



# Study of Dyes and Methods of Their Removal, with a Focus on Studying Their Removal using Photocatalysts Based on Polyoxometalates: Review

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## Abstract

Dyes are important chemicals in industrial uses; however, they are considered hazardous materials because they accompany sewage and are one of the causes of serious diseases such as cancer if not treated properly. The aim of this study is to specify the effect of dyes on the environment and human health and to remove them from water using the photochemical agent (polyoxometalate). By studying two types of Phosphotungstic acid (PTA) and phosphomolybdic acid (PMA) due to the good possibility of loading these acids on other materials using mixing and precipitation ways and without the need for high temperatures, as they are prepared at room temperature. They are also solid materials that are easy to separate, quickly dissolve in water, non-toxic, and do not release dangerous gases, which led to the need to use them in removing dyes, as they gave high efficiency. The research explains a comprehensive review of the use of PTA and PMA acid in Visible light-enhanced degradation of organic dye pollutants for three dyes: methylene blue, methyl orange and chromium B. Previous research is reviewed, with special emphasis on the performance of the photocatalyst, conditions that increase its efficiency, and the proposed mechanisms for the combined photocatalysts of PTA and PMA acids in developing the photocatalytic process. Finally, recent findings in this area are discussed, and possible future research continuations are suggested.

**Keywords:** Dyes, Photocatalyst, Phosphotungstic Acid, Phosphomoldpic Acid

الإزالة التحفيزية للأصبغ العضوية باستخدام المحفزات الضوئية القائمة على البولي-  
اوكسومييتالات: مراجعة

وسام عبد الحسين جبار، مروة فائق عبد الجبار

## الخلاصة:

تعتبر الاصباغ مواد كيميائية مهمة في الاستخدامات الصناعية مع ذلك فانها تعتبر مواد خطرة لكونها مرافقة لمياه الصرف الصحي واحدى المسببات لأمراض خطيرة كمرض السرطان اذا لم يتم معالجتها بشكل صحيح، هدف هذه الدراسة معرفة تأثير الاصباغ على البيئة وصحة الانسان وازالتها من الماء باستخدام العامل الضوئي من (بولي-اوكسومييتالات) من خلال دراسة النوعين حامض الفوسفوتنغستك وحامض الفوسفوموليبدك وذلك لإمكانية التحميل الجيدة لهذه الحوامض على المواد الأخرى باستخدام طرق الخلط والترسيب و بدون الحاجة الى درجات حرارة عالية حيث انها تحضر عند درجة حرارة الغرفة كما انها مواد صلبة سهلة الفصل وسريعة الذوبان في الماء وغير سامه ولا تطلق غازات خطرة مما دعت الحاجة الى استخدامها في إزالة الاصباغ حيث أعطت كفاءة عالية، يوضح البحث اعادة النظر في لاستعمال حامض الفوسفوتنغستك وحامض الفوسفوموليبدك في التحلل الضوئي المعزز بالضوء المرئي للملوثات الصبغة العضوية لثلاث صبغات الميثيلين الازرق والمثيل البرتقالي والروموديوم ب. تم استعراض وتلخيص البحوث السابقة مع التركيز بشكل خاص على اداء العامل المساعد الضوئي والظروف التي تزيد من كفاءته والآليات المقترحة للمحفزات الضوئية المركبة لحامض الفوسفوتنغستك وحامض الفوسفوموليبدك في تطوير عملية التحفيز الضوئي. وأخيرا، تم مناقشة النتائج الأخيرة في هذا المجال، واقتراح استمرارية عمل البحوث المستقبلية الممكنة.

## 1. Introduction

Initial recognized utilize of organic dyes was a lot of four thousand years ago, when indigo blue dye was

found in mummy lids in Egyptian tombs. In 1856, a major development in the industrial dye industry occurred, when Perkin W. H. was able to prepare the



first purple dye using coal tar. Ever after then various modern chemicals dyes have been appended for rise listing of dyes [1][2]. There are over 100,000 Industrially obtainable dyes with more than seven thousand, one hundred and seven tons of dye manufactured per year worldwide , these dyes are great used in a number of manufactures, like texture, food, Books printing and cosmetics, with the cloth manufacturing the greatest use for dyes[3]. The texture manufactures yet mostly use artificial organic dyes. The great diversity in the use of dyes in fabrics leads to complexity in terms of increased competition in the market and thus a greater consumption of these dyes, the impact of the large consumption of these dyes is negatively reflected on the environment. Through the past ten years, environmental concerns related to the increased manufacturing and use of dyes have increased, and these issues are certainly affecting the textile dyes manufacturing in recent times. [4]. The widespread presence of organic dyes in industrial wastewaters from sectors such as paper, textile, and apparel industries results in significant environmental pollution [5],[6] Several studies have reported that approximately ten–twelve percent of dyes, such as Rhodamine B, Methylene Blue[7], Victoria blue[8], Rose Bengal[9], Indigo Carmine[10],Red 120[11], Eriochrome[12], , Black-T[13], and Thymol blue[12], are annually used in textile industries. However, a significant portion (around twenty percent) of these dyes is lost through manufactures and treatment processes, ending up in wastewater. These dye-contaminated wastes contain non-bio removable, extremely toxic, and intensely tinted compounds that pose harm to aquatic creatures.

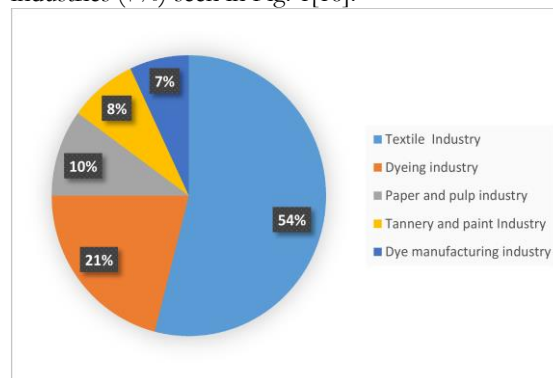
Dyes are visibly apparent in water level at extremely low doses (<1 mg/L) and can contaminate water natures. Therefore, removing dyes from wastewater stands imperative[14]. Dye manufacturing may modify amid ten thousand to seventy-seven thousand tons every year then the casualties are rated about 2% throughout manufacturing and about 10 % throughout uses, and effluents existence threw straight into the nature for emerging nations. Established on the information after 2013, annual manufacturing of fabrics was about thirty million tons, growing each year. Each ton of fabric needs about thirty tons of water for the dyeing operation, while every ton of dye manufacturing needs a rate of two hundred tons of water. That gives an overall of eighty million tons and ninety million tons of water consecutively is referred to dye manufacturing and fabric dyeing operation every year. Taking into consideration the quantity of contaminated with dye (2% - 10% consecutively through their manufacturing and uses), creation the dyestuff manufacturing accountable aimed at around 20% of the overall manufacturing H2O contamination. Hence, it is clear that aquatic contamination since dyes is an standing and rising problematic that requires consideration [15].

