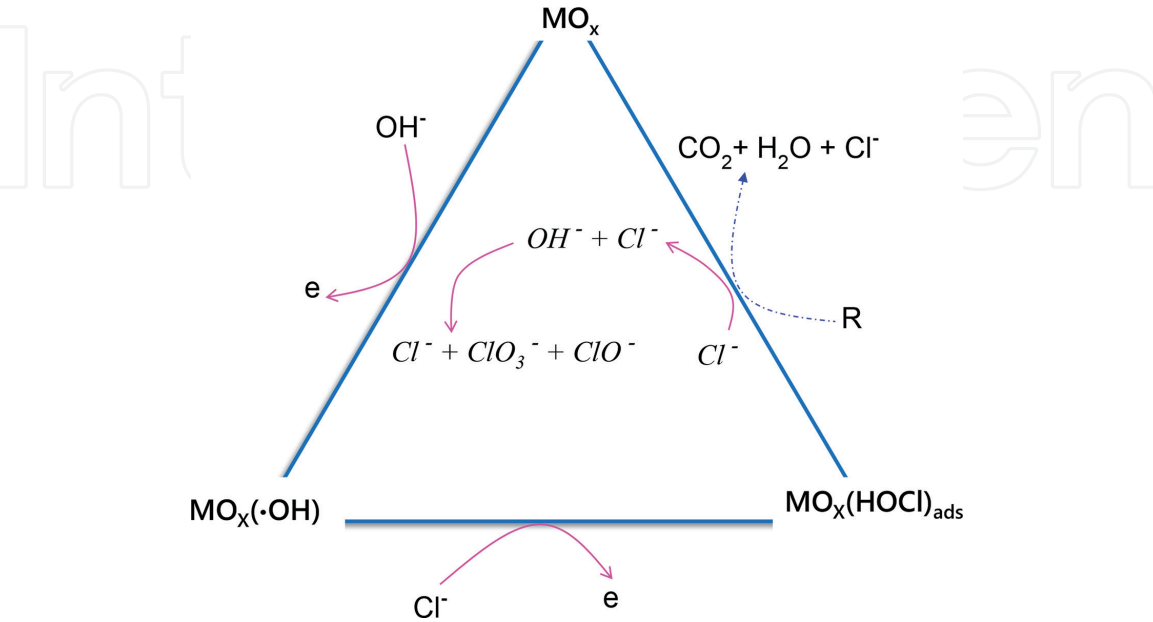


Figure 2.
Mechanism of electrochemical degradation of pollutants in chloride medium.

Panizza investigated electrochemical oxidation of 2-naphthol which was associated with the formation of few chlorinated organic compounds initially, but later as these reactions proceeded, chlorinated compounds were either mineralized to CO_2 or converted to volatile CHCl_3 which escaped off [48].

3. Conclusion

Advance oxidation process has a tremendous power to degrade dyes in aqueous solution. Some of these technologies like electro-Fenton, bio-electro-Fenton, photoelectrocatalytic and photocatalytic techniques and process based on peroxymonosulfate obtain good focus in the last decades. Moreover, the performance of some of these processes has been improved by coupling ultrasound, UV and biological process. The recent development of electrode materials and membranes enhances the efficiency of electrochemical process to remove dyes from wastewater. During the electrochemical process, the cathode also helps to generate active species ($\text{S}_2\text{O}_8^{2-}$, Cl^- , $\text{HO}\bullet$), depending on experimental conditions. Additionally, it has been shown that the integration of different technologies is a good alternative for the degradation of dyes. From our point of view, a lot research has been done, and now it is time to enlarge and apply at pilot and industrial scale. Similarly, reactor should be design to work batch and continues mode and industrial water reusable for different purposes.

