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DEGRADATION OF AZO DYES FROM EFFLUENTS: A MINI REVIEW FOCUSING ON COMPARISON BETWEEN CURRENTLY EXISTING INDUSTRIAL METHODS AND GREEN OXIDATION CATALYSIS TREATMENT INVOLVING Fe-TAML AND H_2O_2

(Degradasi Pewarna Azo daripada Efluen: Sebuah Mini Ulasan yang Memfokuskan Perbandingan Antara Teknik Industri yang Kini Wujud dan Rawatan Pemangkinan Pengoksidaan Hijau Melibatkan Fe-TAML dan H_2O_2)

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Abstract

Dyes are widely used as coloring agents globally in the industrial field, especially in the textile industry. As proof, 10,000 types of dyes have been introduced and are continuously used, reaching a usage viability of 700,000 tons. The widespread use of synthetic dyes is caused by their economic factors, ready availability, superior strength, and ability to cover a wide range of shades. However, the discharge of commercial dyes is increasing at a swift rate as industrialization continues to grow, leading to severe hazards to living organisms due to their toxic and harmful impacts. The discharge of dyes into water reservoirs is a concern because of their high toxicity and bioaccumulation in living organisms. One of the most used commercial dyes, azo dyes, possesses a benzidine function that needs to be treated soon due to its side effects. Dyes contain toxicity and have a strong tendency toward eutrophication. The major globally concerned issues are water and soil pollution. The massive use of these dyes in industrial sectors is the main reason behind these environmental issues. Even at concentrations lower than one ppm, around 10% of the untreated discharged dyes impart an intense color, making the water highly detrimental. As an unwanted consequence, this exhibits an immense environmental hazard to the surroundings. Thorough studies on dye metabolites and their constituents have been developed to reduce the acute diverse effects of dyes. However, a few outdated techniques such as ozonation and chlorination are still being utilized to break down untreated dye discharge for various reasons, including economic factors. In this review, the ability of the green oxidation catalysis method of degradation to degrade dye is reviewed owing to its eco-friendliness and safety.

Keywords: azo dyes, green oxidation, catalysis, degradation of dyes, toxicity

Abstrak

Pewarna telah digunakan secara meluas sebagai agen pewarna di dalam bidang industri global, terutamanya di dalam bidang tekstil. Buktinya, terdapat 10,000 jenis pewarna telah diperkenalkan dan digunakan secara berterusan sehingga mencapai tahap penggunaan 700,000 tan. Penggunaan pewarna sintetik yang secara meluas adalah disebabkan faktor ekonominya yang sedia ada, kekuatan yang unggul, dan kebolehan untuk meliputi julat warna. Pembuangan pewarna komersil telah meningkat secara pantas selari dengan kadar pertumbuhan perindustrian, menyebabkan risiko yang serius kepada hidupan bernyawa telah dikenal pasti kerana impak pewarna yang toksik dan berbahaya. Pembuangan pewarna di dalam takungan air diberi perhatian kerana kesan toksik yang tinggi dan bioakumulasi dalam hidupan bernyawa. Pewarna komersil yang sangat biasa digunakan, pewarna azo memiliki fungsi benzidine yang perlu dirawat dengan segera kerana kesan sampingannya. Pewarna mempunyai toksik yang tinggi dan mempunyai kecenderungan yang kuat terhadap eutrofikasi. Isu utama yang menjadi perhatian secara global adalah pencemaran air dan tanah. Penggunaan perwarna secara berleluasa dalam sektor industri adalah punca utama isu pencemaran ini berlaku. Walaupun pada kepekatan bawah daripada 1 ppm, sekitar 10% pewarna yang dibuang dan tidak dirawat menghasilkan warna yang terang yang menyebabkan kandungan air menjadi sangat berbahaya. Sebagai kesan yang tidak diingini, bahan ini menunjukkan bahaya kepada alam sekitar dan sekelilingnya. Satu kajian yang mendalam mengenai metabolit pewarna dan unsur-unsur ini telah dibangunkan untuk mengurangkan pelbagai kesan pewarna yang berbahaya. Walau bagaimanapun, beberapa teknik yang lama seperti pengozonan dan pengklorinan masih digunakan untuk merawat pewarna yang dibuang dan tidak dirawat atas beberapa faktor termasuk faktor ekonomi. Dalam ulasan ini, kebolehan cara pemangkinan pengoksidaan hijau untuk degradasi pewarna diulaskan kerana ianya mesra alam dan selamat.

Kata kunci: pewarna azo, pengoksidaan hijau, pemangkinan, degradasi pewarna, ketoksikan

Introduction

The critical part of natural dye removal is using the appropriate method without creating environmental problems. As it is known, textile dyes discharge uncountable effluents that extant significant ecological issues. These effluents are mostly from dye manufacturing and textile wet processing industries. About 7 x 107 tons of synthetic dyes are produced annually worldwide, with over 10 000 tons of dyes being used by textile industries [1]. The discharge of dye is likely to rise phenomenally due to the growth in fiber consumption worldwide, such as wool, silk, and leather, which are included in the usage of clothes and bags, among others. Almost all modern dyes are degradation resistant and chemically stable by bleach, sunlight, water, and perspiration in a brief time or even a lifetime [2]. Since its structure contains an aromatic and -N=N- group, it harms the environment by being highly toxic, carcinogenic, and teratogenic [3]. The degradation of the dye-effluent-containing wastewater is quite tricky due to its resistance. Azo dyes are synthetic and organic chemical compounds applied in many industries, such as fabrics, medicine, food, and cosmetics. In addition, azo dyes contain combinations of the azo group chemically represented as (R-N = N-R'), with (-N=N-). Examples of azo dyes are orange (II), tartrazine, Congo red, eriochrome black T, methylene blue, and brilliant green [4]. Dyes in wastewater, especially azo dyes like Orange (II), create aesthetic problem [2] that limits the usage of the water and lessens the effectiveness of wastewater treatment using microbiological method due to its toxicity to the environment and harm to organisms [5].