This study summarizes on considering the previous results of removing common dyes (Methylene Blue, Rhodamine-B, Methylene Orange)

from water using photocatalyst and studying the conditions such as effect of light source, initial concentration of dyes, dose of photocatalyst needed to remove dye, and volume of aqueous solution contaminated with the formula by comparing Where is the removal efficiency for each photocatalyst.

## 2. Uses of dyes and their effect on water

Comparing the discharge of dye effluent from different manufactures, textile manufacturing (54%) makes half of the present dye liquid waste seen in the world-broad environment followed by the dyeing manufactures (21%), paper and pulp manufactures (10%), paint manufactures (8%) and the dye industries (7%) seen in Fig. 1[16].



**Figure (1):** Comparing the discharge of dye effluent from different manufactures

The textile manufacturing is one of the most important uses of dyes, as large quantities of dyes are consumed in this process, the specifics of this procedure and its waste possible are described in Table 1[17].

Generally, textile processes include water and chemical materials. The dyeing operation needs a biggest amount of water, this leads to an increased load of impurities. Growing concern about the color of textile wastewater is returns in government regulation or criteria wanted by most companies[18].

**Table (1):** Water used for every textile industrial process.

Process	Description	Water use (liter/ton) product
Sizing	Lubricating the threads through texture by applying a sizing agent in the shape of a liquid water mixture. Sizing agents are normally polysaccharide-depended, but polymer-depended sizing agents can also be utilized.	500 – 8,200
Desizing	elimination of starch/size protective the thread, normally by enzymatic removal employing $\alpha$ -amylase.	2,500 – 21,000
Scouring	salts, and sizes (if case is procedure previously desizing, or the rest from desizing treatment). cleaning is performed by adding cleaning agent (normally alkali) and other auxiliaries like reducing agent, dispersants, or surfactants.	20,000 – 45,000



Bleaching	elimination of the origin color of the fiber. Important if the desirable textile output is colored in a pastel or greasy color.	2,500 – 25,000
Mercerizing	Refinement of textile stretchy intensity, stabilization, and luster via caustic increment.	17,000 – 32,000
Dyeing	putting color to the textile output by addition a coloring agent. In the dyeing operation, the textile output is soaked in a reservoir keeping dyes.	10,000 – 300,000
Printing	In the printing operation, color is connected to a specified site on the textile output to give an obvious designing.	8,000 – 16,000

### 3. Types of dyes

There are numerous kinds of dyes utilized in fabric manufactures., with the most used dyes is seen in Table 2 [19].

**Table (2):** Characterization of dyes kind

Kind of dyes	Characterization	Application ability	Ref.
Reactive	Dyes including chromophores are fit to react and form covalent ranges with nucleophilic positions in fibers.	Cotton, linen, wool, silk	[20]
Disperse	Dyes with depressed solubility in water awards colour to the fiber via H-range and Van Der Waals force while distracted in the water, rising comparatively depressed fastness.	Nylon, polyester	[21]
Direct	soft-to-use dyes that adhere itself to the fibers by adsorption, following isothermal balance adsorption kinetic precept. Inorganic electrolyte oftentimes inserts to boost dyes uptake.	Cotton, rayon, wool, silk	[22]
Acid	Anionic dyes that are applied in acidic (pH two – six) state. Color is used by ionic bond inter the dye and the fibers. Example of Acid dye: methylene orange.	Silk, nylon	[23]
Basic	Cationic dyes consisting amine-group and having best solubility in alcohol, predominating utilized along with ethanol to shape dye dough. Dyeing by ionic bond inter the dye and the passive, charged compound of the fibers, thus locating the Application ability where most of natural threads is positively-charged. Examples of basic dyes are methylene blue and rhodium B.	Acrylic, rayon (limited suitability)	[24]

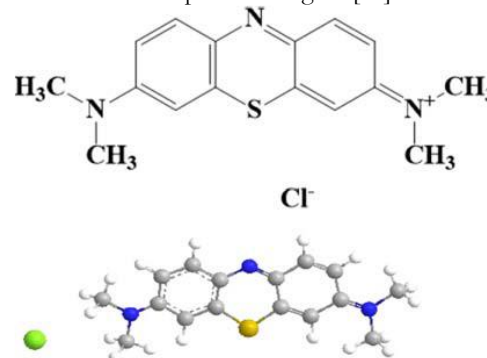
### 4. Common dyes

There are many common dyes, and the most important of these dyes will be presented.

#### 4.1 Methylene Blue

##### 4.1.1 Definition of Methylene Blue

Methylene Blue categorized as an aromatic heterocyclic basic dye with a molecular weight of (319.851) gm/mol. The IUPAC name [7 (dimethylamino) phenothiazine- 3- ylidene] dimethylazanium; chloride It is recognized as a cationic and primary thiazine dye, with a molecular formula of C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>ClS and exhibits high solubility in water. The molecular model , structure of methylene blue and its various character constructions are depicted in Fig. 2 [25].



**Figure (2):** displays the sample and construction of the MB dye particle and the various resonance structures of MB.

##### 4.1.2 Properties of Methylene Blue

Methylene Blue presents as a solid, odorless, dark green powder under standard conditions, producing a blue solution upon dissolution in water [26]. Its melting point falls within the range of 100–110 °C [27]. The coloration of methylene blue is determined by its chromophoric and auxochrome collections. The chromophore collection consists of the N–S conjugate scheme on the dominant aromatic heterocycle, while the auxo-chrome collection includes N-containing collections with only couple electrons on the benzene loop [28]. UV-analysis of methylene blue holds significant importance in photodegradation and adsorption studies, as nearly all assessments are conducted based on its Ultraviolet-visible spectroscopy. The absorption spectroscopy of methylene blue reveals a prominent absorption top at approximately 664 nm corresponding to a methylene blue monomer, alongside a shoulder peak around 612 nm associated with a methylene blue dimer. Additionally, dual bands emerge in the UV area by peaks at approximately 292 and 245 nm, linked to substituted benzene loops [29]. Absorption peaks regularly diminish as the photolysis reaction advancements [30].