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References

- [1] Pearce CI, Lloyd JR, Guthrie JT. The removal of colour from textile wastewater using whole bacterial cells: A review. *Dyes and Pigments*. 2003;**58**:179-196. DOI: 10.1016/S0143-7208(03)00064-0
- [2] Husain Q. Potential applications of the oxidoreductive enzymes in the decolorization and detoxification of textile and other synthetic dyes from polluted water: A review. *Critical Reviews in Biotechnology*. 2006;**26**:201-221. DOI: 10.1080/07388550600969936
- [3] Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*. 2001;**77**:247-255. DOI: 10.1016/S0960-8524(00)00080-8
- [4] Ratna, Padhi B. Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. *International Journal of Environmental Sciences*. 2012;**3**:940-955. DOI: 10.6088/ijes.2012030133002
- [5] Lachheb H, Puzenat E, Houas A, Ksibi M, Elaloui E, Guillard C, et al. Photocatalytic degradation of various types of dyes (alizarin S, Crocein Orange G, methyl red, Congo red, methylene blue) in water by UV-irradiated titania. *Applied Catalysis B: Environmental*. 2002;**39**:75-90. DOI: 10.1016/S0926-3373(02)00078-4
- [6] de Oliveira GAR, Leme DM, de Lapuente J, Brito LB, Porredón C, de Rodrigues LB, et al. A test battery for assessing the ecotoxic effects of textile dyes. *Chemico-Biological Interactions*. 2018;**291**:171-179. DOI: 10.1016/j.cbi.2018.06.026
- [7] Kobylewski S, Jacobson MF. Toxicology of food dyes. *International Journal of Occupational and Environmental Health*. 2012;**18**:220-246. DOI: 10.1179/1077352512Z.000000000034
- [8] Hunger K. Industrial dyes: Chemistry, properties. *Journal of the American Chemical Society*. 2003a;**125**:10144. DOI: 10.1021/ja0335418
- [9] Hunger K. Industrial dyes: Chemistry, properties, applications edited by Klaus Hunger (Kelkheim, Germany). Wiley-VCH: Weinheim. 2003. Xxiv + 600 pp. \$185.00. ISBN 3-527-30426-6. *Journal of the American Chemical Society*. 2003b;**125**:10144-10144. DOI: 10.1021/ja0335418
- [10] Chudgar RJ, Oakes J. Dyes, azo. In: *Kirk-Othmer Encycl. Chem. Technol.* Hoboken, NJ, USA: John Wiley & Sons, Inc.; 2014
- [11] Drumond Chequer FM, de Oliveira GAR, Anastacio Ferraz ER, Carvalho J, Boldrin Zanoni MV, de Oliveira DP. Textile dyes: Dyeing process and environmental impact. In: *Eco-Friendly Textile Dyeing and Finishing*. InTech: IntechOpen; 2013. DOI: 10.5772/53659
- [12] Azbar N, Yonar T, Kestioglu K. Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. *Chemosphere*. 2004;**55**:35-43. DOI: 10.1016/j.chemosphere.2003.10.046
- [13] Rai HS, Bhattacharyya MS, Singh J, Bansal TK, Vats P, Banerjee UC. Removal of dyes from the effluent of textile and dyestuff manufacturing industry: A review of emerging techniques with reference to biological treatment. *Critical Reviews in Environmental Science and Technology*. 2005;**35**:219-238. DOI: 10.1080/10643380590917932