There are physical, chemical, and biological methods to degrade dyes. One of the commonly used physical methods is adsorption, which is performed by removing organic compounds in water involving separating substances from one phase to the surface of another. Adsorption using activated carbon is an efficient process for organic micro-pollutant removals such as pesticides, fertilizers, cosmetics, pharmaceuticals, and personal care products, which are deployed by porous materials [6]. However, the cost of production, as well as the regeneration of activated carbon, is expensive. Various chemical methods have been employed by breaking the chemical bond, such as the azo bond, for degradation and decolorization of the dyes. Examples of chemical methods include ozonation, the Fenton reagent method, and photocatalytic reactions. The drawbacks of chemical methods are their less efficiency, limited versatility, high cost, and utilize a significant amount of energy. Abundant studies and research have taken severe actions, especially in attempting new methods for wastewater purifying treatment with less chemical impact on nature in terms of economically controlled [7]. An escalating number of contaminants continuously flow into the water supply annually, ranging from common contaminants like heavy metals to emerging micro-pollutants such as nitrosamines and endocrine disruptor compounds [7].

The possible method that can be conducted to overcome this kind of drawback is the application of green chemistry with the use of green oxidation catalyst technique through the Fe (III)–TAML-H_2O_2 system. Green oxidation technique is a technique that uses an oxidizing agent, which is safer towards the environment since it consumes less energy, low cost, and is environmentally friendly. The oxidizing agent usually oxidizes dye and eventually degrades its color. With current concerns regarding the treatment of dye effluents, there is an urgent need for a much greener degradation of pollutants. Besides being the greener method, it is also efficient, as proven by research that dye and other contaminants including 17α-ethynyl estradiol can be 100% degraded using this method [8]. In conclusion, it can be proved that Fe (III)-TAML-H_2O_2 systems have substantial potential in providing a greener technology.

Common azo dyes

Orange (II)

Orange (II) dye with IUPAC name [*p*-(2-hydroxy-1-naphthylazo) benzenesulfonic acid sodium salt]$^+$ as shown in Figure 1 with a molecular formula of $C_{16}H_{11}N_2NaO_4S$ is a most common anionic dye that is water soluble. (Usage) It is commonly used in industry for a range of raw materials such as nylon, aluminum, cosmetics, wool, silk, and detergents [9]. (Harmful effect) The orange (II) dye causes severe health issues in humans. The toxicity of orange (II) dye can cause upper respiratory tract, mucous membrane, eye, and skin irritation after ingestion. It can also lead to anemia, which can cause severe nausea, headaches, and water-borne diseases such as bone marrow loss [9]. Chronic toxicity is developed from the electron-withdrawing character of the azo group, which causes electron deficiency and reduces to carcinogenic amino compounds [10]. However, it is proven that azo dyes are able to permeate.

Organisms affect their metabolic processes by reacting with reducible chemicals produced. Production of 1-amino-2-naphthol from reduced Orange (II) dye can stimulate tumors in the bladder. In addition, Orange (II) dye can undergo enzymatic breakdown effortlessly and produce aromatic amines that can cause methemoglobinemia [11] and tend to oxidize the hem iron of hemoglobin from Fe(II) to Fe(III) and block oxygen-binding activity [12]. Besides, ingestion of Orange (II) dye is considered genotoxic [9]. Therefore, the dye needs to be removed, especially from the environment, to prevent the toxicity of the dye. The toxicity and carcinogenic nature are shown by removing Orange (II) dye by biodegradation and photosensitization on TiO_2 particles. The biodegradation of Orange (II) dye is carcinogenic towards the metabolic intermediates [2]. The generation of toxic intermediates during the process is possible and most likely to occur from the high solubility of the dye in water. There are some works of orange (II) dye removal reported. However, most of them revealed some side effects and need to be more environmentally friendly. Several degradation methods used in the degradation of Orange (II) dye include Fenton's reagent, photocatalyst, and heterogeneous [13].

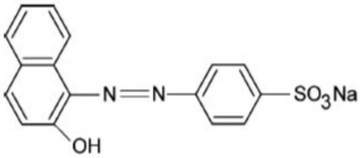

Figure 1. Structure of Orange (II) [p-(2-hydroxy-1-naphtlyazo) benzene sulfonic acid sodium salt]

Tartrazine

Tartrazine (Yellow Dye No.5), as shown in Figure 2, is an anionic azo dye widely used in the food industry as a coloring agent. Tartrazine originates from coal tar, which has been identified to have high toxicity and the ability to cause mutations in living things due to its high solubility in water. The high solubility in water makes the tartrazine interact with the body and form allergic reactions when in contact with the cellular processes in the body. Tartrazine is potentially phototoxic [14] and proved as a possible cause of angioedema, urticaria, and asthma [15]. Since food azo dyes are not eco-friendly [16] as it is non-biodegradable, the conventional biological treatment processes are inefficient for degrading these dyes in wastewater. Hence, physio-chemical processes are typically used for azo dyes wastewater treatment. However, the removal processes produce a lump of sludge that requires good treatment. This dye has been degraded by the benzoic acid/TiO_2 system with 99.08% removal within 90 minutes [17]. The optimum H_2O_2 concentration for T degradation is 2 mM. Under experimental conditions, 95% of the T can be degraded by a novel Fe-composite (NZ-A-Fe) containing iron in a natural zeolite [18].