##### 4.1.3 Degradation of Methylene Blue

Methylene Blue serves as a typical organic dye known for its stability under visible light irradiation [31]. Its resilience poses challenges for efficient degradation solely through photolysis or catalysis. Research indicates that only 7.9% of methylene blue dye undergoes photolysis after 10 hours of irradiation [32], while mere 10% degradation occurs within 24 hours in the existence of a photocatalyst low light radiation [33]. Notably, negligible decomposition is observed without a catalyst under visible light as well as in acid and equal mediums, both in the opaque and

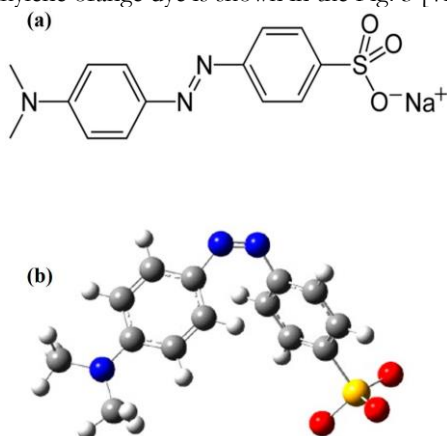


under sun light radiation. Conversely, photolysis accelerates in basic mediums due to the rapid formation of hydroxyl ions, which leads to dye degradation. Temperature elevation shows minimal impact, with degradation ceasing entirely under an argon atmosphere [34]. Photodegradation of methylene blue is an effective get closer because methylene blue can similarly purpose as a photosensitizer[35]. The minor/limited degradation experiential in methylene blue deprived of photocatalysts might be credited to the photosensitized phenomenon of methylene blue particles observed after radiation with dissimilar light devices [36]. Methylene blue exhibits light absorption within the five hundred–seven hundred nm region, generating mono and trilogy classes through electronic change and inter-system passageway, eventually undergoing self- dissociation to some reach [37].

## 4.2 Methylene Orange

### 4.2.1 Definition of Methylene Orange

Methylene orange can be defined as an anionic azo color, containing elevated chemicals constancy[38], and it belongs to the sulphonate azo class[39]. IUPAC noun of methyl orange is Na 4- [(4-dimethylamino) phenyl-diazinyl] benzenesulfonate, reign a molecular formula of  $C_{14}H_{14}N_3NaO_3S$ , a molar weight of 327.33 g/mole, and a volumetric mass of 1.28 g/cm<sup>3</sup> [40]. The chemical form of methylene orange dye is shown in the Fig. 3 [41].



**Figure (3):** (a)The chemical form of methylene orange dye, (b)the enhanced methylene orange molecular form.

### 4.2.2 Properties of Methylene Orange

Partly solvable in water, very soluble as the water temperature increases, and unsolvable with ethanol. It is an orange–yellow dust, melting degree is better than three hundred Centigrade [42]. Behave as weak acid, viewing about 6.5 pH when liquified in H<sub>2</sub>O, and works as a pH detector (colour variations from red to yellow range (3.1–4.4)[43] methylene orange shows a red dye in the acidic solution, and in basic solution it demonstrate an orange dye [44]. The azo family, sulfur family and aromaticity of methylene orange give it a strong coloring, chemicals constancy, poisoning and depressed bioremoval [45]. methyl orange dye has different processing and lab uses[46].

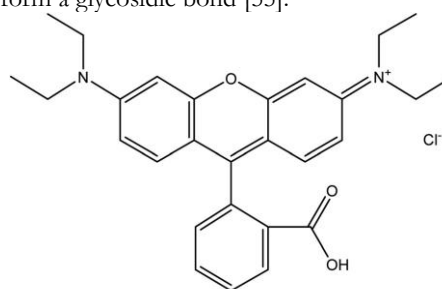
### 4.2.3 Degradation of Methylene Orange

Methylene orange is complicated to break down utilizing conventional technique in natural states, these techniques can stack impurities state of dissociation them [47]. Methylene orange color is not biodegradable, due to its chemical formula of complex aromatic [48]. Many techniques are studied for methylene orange elimination, like adsorption, bioremoval, phytoremediation ozonation, coagulation/flocculation and photoremoval. It has multiplex molecular forms, which make their degradation from effluent water complicated when utilizing conventional process techniques [49]. Photoderemoval has preferences over the further stated conventional methods because of its system easiness, full impurity mineralization, lowest price, no/smaller hurtful after-effect production and its capacity to remove at room temperatures and pressure [50]. The photodegradation process generally needs a photocatalyst or semiconductor, lamp device type, vessel process, contaminated dye and the presence of air [51].

## 4.3 Rhodamine B

### 4.3.1 Definition of Rhodamine B

Rhodamine B dye is a widespread that is most used in textile manufactures for dyeing textile. In addition, another's manufacturing like papers, plastics, printing, biomedical and leather manufacturing. Rhodamine B is usually used as a coloring operator, light sensitizers and H<sub>2</sub>O<sub>2</sub> tracer[52]. Referring to IUPAC terminology, rhodamine B is named N-[9-(ortho-carboxy-phenyl)-6-(diethyl-amino)-3H-xanthen-3-yl] diethylammonium chloride. A molecular wt. of (479.02) gm/mol and shows ultimate absorbance at a wavelength of 554 nm.[53]. The standard chemical form of rhodamine B (C<sub>28</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>3</sub>) is seen in Fig. 4. In the case, the closed structure, which is colorless, is preferred, while the open structure, which is colorful, is preferred, while the open with acidic acids[54]. It is a basic red pigment that is highly soluble in H<sub>2</sub>O, and its soluble structure can easily be removed from C<sub>2</sub>H<sub>6</sub>OH or C<sub>4</sub>H<sub>9</sub>OH. Mostly, the research of rhodamine B consists of modifying the amino groups of the xanthine components by linking the parts to form a glycosidic bond [55].



**Figure (4):** Structure chemical of Rhodamine B

### 4.3.2 Properties of Rhodamine B

Soluble dye in H<sub>2</sub>O, have melting point = 165 °C, and  $\lambda_{max}$  = 543 nm , class = basic dye; color = basic violet 10; electrical conductivity (20 mg l<sup>-1</sup> solution) K = 0.015 s m<sup>-1</sup> [56]. Touch with Rhodamine B can harm the eyes, increase sharp oral irritation, and cause harm to humans [57].





### 4.3.3 Degradation of Rhodamine B

Many wastewater process choices have been explored for removal color and removal rhodamine B in H<sub>2</sub>O. These process choices contain technique founded on biologic, physic, or chemical basics. A protuberant instance of these technique choices is the adsorption treatment which is highly economic and environment favorable[58].

Photocatalysis has been extensive researched to degraded rhodamine B in a liquid mixture. The technique is also simple to work and environment favorable. Yet, opposite the adsorption system, photocatalysis can full mineralize rhodamine B particles in liquids water mixtures[59].