- [14] Yagub MT, Sen TK, Afroze S, Ang HM. Dye and its removal from aqueous solution by adsorption: A review. *Advances in Colloid and Interface Science*. 2014;**209**:172-184. DOI: 10.1016/j.cis.2014.04.002
- [15] Nidheesh PV, Gandhimathi R, Velmathi S, Sanjini NS. Magnetite as a heterogeneous electro Fenton catalyst for the removal of Rhodamine B from aqueous solution. *RSC Advances*. 2014;**4**:5698. DOI: 10.1039/c3ra46969g
- [16] Gupta VK, Jain R, Nayak A, Agarwal S, Shrivastava M. Removal of the hazardous dye-Tartrazine by photodegradation on titanium dioxide surface. *Materials Science and Engineering: C*. 2011;**31**:1062-1067. DOI: 10.1016/j.msec.2011.03.006
- [17] Hussain S, Gul S, Khan S, Rehman H, Ishaq M, Khan A, et al. Removal of Cr(VI) from aqueous solution using brick kiln chimney waste as adsorbent. *Desalination and Water Treatment*. 2015a;**53**:373-381. DOI: 10.1080/19443994.2013.837001
- [18] Mittal A, Kurup L. Column operations for the removal and recovery of a hazardous dye 'acid red -27' from aqueous solutions, using waste materials - bottom ash and de-oiled soya. *Ecol. Environmental Conservation*. 2006;**12**:181-186
- [19] Thiam A, Sirés I, Brillas E. Treatment of a mixture of food color additives (E122, E124 and E129) in different water matrices by UVA and solar photoelectro-Fenton. *Water Research*. 2015;**81**:178-187. DOI: 10.1016/j.watres.2015.05.057
- [20] Moreira FC, Boaventura RAR, Brillas E, Vilar VJP. Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters. *Applied Catalysis B: Environmental*. 2017;**202**:217-261
- [21] Nidheesh PV, Gandhimathi R, Ramesh ST. Degradation of dyes from aqueous solution by Fenton processes: A review. *Environmental Science and Pollution Research*. 2013;**20**:2099-2132. DOI: 10.1007/s11356-012-1385-z
- [22] Li X, Jin X, Zhao N, Angelidaki I, Zhang Y. Novel bio-electro-Fenton technology for azo dye wastewater treatment using microbial reverse-electrodialysis electrolysis cell. *Bioresource Technology*. 2017;**228**:322-329. DOI: 10.1016/j.biortech.2016.12.114
- [23] Ikhlaq A, Kasprzyk-Hordern B. Catalytic ozonation of chlorinated VOCs on ZSM-5 zeolites and alumina: Formation of chlorides. *Applied Catalysis B: Environmental*. 2017;**200**:274-282. DOI: 10.1016/j.apcatb.2016.07.019
- [24] Pereira GF, El-Ghenymy A, Thiam A, Carlesi C, Eguiluz KIB, Salazar-Banda GR, et al. Effective removal of Orange-G azo dye from water by electro-Fenton and photoelectro-Fenton processes using a boron-doped diamond anode. *Separation and Purification Technology*. 2016;**160**:145-151. DOI: 10.1016/j.seppur.2016.01.029
- [25] Erkurt EA, Erkurt HA, Unyayar A. *Decolorization of Azo Dyes by White Rot Fungi*. Berlin, Heidelberg: Springer; 2010. pp. 157-167
- [26] van der Zee FP, Villaverde S. Combined anaerobic-aerobic treatment of azo dyes—A short review of bioreactor studies. *Water Research*. 2005;**39**:1425-1440. DOI: 10.1016/j.watres.2005.03.007
- [27] Aksu Z. Application of biosorption for the removal of organic pollutants: A review. *Process Biochemistry*. 2005;**40**:997-1026. DOI: 10.1016/j.procbio.2004.04.008