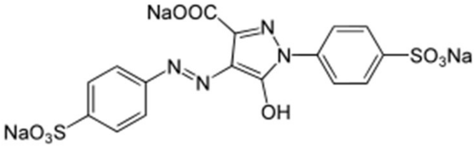

Figure 2. Chemical structure of tartrazine

Congo red

Figure 3 shows the structure of Congo red dye or knowns as sodium salt of 3,3′-([1,1′-biphenyl]-4,4′-diyl) bis (4-aminonaphthalene-1-sulfonic acid). Congo red is water soluble and yields a red colloidal solution. It is a well-known dye belonging to an anionic group commonly used in most industries, including the textile and paper industry. As an additional usage, it plays a vital role in diagnosing amyloidosis for amyloid as a pH indicator [19]. In addition, it also helps to detect free hydrochloric acid in gastric contents. Congo red adversely affects the human body, leading to diseases such as platelet aggregation, thrombocytopenia, and disseminated micro-embolism by lowering blood protein content [20]. Regarding this severe problem, several methods have been studied for successfully degrading Congo red using different nanomaterials [21] such as TiO_2 nanoparticles and bimetallic Fe–Zn nanoparticles [22].

The commonly used metallic nanoparticles such as Ru act as electron donors in azo bond conversion using a reducing agent through electron transfer. As desired results, the degradation rate of Congo red has increased by 200% [23]. Extract from Chinese spinach leaf, *Amaranthus gangeticus Linn,* has been used to synthesize silver nanoparticles with good catalytic efficiency by 50% within 15 minutes [24] for degrading Congo red dye. In addition, the biogenic silver nanoparticles with Senna leaf demonstrated 89.6% degradation of Congo red, onion silver nanoparticles, and acacia catechu with 96% and 97% degradation, respectively [25].

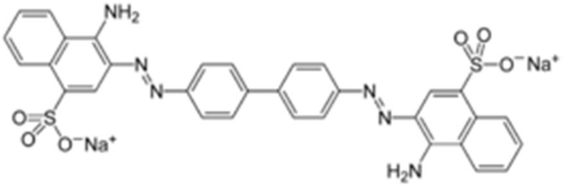

Figure 3. Chemical structure of Congo Red dye

Eriochrome Black T

Eriochrome Black T or Sodium 1-[1-Hydroxynaphthylazo]-6-nitro-2-naphthol-4-sulfonate structure is shown in Figure 4. It is commonly utilized in silk, wool, and nylon dyeing. It is also widely used in today's laboratories to determine the pre-accurate estimation of Zn^{2+}, Ca^{2+}, and Mg^{2+} ions [26]. Carcinogenic azo dye is one of the trademarks of Eriochrome Black T with its intermediate product called Naphthoquinone, which is toxic and not a desired product [27]. A severe problem has arisen worldwide for successfully treating Eriochrome Black T-containing effluent since it can potentially be harmful if not well treated [28]. Nevertheless, the breakdown of Eriochrome Black T has been carried out by numerous researches as a future need basis using different nanomaterials.

It was successfully found that the photocatalytic degradation of Eriochrome Black T has been enhanced to 88% with crystalline anatase TiO_2 under basic conditions around pH 11.0, which occurred from the higher concentration of hydroxyl radicals [29]. Generally, TiO_2 nanostructures of different shapes with Fe^{3+} and Pt^{4+} impregnation [30] successfully photodegraded Eriochrome Black T by about 82% within 90 mins under UV irradiation.

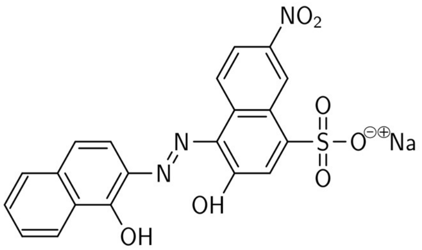

Figure 4. Chemical structure of Eriochrome Black T

Methylene blue

Methylthioninium chloride, commonly called Methylene blue, is a common thiazine dye used as a chemotherapeutic agent and anti-malarial in aquaculture [31]. The structure of methylene blue is shown in Figure 5 below. This dye gives side effects such as headache, shortness of breath, vomiting, high blood pressure, and allergic reaction [32]. Thiazine dye can effectively undergo degradation by a variety of nanomaterials, including copper-supported clay nanocomposite [33], ZnSe/Graphene nanocomposites, and titanium dioxide [34]. The implementation of Cu-supported organo-treated clay can result in the complete removal of the dye. However, 99.6% degradation efficiency has been obtained [35] using ZnSe/Graphene nanocomposites.