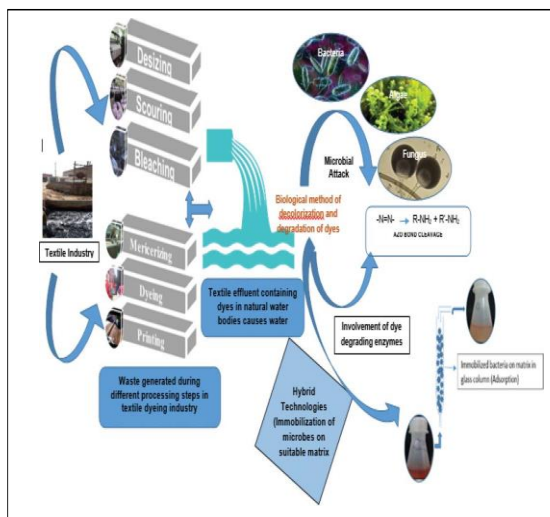
## 5. Removal dyes

### 5.1 Kinds of Removal dyes:

Various kinds of dyes and dye removal technique exist, including biological (like protein degradation), chemical, and physical approaches. Protein degradation and adsorption are considered highly efficient dye removal strategies, known for their effectiveness in removing dye particles from wastewater within a short period of time, without generating harmful by-products [60].

#### 5.1.1 Biological techniques for the Removal of Dyes

Biological techniques, such as algae, microbes, fungi, and yeasts, are recommended for applications involving the degradation and retention of various manufactured dyes. These natural organisms have the capability to break down and absorb a wide range of manufactured dyes, making them valuable in wastewater treatment and dye removal processes, as shown in Fig. 5 [61].



**Figure (5):** The waste generated during processing stages in textile industries and different biological methods utilized for effluent treatment.

#### 5.1.2 Physical techniques for the Removal of Dyes

Various physical techniques, including membrane separation, ion exchange and adsorption, are employed for the removal of dyes from wastewater, Table 3. Show the removal of dyes by multi physical experiments[62].

**Table (3):** The removal of dyes by multi physical experiments

Physical techniques	DYES	Removal efficiency%
1 Membrane filtration		
Ultra Filtration	Reactive black5	70
Nano Filtration	Reactive black5	99
2 Ion exchange		
anion exchange membrane	Congo red	98
basic anion exchange resin	Acid orange7	75
3 Adsorption		
activated carbon prepared from rattan sawdust		>99%

##### 5.1.2.1 Membrane filtration

Membrane filtration is a technique that includes several types of filtrations such as Micro Filtration, Ultra Filtration, Nano Filtration and reverse osmosis, represents a Modern processing technology for the removal of color, chemical oxygen demand and biochemical oxygen demand. The basis of this work lies in the determination of the pore dimensions of the membrane, which dictates whether particles are allowed to pass through or are retained on the barrier's surface [63]. When particles exceed the pore size of the membrane, they are unable to pass through. Ultrafiltration is effective for separating particles scaling between 0.05 - 0.15 micrometer, making it appropriateness for treating inorganic grains or organic colloids [64]. The outcomes indicated that the removal remained higher than 70% even at a dye dosage of 0.5 g/L. Therefore, Ultra Filtration membrane alone may not be appropriate for dye degradation. NF membranes, with pore sizes in the scale from one to ten angstroms, are capable of separating particles at the nanometer scale. NF technology, which combines the features of UF and RO, offers advantages such as bigger flux permeation, greater keeping of salts multivalent, comparatively lower investment, low operation and servicing prices compared to UF and RO individually[65].

##### 5.1.2.2 Ion exchange

Ion exchange have achieved top efficiency when used, which has made them of great interest, little prices, and distinctive quality for implementation in water purification, heavy mineral degradation, and handling of liquid fabric waste. Ion exchange process effectively clears dyes from liquids mixtures by use powerful reactions between charged dyes and practical bands on ion exchange resins. Resins can be divided into four principal groups: anion exchange membranes, cation exchange membranes, cross-linkage membranes, and other ion exchange membranes. Among these, anion and cation exchange membranes are the generally often applied to remove dye. Anion exchange membranes contain positively charged bands, which facilitate the passage of anions while rejecting cations [66].

##### 5.1.2.3 Adsorption:

This physio-chemical process has been identified as the most straightforward and cost-effective technique for the degradation of dyes from textile effluents. A variety of low-cost materials, including agricultural



waste material, naturally occurring fabrics, and processing waste materials, have been tested for the removal of dyes [67]. As an example of the adsorption process using activated carbon is shown in Fig. 6.

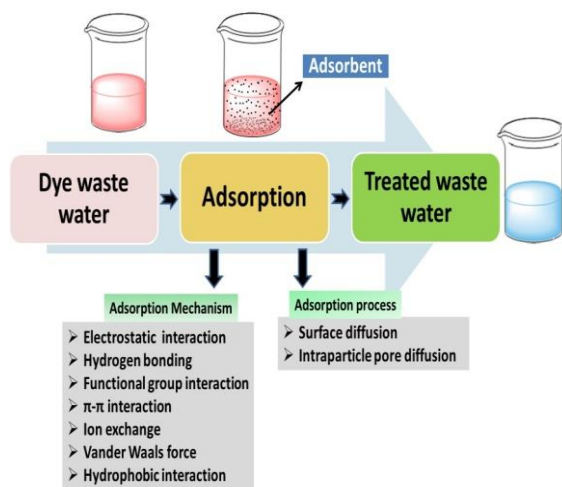


Figure (6): Depicts a schematic presentation of the adsorption process [68].

#### 5.1.2.3.1 Activated Carbon:

Activated carbon has been shown to be an operative adsorbent for the elimination of a wide variety of organic and inorganic dirties dissolved in liquid medium, or from gaseous ambience. In fact, activated carbon is a primitive form of graphite with an indiscriminate or amorphous form, which is immensely porous, exhibiting a large scale of pore dimensions, from visible voids, cracks and slits of molecular sizes. The broad benefit of activated carbon is due to its chemical and mechanical fastness, large adsorption ability and a large degree of surface reaction[69]. Fig. 7 shows the adsorption process of dyes molecules using activated carbon.

#### 5.1.2.3.2 Clays:

Clays are natural aluminosilicates containing small amounts of mineral particles and organic components. They are widely recognized for their effectiveness as adsorbents due to their big surface area, high cation conversation capacity, chemical and mechanical constancy, and layered shape. Common clays are typically employed for the removal of cationic dyes like MB because of their normal negative charge[70].

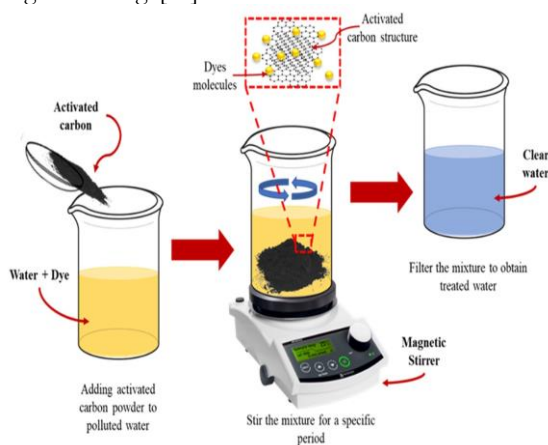


Figure (7): The adsorption mechanism of activated carbon for dye particles[71].