- [28] Martínez-Huitle C a, Brillas E. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review. *Applied Catalysis B: Environmental*. 2009;**87**:105-145. DOI: 10.1016/j.apcatb.2008.09.017
- [29] Modirshahla N, Behnajady MA. Photooxidative degradation of malachite green (MG) by UV/H₂O₂: Influence of operational parameters and kinetic modeling. *Dyes and Pigments*. 2006;**70**:54-59. DOI: 10.1016/j.dyepig.2005.04.012
- [30] Hussain S, Steter JR, Gul S, Motheo AJ. Photo-assisted electrochemical degradation of sulfamethoxazole using a Ti/Ru 0.3 Ti 0.7 O₂ anode: Mechanistic and kinetic features of the process. *Journal of Environmental Management*. 2017;**201**:153-162. DOI: 10.1016/j.jenvman.2017.06.043
- [31] Nilsson A, Ronlán A, Parker VD. Anodic oxidation of phenolic compounds. Part III. Anodic hydroxylation of phenols. A simple general synthesis of 4-alkyl-4-hydroxycyclo-hexa-2,5-dienones from 4-alkylphenols. *Journal of the Chemical Society, Perkin Transactions 1*. 1973:2337-2345. DOI: 10.1039/P19730002337
- [32] Sirés I, Brillas E, Oturan MA, Rodrigo MA, Panizza M. Electrochemical advanced oxidation processes: Today and tomorrow. A review. *Environmental Science and Pollution Research International*. 2014;**21**:8336-8367. DOI: 10.1007/s11356-014-2783-1
- [33] Zhang F, Feng C, Li W, Cui J. Indirect electrochemical oxidation of dye wastewater containing acid Orange 7 using Ti/RuO₂-Pt electrode. *International Journal of Electrochemical Science*. 2014;**9**:943-954
- [34] Hussain S, Gul S, Steter JR, Miwa DW, Motheo AJ. Route of electrochemical oxidation of the antibiotic sulfamethoxazole on a mixed oxide anode. *Environmental Science and Pollution Research*. 2015b;**22**:15004-15015. DOI: 10.1007/s11356-015-4699-9
- [35] Rocha JHB, Gomes MMS, Fernandes NS, Da Silva DR, Martínez-Huitle CA. Application of electrochemical oxidation as alternative treatment of produced water generated by Brazilian petrochemical industry. *Fuel Processing Technology*. 2012;**96**:80-87. DOI: 10.1016/j.fuproc.2011.12.011
- [36] Comninellis C, Nerini A. Anodic oxidation of phenol in the presence of NaCl for wastewater treatment. *Journal of Applied Electrochemistry*. 1995;**25**:23-28. DOI: 10.1007/BF00251260
- [37] Panizza M, Cerisola G. Direct and mediated anodic oxidation of organic pollutants. *Chemical Reviews*. 2009;**109**:6541-6569. DOI: 10.1021/cr9001319
- [38] Garcia-Segura S, Vieira dos Santos E, Martínez-Huitle CA. Role of sp³/sp² ratio on the electrocatalytic properties of boron-doped diamond electrodes: A mini review. *Electrochemistry Communications*. 2015;**59**:52-55. DOI: 10.1016/j.elecom.2015.07.002
- [39] Tavares MG, da Silva LVA, Sales Solano AM, Tonholo J, Martínez-Huitle CA, Zanta CLPS. Electrochemical oxidation of methyl red using Ti/Ru 0.3Ti 0.7O₂ and Ti/Pt anodes. *Chemical Engineering Journal*. 2012;**204-206**:141-150. DOI: 10.1016/j.cej.2012.07.056
- [40] Radjenovic J, Sedlak DL. Challenges and opportunities for electrochemical processes as next-generation

Technologies for the Treatment of contaminated water. *Environmental Science & Technology*. 2015;**49**:11292-11302. DOI: 10.1021/acs.est.5b02414

treatment of wastewater containing organic pollutants. In: *Electrochemistry for the Environment*. New York: Springer; 2010. pp. 25-54

[41] Abdesslem AK, Oturan MA, Oturan N, Bellakhal N, Dachraoui M. Treatment of an aqueous pesticides mixture solution by direct and indirect electrochemical advanced oxidation processes. *International Journal of Environmental Analytical Chemistry*. 2010;**90**:468-477. DOI: 10.1080/03067310902999132

[48] Panizza M, Cerisola G. Electrochemical oxidation of 2-naphthol with in situ electro-generated active chlorine. *Electrochimica Acta*. 2003;**48**:1515-1519

[42] Martínez-Huitle C, Ferro S, De Battisti A. Electrochemical incineration of oxalic acid. *Electrochimica Acta*. 2004;**49**:4027-4034. DOI: 10.1016/j.electacta.2004.01.083

[43] Rajkumar D, Kim JG. Oxidation of various reactive dyes with in situ electro-generated active chlorine for textile dyeing industry wastewater treatment. *Journal of Hazardous Materials*. 2006;**136**:203-212. DOI: 10.1016/j.jhazmat.2005.11.096

[44] da Silva RG, Aquino Neto S, de Andrade AR. Electrochemical degradation of reactive dyes at different DSA® compositions. *Journal of the Brazilian Chemical Society*. 2011;**22**:126-133. DOI: 10.1590/S0103-50532011000100017

[45] Bonfatti F, Ferro S, Lavezzo F, Malacarne M, Lodi G, De Battisti A. Electrochemical incineration of glucose as a model organic substrate. II. Role of active chlorine mediation. *Journal of the Electrochemical Society*. 2000b;**147**:592-596

[46] Bonfatti F, De Battisti A, Ferro S, Lodi G, Osti S. Anodic mineralization of organic substrates in chloride-containing aqueous media. *Electrochimica Acta*. 2000a;**46**:305-314. DOI: 10.1016/S0013-4686(00)00586-7

[47] Panizza M. Importance of electrode material in the electrochemical