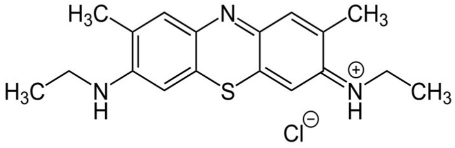

Figure 5. Chemical structure of methylene blue dye

Brilliant green

Brilliant green (zelyonka or zelenka), as shown in Figure 6, is a universally known cationic dye used as a biological stain and an antiseptic [36]. This dye displays an explicitly tremendous effect on gram-positive bacteria. This Brilliant green is highly carcinogenic to target organs and lungs after ingestion [37]. About 92% of the dye has been adsorbed by nano ferrites effectively under optimized conditions [38]. TiO_2 nanoparticles and Graphene oxide are usually doped with alkaline earth metal ions such as Sr^{2+}. Graphene oxide nanoparticles showed a degradation value of 93% in 10 min [39], while 96% of degradation efficiency was obtained when doped with TiO_2 nanoparticles within 1 hour [40].

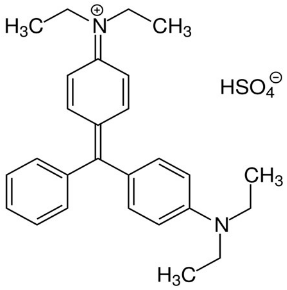

Figure 6. Chemical structure of the brilliant green dye

Current approach used in dye wastewater treatment place for dye degradation

Since dyes started being used in the textile industry, comprehensive treatment methods have yet to be introduced for dye wastewater treatment. As there are few techniques introduced since then, oxidation, anaerobic treatment, adsorption, and coagulation are majorly used methods in physical and chemical treatments for effluents containing various dyes. Therefore, there are some current approaches used in dye wastewater treatment places for dye degradation, which are direct chemical oxidation, oxidative processes with H_2O_2, ozonation, oxidation processes with sodium hypochlorite, photochemical oxidation process, electrochemical oxidation process, and combination of advanced chemical and biological processes.

Direct chemical oxidation

Direct chemical oxidation is an old conventional method for degrading water-soluble dyes in textile wastewater. Nonetheless, water-insoluble disperse dyes have chlorine decolorization resistance, making decolorization of reactive dyes require extended time for treatment. Moreover, dye chromophores with an amino or substituted amino group are susceptible to rapid chlorine decolorization. The chlorine treatment produces toxic chlorinated organics including halogenated hydrocarbons that harm humans and the environment [41]. The general advantages of chemical oxidation are rapid reaction rates, mineralization of organics, and removal of soluble and insoluble dyes, with the overall disadvantage of not being suitable for dispersed dyes. They release toxic compounds such as aromatic amines and involve complex chemistry [42].

Oxidative processes with hydrogen peroxide

The oxidative process with hydrogen peroxide (H_2O_2) is an alternative wastewater treatment that has been done using two systems: a homogenous system and a heterogenous system [43]. A homogenous system uses UV light, chemical activators, and soluble catalysts (Fenton reagents). The Fenton reagent utilizes hydrogen peroxide, which is then activated by iron salts and Fe^{2+} salts. This is done without UV producing hydroxyl radicals (OH). These radicals are strong oxidants than H_2O_2 and ozone but are harmful to environments when released into thin air. At the same time, the heterogenous system uses semiconductors like TiO_2 and modified zeolites with Fe and Al, such as FeY11.5 and FeY5.

The homogenous catalytic oxidation demonstrated color removal of 56.20% at a pH of 4 for Remazol Rose RB and Remazol Arancio 3R dye-containing effluents [44] with a minimal 0.18 M of H_2O_2 and 1.45 mM of Fe^{2+}. Meanwhile, heterogenous catalytic oxidation led to color removal of 53% - 83% at pH 3-5 for Procion Marine H-pEXL dye-containing effluents [45] with H_2O_2 and FeY11.5 within 10 mins. As for H_2O_2 and FeY5 at pH= 5 using the same textile effluent in the treatment, 95% color removal was achieved within 10 min of oxidation and 97% for 60 min of oxidation [46].

Ozonation process

Ozonation is the most straightforward process, which depends on oxidizing agents and ozone. The ozone efficiently decomposes organic pollutants from industrial effluents and cleaves aromatic rings in textile dyes. Ozone with conjugated double bonds decomposes organic dyes and produces carcinogenic compounds. This process has most probably been used with a physical method to reduce its toxicity with extra costs required. Based on several studies, it was proven that ozone can react with dye molecules either directly or indirectly [47]. Since the ozone molecule is an electron acceptor, the hydroxide ions catalyze the ozone decomposition into hydroxyl radicals ($\cdot OH$) in effluents through the direct pathway. However, due to its complicated process, the indirect path is not recommended for industrial dye degradation.

The main advantages of ozonation are that ozone does not affect wastewater in terms of volume and minimizes the production of extra sludge apart from its application in a gaseous state. The disadvantages of ozonation include its destabilization by the temperature, the short half-life of around 20 min, and the installation of an ozonation plant that requires additional cost. The combination with irradiation [48] improves the performance of ozonation. In a study, the treatment of wastewater containing dye effluent indicated color removal of 62% with ozone [49], followed by chemical coagulation using $Ca(OH)_2$.