### 5.1.3 Chemical Methods for the Removal of Dyes

Chemical methods for dye removal involve the use of chemicals or its essentials to eliminate dye, include Fenton reaction elimination, ultraviolet irradiation, electrochemical degradation, ozonation, treatment by photochemical, and accelerated oxidation. While some chemical removal methods, like electrochemical degradation, can be efficient, they often come with higher costs compared to biological and physical dye removal methods [72].

The primary objective of conventional processes is to remove color from wastewater by extracting dye particles from the dye bath effluent, without causing partial dissolution of dyes. Partial dissolution could cause to the release of hurtful and poisonous aromatic components. However, a main drawback of this method is the generation of sludge [73].

## 6. Kinds of Catalysis Used in Dye Removal

### 6.1 Homogeneous Catalysis

Homogeneous catalysis can be defined as a catalytic system in which the reactants and catalyst components are mixed together in a single stage, often the liquid phase [74]. But the problems of using this type of catalysts are the difficulty of recycling them after the reaction for use in multiple cycles due to their homogeneity with the mixture, which increases the additional cost in manufacturing for the purpose of separating them from the products using distillation[75], and they also consume a large quantity of water[76]. An example of the use of homogeneous photocatalysts in the homogeneous process: UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+2</sup> was applied to the removal of Reactive Blue 21 [77], UV/H<sub>2</sub>O<sub>2</sub> was applied to the removal of a number of dyes such as Reactive Yellow 145 and Orange 122, Reactive Red 239, Reactive Blue 222 and Reactive Blue 21 [78],and UV/Fe<sup>+3</sup>/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> applied to remove methylene orange dye[79].

### 6.2 Heterogeneous Catalysis

Representing most of the processes currently used in removing dyes, the heterogeneous catalytic process is described by the ability of semiconductors to generate charge carriers under light irradiation, followed by the generation of free radicals represented by •OH which led to the dismantling of the dye and the formation of carbon dioxide and water. Therefore, Heterogeneous catalysis is characterized by the complete removal of the dye, in addition to the fact that it does not require external conditions except for the availability of a light source such as sunlight and air, and its low cost, reusability, and non-toxicity. The catalyst can be loaded onto different types of materials, such as graphene oxides, carbon nanotubes, polymers and glass[80].

## 7. Photocatalyst

Over the past twenty years, the utilization of photocatalysis has significantly increased. Photocatalyst is recognized as a green innovation that has been successfully applied to water purification,



environmental remediation, and specific organic transformations carried out under ambient conditions, such as atmospheric pressure and room temperature. With rising worries about energy and environment issues, Photocatalytic processes will play a very influential role [81].

### 7.1 Benefits Photocatalysis

The following advantages highlight why Photocatalyst is considered the perfect technology for waste water treatment:

- Photocatalyst generates harmless by-products, which is a great benefit.
- Organic dyes are totally eliminated concurrently with an active Photocatalyst.
- The band gap of the photocatalytic substance uses of ultraviolet light can be applied rather of sun light.
- Provides sufficient oxygen in the environment for dye decomposition during photocatalysis.
- Researchers prefer semiconducting metal oxide photocatalysts for photocatalysis due to their inexpensiveness, chemical stability, recyclability, and harmless nature.
- Photocatalysis is a price-effective and environmentally friendly planning for dye removal[82].

### 7.2 Photocatalytic Mechanisms

The photocatalytic discoloration of a dye is thought to take place based on the below mechanism: At a catalyst is exposed to solar light, there is a move of electrons from the valence range to the conduction range.

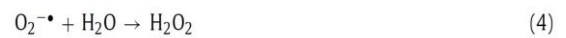
This movement result to the generation of an electron- hole pair[83].



Constitute the electrons in the conduction range and the electron vacancy in the valence range, Consecutively. Both of these units can fare to the catalyst surface; accordingly, they can react with other types existing on the surface in a chemical interaction. usually  $h^+_{vb}$  is able to produce the OH radical easily, while  $e^-_{cb}$  is capable of produce the superoxide radical anion of  $O_2$  [84].



The blocks the reassemble of the electron and the hole that are generation in the beginning step. Subsequently, The hydroxyl radicals and oxygen radicals generate in the subsequent steps .which can then interact with the dye to shape other types , which are accountable for the discoloration of the dye.



A schematic description of the mechanisms of oxidative types production in a photocatalyst study is Explained in Fig.8 [85], The formation of photocatalysts and the generation of electron- hole pairs are linked to the degradation of pollutants in water ,as shown in the Fig. 9.

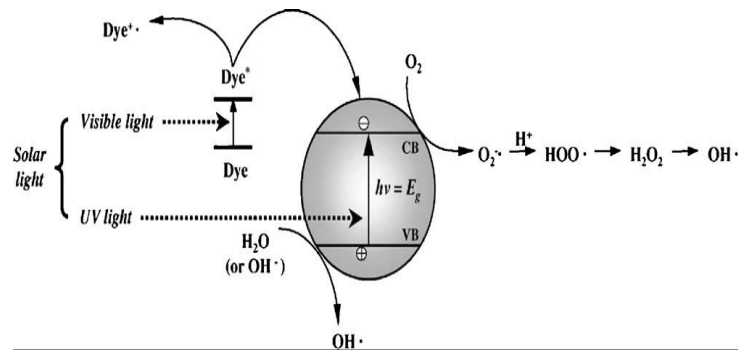


Figure (8): Diagram Explaining the forming of oxidants in photocatalyst study.

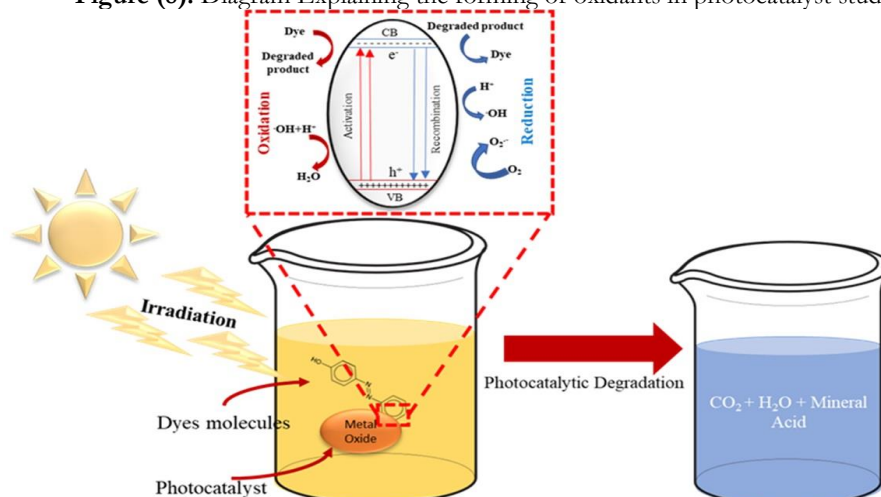


Figure (9): Diagram depicting the Photocatalytic Degradation process of toxic dyes.