Oxidation process with sodium hypochlorite

The oxidation process with sodium hypochlorite starts when the Cl^- ion attacks the amino group in the dye molecule, followed by initiation and azo-bond cleavage acceleration. This dye removal and decolorization process can be favored by increasing the chlorine concentration and decreasing pH [50]. The dye-containing amino or substituted amino groups on the naphthalene ring, such as naphtylamino-sulphonic acid and amino-naphthol, are most vulnerable to the decolorization of chlorine. Thus, this process is unsuitable for dispersing dye. The negative effect of this treatment is that it is prone to release aromatic amines and toxic molecules into water, making it a less desired treatment. Furthermore, pigments used worldwide contain chlorine of approximately 40% [51], while this method uses less than 0.02% of the total chlorine production.

Photochemical oxidation process

The presence of H_2O_2 is most necessary for the photochemical process. This process decomposes dye molecules into low-weight organic molecules such as water, carbon dioxide, hydrides, and inorganic oxides. The additional by-products produced are organic and inorganic acids, organic aldehydes, and halides, which vary depending on the initial materials used in decolorization treatment. The generation of hydroperoxide radicals is shown in Equation 1, while hydroxyl radicals as shown in Equation 2 will initiate the dye decomposition.

$$H_2O_2 + HO\cdot \rightarrow HO_2\cdot + H_2O \qquad (1)$$

$$H_2O_2 + h\upsilon \rightarrow 2HO\cdot \quad (2)$$

The treatment is set up in a batch or continuous column unit and mainly depends on the dye structure, pH, and intensity of the UV radiation. This photo-oxidation treatment displayed color removal around 81% - 94% after 1 hour with 88 mM H_2O_2 with minimal pH at 4 [52] for Acid Red G dye-containing effluent.

Electrochemical oxidation process

The electrochemical treatment is a unique treatment that presents high removal efficiencies and pollution control for dispersed and metal complex dyes known as acid dyes. The oxidizing agent in the electrochemical process is hypochlorous acid or hypochlorite ion produced from naturally occurring chloride ions [53]. The by-products are commonly less hazardous than any other oxidation process discharged into the water without health precautions or environmental risks.

Some advantages of this treatment include the requirement of no additional chemicals, simplified operation, prevention of the production of unwanted by-products, and minimization of all emissions such as the emission of solid waste, liquid effluent, and gases [54]. Electrochemical oxidation is believed to be an economical and efficient treatment for recycling textile wastewater. However, since the metallic electrode in the cell generates metallic hydroxide, this process has usage limits.

The color removal for the effluent containing blue-26 anthraquinone dye demonstrated the highest percentage within 220 min of electrolysis, a higher rate at neutral pH of 7 using NaCl, and a current density of 4.5 A/dm^2 [55]. The color removal obtained was 95.2% for the same dye-containing effluent in a flow reactor working at a rate of 5 mL/min and a current density of 29.9 mA/cm^2.

Combination of advanced chemical and biological processes

Photodegradation and biodegradation are the most appropriate methods for degrading the harmful compounds in wastewater. Aromatic hydrocarbons and phenols use photodegradation to degrade effluents containing dye. Generally, the pollutants are eliminated using biodegradation by microbes. Implementation of chemical oxidation together with biological processes proves the enhancement of efficiency and lowers operating costs [56].

The process begins when H_2O_2 and Fe (II) are operated in optimum requirements in the combined process. At 25 °C, the biological reactor was operated for 10 cycles for 12 hours per cycle. After adjusting to neutral pH in the first cycle, the biological reactor was supplemented with 2.5 L of wastewater. Adding 2.5 L of activated sludge made the final volume 5 L. The reactor was supplemented with 2.5 L of effluent to compensate for the quantity of treated effluent released. Chemical Oxygen Demand (COD) and Dissolved Organic Carbon (DOC) were examined at the end of each cycle. Automatic unit control and data acquisition were attained using Lab View 5.0 software [57]. The advantages of this method are enhanced efficiency and lower operating costs. This system significantly achieved 99% of color removal, COD removal of 88%–98%, and 91%–98% of DOC removal. Furthermore, this combined system reduced operating costs by 24–39%. The by-products include DCIP reductase, veratryl alcohol oxidase, riboflavin reductase, azo reductase, and laccase. However, this method involves complicated processes with high maintenance costs.

Proposed approach in degradation of Orange (II) dye in wastewater

This part explains the oxidation of the Fe-TAMLs/ H_2O_2 System (Oxidative Catalysis), the general procedure for degradation of Orange II by Fe(III)TAML-H_2O_2, and toxicity measurements of Orange (II) dye. This method can potentially reduce cost as the reagent requirement can be decreased as oxidation efficiency.

Oxidation of Fe-TAMLs/ H_2O_2 system (oxidative catalysis)

Collins and Lenoir developed a landmark example based on a Fe (III) metal center coordinated to a tetra-amido macrocycle that coordinates the metal with four anionic amide groups (Fe-TAML). The activation of H_2O_2 acts as a terminal oxidant owing to its highly active characteristics toward the complete degradation of different species in aqueous solutions such as resistant chlorinated phenol derivatives, water effluents, and dyes from paper industries [58]. This green oxidation method is a notable application involving the total degradation of organophosphorus pesticides such as Parathion and Fenitrothion with a prevalent agricultural use [59].

Iron (III)-Tetra Amidato Macrocyclic Ligand (TAML) is a unique catalyst suitable for commercialized industrial uses in wastewater treatment. The development of this catalyst started over 20 years, which revealed its unique properties. Common biochemical elements form this catalyst with little or no toxicity properties impacting its biodegradable functionalities. It has high stability in various ranges of pH and is also water-soluble. Besides, it is effective at minute concentrations from 0.1 to 4 ppm.

Fe-TAML catalysts that exhibit oxidation catalysis act as among the finest green catalysts [60]. The use of hydrogen peroxide as an essential source of oxidizing equivalent can be done flawlessly by TAML oxidant activators [61]. The oxidation mechanism of catalysis by Fe (III)-TAML is crucial for industrial and academic purposes. The synthetic oxidation catalyst process displays unprecedented selectivity and high reactivity water while utilizing environmentally friendly oxidants. This research could be a milestone in the further development of green chemistry in the future [61]. Green oxidation catalysis is a frontier at risk elimination for further development. Green procedures that decrease risk detoxify effluent streams and serve as substitutes for polluting processes have been used in several circumstances. Further improvement of TAML systems is potentially suitable for various new green applications from the intermediate, which allows the process.

The dye is reduced by TAML activators when compared with incumbent technologies. The TAML risk reduction theory is supported by mechanistic understanding developed by previous studies proposed in Fenton chemistry, which served as a foundation for developing efficient catalysts [62]. The Fe (II) salts activate the oxidation process in the presence of H_2O_2 known as Fenton chemistry. This chemistry induces the generation of radical species in solution and a wide range of organic substrates with poor selectivity [63].

The tendency to decompose the oxidant, which implies the need for over-stoichiometric amounts of H_2O_2, is one of the main drawbacks of this system [64]. It also requires help controlling the coordination of the oxidation state of the metal and geometry, which undoubtedly leads to the coexistence of some analogous oxidation processes. Nevertheless, it appears to be fine and produces toxic by-products like other wastewater treatment methods, whereas only produces organic compounds in excess amounts. Catalytic oxidation processes can be found in applications including environmental clean-up using soluble iron complexes. Compared to the electrochemical method, this system is cost-effective and relies on readily available and inexpensive reagents such as hydrogen peroxide and ferrous ions. Besides, it is simple to set up and operate and can be applied to a wide range of wastewater samples or dye formulations. It is easy to control the reaction conditions such as pH, temperature, and dosage of H_2O_2, in addition to its high degradation efficiency.

General procedure for degradation of Orange II by Fe(III)TAML-H_2O_2

Under isothermal conditions, Orange (II) was added along with buffered solution stirring at a precision temperature of ± 0.5 °C. Then, the final concentration of H_2O_2 of 0.01 M was achieved after a diverse amount of 30% H_2O_2 was added. The absorption band for Orange (II) at the maximum was then examined. More precisely, it was only done once using a UV-Vis spectrophotometer. Lastly, quenching of the mixture was carried out by an appropriate method for the analysis, which involved adding a quenching agent to neutralize the oxidizing species and stop the reaction. A sodium bisulfite solution was prepared by dissolving a proper amount of sodium bisulfite powder in deionized water. The concentration of sodium bisulfite should be sufficient to react with the excess hydrogen peroxide and oxidizing species present in the mixture. Once the desired reaction time has elapsed, the sodium bisulfite solution was carefully added to the reaction mixture. The amount of sodium bisulfite required depends on the specific reaction conditions and the concentration of the oxidizing agents. It was typically added in excess to ensure complete quenching. After that, the reaction mixture was thoroughly mixed to ensure proper contact between the quenching agent and the reactive species. The mixture was allowed to stand briefly to provide a complete reaction and neutralization of the oxidizing agents.

Toxicity measurements of Orange (II) Dye

The toxicity of the dye and degradation products was analyzed using *Daphnia magna* of one day born at different concentrations of *Daphnia magna* (0.8, 1.3, 2.2, 3.6, 6.0, and 10.0 mg/L). Laboratory-grown daphniids were fed with *Scenedesmus subspicatus chodat,* cultured microbes. Doubly distilled water was used to prepare all the solutions at 20 °C under room temperature. Then, each test beaker was filled with 10 daphniids and 50 mL of final volume to identify the toxicity levels by immobilization test method for 24 hours of exposure. Results were evaluated based on the immobilization percentage obtained by dividing the number of immobilized organisms by the total organisms. The toxicity of wastewater samples is considered toxic when the immobilization percentage is higher than 50% [65].

Main findings for degradation of Orange II by Fe(III)TAML-H_2O_2

In optimizing the degradation of Orange (II) dye, the parameters involved were the concentration of Fe-TAML, H_2O_2, and pH. Initially, the Fe-TAML catalyst (0.5 μM) and H_2O_2 (16 mM) showed the color removal of 41% from wastewater in the Fe-TAML-H_2O_2 system after 30 minutes at 50 °C in the first trial [66] as shown in Figure 7(a). Moreover, the reduction of color differed from 9% to 42%, which led to the final color of 495 ± 68 CPU over seven repetitions without any mixings. The final color of 348 ± 8 CPU while mixing was used. The production of hydroxyl radicals occurred with the reaction between aqueous Fe^{2+} salts and H_2O_2 solutions. The color evaluation was performed by ultraviolet-visible spectroscopy (UV-Vis).