## 7.3 Parameters Influencing Photocatalysis

### 7.3.1 Initial Dye Concentration

Dye granules contain different functional groups. The function of the dye affects the interaction between the dye and the photocatalyst substrate and these functions vary from one dye to another [86]. In general, increasing the reactant concentration leads to a rise in the reaction rate, but the photoremoval performance of the dyes drop with the growing of the initial dye concentration due to the drop in the percentage of active sites, the drop in the percentage of ( $\bullet\text{OH}$ ) and the absorption of light instead of its diffusion to the surface of the photocatalyst [87][88].

### 7.3.2 Catalyst Amount

The removal of dye is influenced by the quantity of the Photocatalyst. Rising the quantity of catalyst increase the photoremoval of dye, a phenomenon recognized as heterogeneous Photocatalytic. The augmentation in catalyst quantity effectively rise the number of active sites on the photocatalytic surface, thereby leading to a higher number of  $\bullet\text{OH}$ , which actively participate in the degradation of dye mixture [89]. However, after a specific step of catalyst quantity, the solution turn out thick, obstructing UV radiation from reaching the interaction site, and consequently, the removal process get started to decrease [86].

### 7.3.3 Morphology, Surface Area and Size

The surface area and dimensions of photocatalyst, mostly mentioned as surface morphology, are critical factors impacting the rate of photocatalytic removal of pollutants in water. Surface morphology affected by the adsorption of contaminants onto its surface, a phenomenon referred to photo mineralization [90]. Nano measure semiconductor materials work as high-quality photocatalysts compared to bulk equivalent because of their electrical, high visual, and photocatalyst features [91]. In general, nano molecules of very little dimensions show raised surface area, guiding to the generate of numerous active sites. These active sites play an important role in directly adsorbing pollutants onto the surface by efficiently absorbing photons, thereby facilitating best mineralization [92].

### 7.3.4 pH of Solution

The work of photocatalyst is greatly affected by the pH of the mixture, making it a critical factor in wastewater process [93]. The pH scale straightway affects the surface charge features of the photocatalytic and thereby affect the oxidation potential of the interaction [94]. The pH of the solution alters the electrical twice layer of the solid electrolyte interface. Therefore, impacting the sorption-desorption system and the separation of photoproduced  $\text{H}^+/\text{e}^-$  pairs on the surface of the semiconductor photocatalytic [95]. The pH scale not only in a large way impacts the generation of hydroxyl radicals but similarly influences the charge on the photocatalyst molecules and the sites of the valence and conduction ranges [96]. Given that waste-liquid from different manufacturing operations is discharged at various pH scales, it is important to observance the effects of this factor for photodegradation researches [97]. The cationic behaviour of MB favours larger scales for pH, as its

adsorption is enhanced according to these terms. This phenomenon refers to improved photocatalyst removal [98]. Likewise, it was notice that MB removal happen at a quick rate in a basic solution differentiated on an acidic solution [99]. while the anionic behavior of methylene orange gave better photoremoval results in acidic medium compared to basic medium [100] [101].

### 7.3.5 Light Energy

The intensity, wavelength, and duration of light exposure affect the quantum efficient and Motility of photocatalyst removal processes. Illumination irradiation presents the needed energy for electron excitation from the valence range to the conduction band of the catalytic. The intensity of the light origin decided the fully energy obtainable, while the wavelength dominate the energy of every photon, making both factors critical [102], for efficient removal of organic contaminates, the catalyst must be active across the entire solar spectrum. However, generally used photocatalysts like  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{SnO}_2$  are primarily active under UV light, which forms just a tiny part of the solar spectrum [103]. Because their large band gap, not all photocatalysis make use of visible and infrared rays. Positively, in spite of comprising an important portion of solar power [104].

### 7.3.6 Irradiation Time

The period of solar light submission is a crucial factor to set the photoremoval capacity of photocatalytic for dye removal [105]. Researches show that prolonged radiation leads to raised light and therefore decolourization of dyes, attributed to the escalated production of reactive types with extended interaction periods [106]. The removal rate is quick but suddenly slows down with raised radiation period [107]. Nevertheless, as the interaction progresses after a specific time point, filling the residual active sites becomes more difficult because the repulsive forces between surface molecules and those in the bulk phase. Subsequently, the removal percentage leaning to stability and stays comparatively fixed during time [108].

### 7.3.7 Oxidizing agent

In photocatalyst, various reactive radicals and oxygen species are considered essential benefactors to the removal of organic dyes [109]. The presence of oxidants grows removal effectiveness and decreases reaction time by generating reactive oxygen species [110]. raising the dosage of  $\text{H}_2\text{O}_2$  enhances Photodegradation effectiveness by generating additional  $\bullet\text{OH}$  radicals and exploiting  $\text{H}_2\text{O}_2$  capability to trap electrons [111]. The extension of  $\text{H}_2\text{O}_2$  conspicuously decreases the interaction time wanted for dye removal [112]. For instance, in a study by crystal violet dye was removed over a lengthy period of 280 minutes, but with the extension of  $\text{H}_2\text{O}_2$ , efficient removal was achieved in just 60 minutes. However, excessive concentration of  $\text{H}_2\text{O}_2$  can give to the production of less potent  $\bullet\text{O}_2\text{H}$  (hydroperoxy) radicals [113], which although operative oxidants, possess least oxidation potential compared to  $\bullet\text{OH}$  radicals [114][115]. Azo dyes are predictable to subject relatively rapid removal in the existence of hydrogen peroxide





[116]. It has been concluded that the percentage removal get bigger with an increase in the initial dosage of  $H_2O_2$  up to a crucial rate, beyond which more removal is constrained [117].

#### 7.4 Polyoxometalates (POMs)

Polyoxometalates (POMs) have well-knew inorganic metal-oxygen anionic clusters and coordinations. POMs collected with right counter cations mostly composes solid substances which offer about distinctive properties in several fields of catalysis and photoelectrochemistry, a kind solid POM component which is consist of inorganic monovalant cations [118]. A lot different items can work as heteroatoms in heteropoly compounds with different coordination statistics: 4-coordinate (tetrahedral) in Keggin and Wells-Dawson forms (for example  $PO_4^{3-}$ ,  $SiO_4^{4-}$ , and  $AsO_4^{3-}$ ); 6-coordinate (octahedral) in Anderson-Evans forms (e.g.,  $Al(OH)_6^{3-}$  and  $TeO_6^{6-}$ ); and 12-coordinate (Silverton) in  $[(UO_2)Mo_{12}O_{30}]^{8-}$ . Fig. 10 displays traditional POM forms in polyhedra illustrations [119]. Keggin-kind  $[PM_{12}O_{40}]^{3-}$  ( $M = W, Mo$ ) anions is studied vrey deep, POMs have been product as photocatalysts with growing interest in a few years ago, such as a photocatalyst which does best action in the removal of heavy mineral ions or impurites in water[118].

Heteropoly acids are commonly supported on solid substrates such as silica, carbon, molecular sieves, clay, alumina, titania, and resin[120].

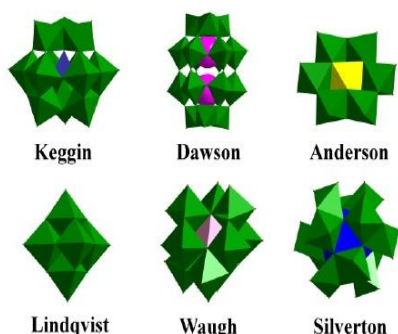


Figure (10): Some traditional POM forms in polyhedra representations

#### 7.4.1 Benefits of POMs

Hetero-polyoxometalates are named green catalysts for of the following purposes:

- The powerful acidity of hetero-polyoxometalates contrasted with liquid acids lead to a considerable lower in the quantity of wanted catalyst.
- They are solid and this ease the sorting and reemploy of materials.
- it is non- poisonous.
- No want for solvent in many reactions.
- It operate at soft temperature in most reactions.
- Perfect activity in the production of substances.
- Dangerousgases or poisonous materials are not created through the reactions catalyzed with POMs
- Multi reactions are procedured at ambient pressure and temperature[121].

#### 7.4.2 Phosphotungstic acid (PTA)

Phosphotungstic acid has the chemical formula  $H_3PW_{12}O_{40}$  in acid form, the Keggin form represents  $(PW_{12}O_{40})^{3-}$  negative charge, in which the centric atom is phosphorus and the addendum atoms are tungsten, is usually consider as an acid catalyst for it has been shown to be the powerful acid [122] PTA is the strongest acid in the series of heterocyclic acids [120]. Fig. 11 display form of PTA[123].

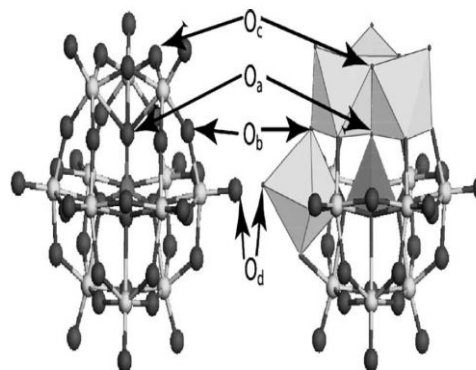


Figure (11): Keggin-form of PTA

#### 7.4.3 Phosphomolybdic Acid (PMA)

Phosphomolybdic acid ( $H_3PMO_{12}O_{40}$ ) was chosen to study the practicability of the research. PMA has a traditional Keggin form with single P atom in the middle that is surrounded by twelve octahedron  $MoO_6$ -units linked with every other by twenty four bridging  $O_2$  atoms. Further twelve corner  $O_2$  atoms supplement the form, every of them which is double-bonded with an extra Mo atom. With thirty six  $O_2$  atoms, PMA provides a range of coordination locations, counting the one corner location, the bridge location (the  $O_c$ -Obr-bridge location), the threefold hollow location ( $3-H_{Oc}$  and  $3-H_{Obr}$ ) and the 4-fold hollow location ( $4-H$ ), as shown in Fig. 12 [124].

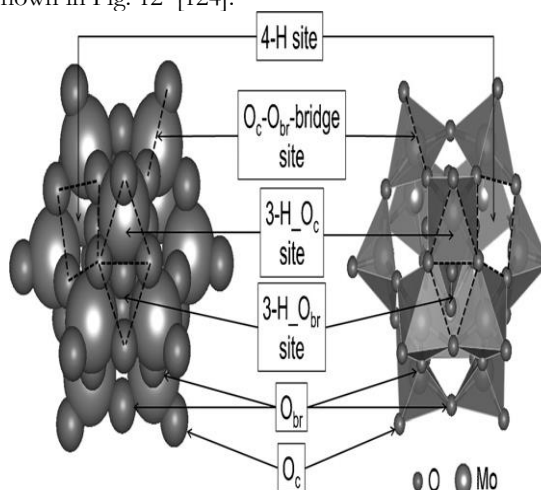


Figure (12): Various kinds of surface O atoms on P atom Keggin-formed anion PMA. The P atom in the middle is unobserved into the external sphere O and Mo atoms.

## 8. Previous works

Zanjanchi M.A. et al. 2009. Studied the use of PTA and  $TiO_2$  loaded on the parent purely siliceous MCM-41 as photocatalyst was investigated by



impregnation way to remove methylene blue dye from water. The results showed removal efficiency reached to 100% within 15 minutes for a 30 mg/L methylene blue solution containing a dose of 100 mg/100 ml. Adsorption plays an important role in the very high efficiency of this photocatalyst for methylene blue removal, the presence of PTA-TiO<sub>2</sub> complex structure makes the most active material for complete removal of methylene blue, This research is excellent in terms of the final result of dye removal [125].

**Wang W. et al. 2010.** Studied the use of PTA and silicotungstic acid in preparing photocatalyst to remove methylene orange dye from water under a metal halide lamp and the experiments were carried out in a closed box. The results showed that the removal reached 93.6% at a dose of 8.89 gm/L of catalyst, a dose of 5.56 mg/L of methylene orange, and a lighting time of 80 minutes This research demonstrated the high quality of PTA in oxidizing dye-contaminated water in the presence of a light source using small quantities. It also studied the effect of the quantity of catalyst, as increasing it increases the removal rate, and studied the concentration of the dye, as increasing it decreases the removal rate [126].

**Song S. et al. 2015.** Studied the use of PTA loaded on Cadmium sulfide to remove Safranin T dye from water. The results of this work show that PTA/CdS with mass ratio of PTA of 30 weight% exhibiting the top photocatalytic activity for removal of Safranin T under acid state, 50mg catalyst adding to 100mL Safranin T (20mg/L) solution, with stirring and remain the pH=4. The removal rate of Safranin T 84.3% below UV lamp irradiation for 120 minutes[127].