The maximum color removal of 44% was obtained under the most favorable conditions of the catalyst at 1 μM and H_2O_2 at 16 μM, which suggests its ability to reduce cost and time significantly, as claimed by Pinzon-Espinosa [67]. Maximum color removal of about 55% as shown in Figure 7(b) was reached within approximately four hours. Based on Fe-TAML catalyst degradation characteristics that can speed up the rate of reaction and lower the activation energy, color removal will reach its maximum within one hour with conditions of catalyst at 3 μM and H_2O_2 at 20μM.

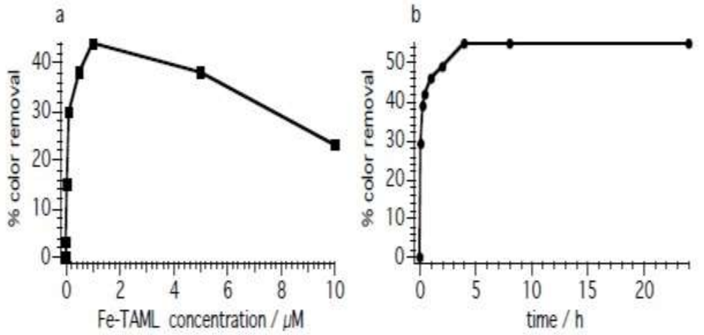

Figure 7. Effects of color removal dependence on Fe-TAML concentration (30 min)

Color removal probability was tested using Fe-TAML-H_2O_2, which might be caused by the reaction with catalyst breakdown derivatives, which are free Fe^{2+}/Fe^{3+}. The reactions were examined when the Fe-TAML catalyst was replaced by $FeCl_3$ [51]. The concentration of Fe^{3+} was similar to the catalyst concentration of Fe-TAML, which was about 1μM. There was no effect observed following the addition of

Fe^{3+}. Hence, the Fe-TAML-H_2O_2 combination is responsible for the degradation of the color. The H_2O_2 concentrations and reaction time, along with the optimization of the catalyst (by investigating the concentration, reaction time, and pH of the solution), were examined. The system's efficiency was demonstrated by a significant surge in color removal within a slight array of catalyst concentrations of 0.05 to 0.1 µM. Since Fe-TAML catalyzed H_2O_2 disproportionation at catalyst concentration larger than 5 µM, less color was removed [68].

The oxidation of Orange (II) was monitored by electronic spectroscopy. The dye has an intense absorption band with a maximum of 485 nm in water. Hydrogen peroxide oxidized Orange (II) very slowly, while Fe (III)-TAML activators immensely increased the rate. The spectral changes observed during catalyzed oxidation of Orange (II) dye are presented in Figure 8 below:

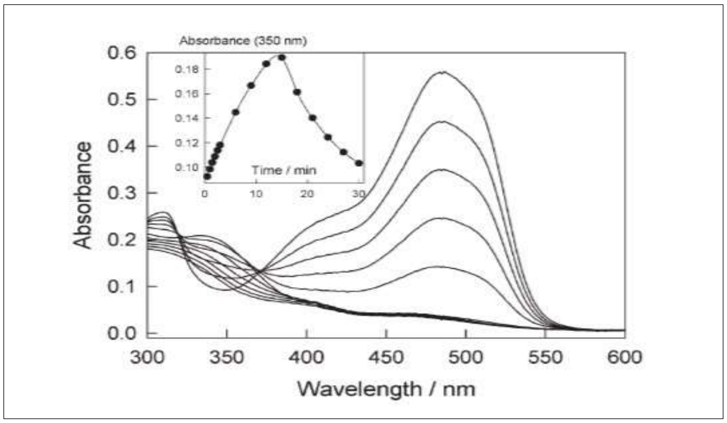

Figure 2. Spectral changes of Orange (II) catalytic oxidation

During treatment with the Fe-TAML-H_2O_2 system, the complex nature of the effluent brings difficulty in determining a high degree of certainty. The complexity of the effluent can arise from various factors, such as the presence of multiple contaminants, varying concentrations of pollutants, and diverse chemical compositions. These complexities make it difficult to precisely predict the treatment process's outcome and determine the certainty level in achieving desired results, thus may require a combination of scientific understanding, practical experience, and ongoing refinement of the treatment approaches. Still, several chemical analyses and spectroscopic methods can provide certain conceptions, including UV-Vis spectroscopy [66]. Firstly, the difference in ionization spectra revealing phenolic α-carbonyl and phenolic group structures in the sample of effluent fragment ions can provide evidence of the presence of phenolic alpha carbonyl groups in the sample. Phenolic alpha carbonyl groups typically refer to a carbonyl (C=O) group adjacent to a phenolic (OH) group. These groups can exhibit specific characteristic peaks in ionization spectra. The fragment ions can provide evidence regarding the presence of phenolic alpha carbonyl groups in the sample. Phenolic groups, referring to compounds containing a hydroxyl (OH) group attached to an aromatic ring, also exhibit characteristic features in ionization spectra. In mass spectrometry, phenolic compounds can produce a molecular ion peak (M+) corresponding to the intact molecule with the hydroxyl group.

The second treatment step involved exposing the Fe-TAML-H_2O_2 effluent to sodium periodate as oxidants using an oxidative procedure to maintain the facile, one-pot conversion approach [69]. Thirdly, the removal of aliphatic double bonds like stilbenes or alkenes from the treated material was demonstrated by controlled hydrogenation and effluents treated with Fe-TAML-H_2O_2. Lastly, groups of carbonyls like quinones and α-carbonyls were reduced using sodium borohydride indicating two types of structures that were eliminated from the treated samples. However, Fe-TAML-H_2O_2 treatment removed the mentioned structure efficiently. Some methods could ensure the structure is eliminated from the effluent, which include UV-Vis spectroscopy, high-performance liquid chromatography (HPLC), mass spectroscopy, and total organic carbon (TOC) instrument. Apart from that, some studies revealed that lowering the concentration of starting color is possible with Fe-TAML catalyst, even in the absence of H_2O_2. Non-aqueous chemistry describes that Fe-TAML catalyst can rapidly activate O_2. Direct reaction of the Fe-TAML catalyst with O_2 reduces the Fe-TAML catalyst. The catalyst then reacts with oxygen to oxidize other chromophores. [70]. As seen in Figure 9, the Fe-TAML catalyst is pH dependent. Meanwhile, pH 11 shows a higher initial rate compared to pH 9.

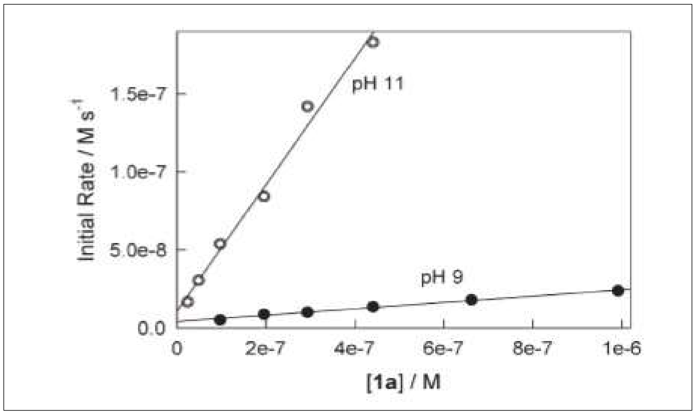

Figure 3. Initial rates of catalyzed bleaching of Orange (II) dye by H_2O_2 as a function at pH 9 and 11. Conditions:[Orange (II)] 4.5 x 10^{-5} M, [H_2O_2] 3.3 x 10^{-4} M, 25 °C

The evaluation of toxicity was done before and after the degradation. The non-toxic compounds, such as more minor aromatic compounds, carboxylic acid, and inorganic ions, were produced as degradation products. The initial toxicity of Orange (II) decreased after the treatment. The test sample's value measured toxicity using one-day-old *Daphnia magna* exposed to different dye concentrations. The percentage of immobilized or decreased *Daphnia magna* was calculated by plotting a dose-response curve representing the dye concentration versus the response (mortality or immobilization) of Daphnia magna. Later, the median lethal concentration (LC50) was determined, which is the concentration at which 50% of the Daphnia Magna are immobilized or deceased. This value indicates the toxicity of the Orange (II) dye to the test organism. The larger the number of values, the smaller the toxicity level. Figure 10 illustrates the effects of orange (II) and the degradation on the immobilization of D. Magna, showing maximum toxicity of 20% observed in both experiments. Daphnia *magna* in the control tubes showed zero mortality. This result demonstrates that the Fe (III)–TAML catalyzed degradation of Orange (II) by H_2O_2 is safe and free from the formation of toxic oxidation products [71].

Conclusion

Green oxidation catalysis treatment involving Fe (III)–TAML-H_2O_2 system has been proven to significantly impact the degradation of azo dye compared to other existing industrial methods. Based on this study, the system significantly degraded Orange (II) dye into non-toxic organic and biodegradable products. Meanwhile, the other method harms the environment and consumes more energy and cost. Extensive mineralization can be observed in its green chemistry principles, such as synthesized biofuels and green ZnO [72]. Oxidation has the potential to occur quickly compared to other chemical systems formerly conducted. The ecotoxicological examination suggests that the described method is much more environmentally harmless than metal catalysts including ruthenium (Ru) or osmium (Os). Thus, the application of green chemistry in the oxidation catalysis treatment involving the Fe (III)TAML-H_2O_2 system is greatly needed to treat dye effluents. In summary, Fe (III)TAML-H_2O_2 system has been significantly proven to carry substantial potential in providing a greener technology.

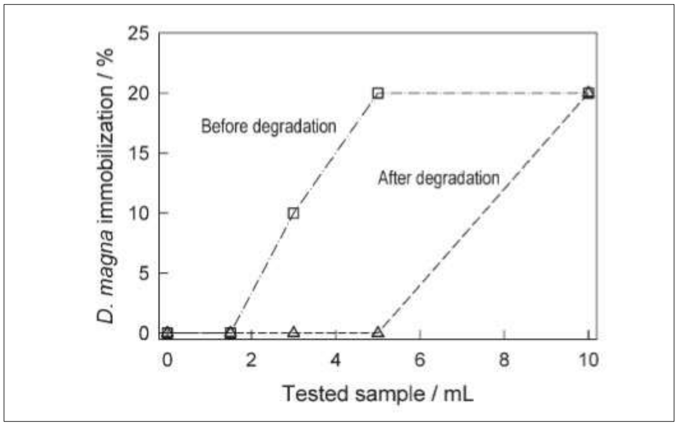

Figure 4. Effects of Orange (II) and its degradation products on immobilization of *Daphnia magna*. Conditions: [Orange II] 1 x 10^{-4} M, [H_2O_2] 1 x10^{-2} M, 25°C, pH 10 (0.02 M carbonate)

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