**Farhadi S. et al. 2016.** Studied the use of PTA supported on aminosilica -type LaFeO<sub>3</sub> nanoparticles to prepare LaFeO<sub>3</sub>@SiO<sub>2</sub>-NH<sub>2</sub>/PTA to remove methylene blue dye from water, at 25 °C with existence of visible light irradiation employing a 400W mercury light with a 420 nm cutoff filter as the light source. In each test, 25 mg of catalyst and 2 mL of Hydrogen Peroxide (0.1 mol/L) were added into 50 mL of methylene blue (25 mg/L) liquid solution in a Pyrex vessel , the result showed removal efficiency reached 100% within 15 minutes , which indicates that this study gave a great result with the fastest total removal rate [128].

**Li X. et al. 2016.** Studied the use of 150 mg KCl and 300 mg PTA at 140 °C for 12 h to prepared K<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O molecules to remove Rh-B dye from water. Photocatalyst showed a good effective photoremoval ability with activating H<sub>2</sub>O<sub>2</sub> in this study, which can degrade dye pollutants completely after a visible light radiation of 90 min., the visible light origin was a 500-W halogen light, 25 mL solution including H<sub>2</sub>O<sub>2</sub> and rhodamine B dye, Initial dose: rhodamine B =0.2 × 10<sup>-4</sup> M, H<sub>2</sub>O<sub>2</sub>=0.002 M[118].

**Zhou J. X. et al. 2017.** Studied the use of PMA, metal-organic gel and Chromium nitrate nonahydrate to prepare PMA@MOG-Cr and studied photocatalytic activities by photoremoval of

methylene orange, MB, and rhodamine B dye solutions below the irradiation of a 50 W Xe light in the air and at room temperature. The range between the light and the vessel the solution was specified at 15 cm. (0.01) g of photocatalyst was added to 50 mL of a liquid water solution with methylene orange, methylene blue, rhodamine B (10 mg/L) in a 50 mL cylindrical pyrex container. Before lighting, the solution was in the magnetic stirrer device in the dark for 60 minutes to attain adsorption/desorption balance, followed by adding 1 mL of 30% H<sub>2</sub>O<sub>2</sub> to the solution. To measure photocatalytic activity under visible radiation, a 420 nm UV cutoff filter was used to provide visible light. The results showed photoremoval efficiency 97% for methylene blue dye and 99% for rhodamine B at 60 minutes. The final result shows that this research showed good results for the two different dyes [6].

**Joseph J. et al. 2019.** Studied the use Micro-sized ammonium phosphomolybdate (NH<sub>4</sub>)<sub>3</sub>PMO<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O (APM) molecules were prepared under natural status and characterized.0.125 gm of APM was added to the solution (25 mL of 10-5 M methylene blue) was preserved with stirring for 5 minutes under UV lamp. then it was left quit for 60 minutes. It was able to remove methylene blue and malachite green from dye-polluted water in the pH range 1-6. Dye removal efficiency (94.6%) was achieved when 10-5 M methylene blue solution (pH = 5.0±0.1) with (APM). The effect of both sunlight and UV light on the rate of removal was also studied, and their results for dye removal were similar. This study was distinguished from other studies by the stability of the catalyst despite reuse for 16 cycles [129].

**Li J. et al. 2019.** Studied the use of PTA, ammonia and reduced graphene to prepare oxide (NH<sub>4</sub>PW-1RGO-1.0 g/L) prepared by hydrothermal way used as Photocatalyst to remove methylene orange dye from water, under 20W UV light, major wavelength (254 nm) and initial dose of MB10 mg/L. The results showed removal rate at 96.86% with 150 minutes, which is a good result. Although it achieved a good removal result, the stability of the catalyst after only three cycles decreased significantly, as the removal rate reached 63.8% [130].

**Li P. et al. 2020.** Studied the use of PTA and silicon carbide to remove rhodamine B dye from water. When loaded on SiC powder 20%, it gave a photocatalytic activity. The results showed removal rate of rhodamine B at 180 minutes was 77%. Under the action of oxidizing agent (H<sub>2</sub>O<sub>2</sub>), the removal rate of rhodamine B by photocatalyst at 180 min was increased to 87%. The free radical capture experiment showed that hydroxyl radical (·OH) is the major photocatalytic effective species, which reacts with rhodamine B and decomposes rhodamine B into CO<sub>2</sub> and H<sub>2</sub>O. The photogenerated holes on the surface of PTA can straight react with rhodamine B molecules to disintegration of rhodamine-B molecules, which function a confirmed role photocatalysis[123].

**Taghdiri M. et al. 2021** Studied prepare photocatalyst from phosphomolybdate-hexamine-nickel (PMA-HMT-Ni), which is prepared by mixing



and then drying until it is ready as a green solid. The results showed removal efficiency of methylene blue in the photocatalytic process with PMA HMT-Ni 98.4 % at solar light, dose of MB 15 mg/l with 80 minutes[131].

**Wei S. et al. 2022.** Studied the use of PTA deposited on the electropositive ZIF-67 to prepare photocatalyst PTA @ZIF-67 to remove methylene blue dye from water. Results showed that PTA @ZIF-67 had very good adsorption capability toward cationic methylene blue. The optimal ZIF-67-0.2 PTA sample with a PTA dosage of 9.9 weight % offered an adsorption capability of 446.4 mg g<sup>-1</sup>. ZIF-67-0.2 PTA displayed perfect reusability; the removal efficiency was 99.6% with time 180 minutes.

This research showed an excellent result in terms of recyclability, as although the number of cycles reached eight cycles, the removal rate did not decrease much and reached 87.2% [132].

**Praveendaniel M. et al. 2023.** Studied the use of titanium dioxide doped with phosphomolybdic acid to prepare photocatalyst by a blending way for 60 minutes, to remove methylene blue dye from water. The composites were heated in an air oven at 110°C for 30. Condition: Methylene blue = 50 ppm; Temperature = 33°C; and catalyst dose of 0.05 M, the results showed removal efficiency about 99% for 180 min. In this study, TiO<sub>2</sub> was used, which is considered the best model for semiconductors[133].

**Table (4)** Applications of different types of polyoxometalates loaded with materials for the removal of organic pollutants by photocatalytic process, (D: Dose of photocatalyst, C<sub>0</sub>: Initial concentration, V: Volume, LS: Light source, M: Molarity, W: Watt, g: gram, L: litter, m: milli, nm: nano meter).

No.	Photocatalyst	Organic pollutant	R %	Time (min.)	Conditions	Reference
1	PTA /TiO <sub>2</sub>	MB	96	60	LS: 125 W (mercury light), D:1.25 g/L, C <sub>0</sub> : 50mg/L., V: 200mL.	Yang Y. et al. 2005 [134]
		Rh- B	98	60		
		MO	72.4	240		
2	PTA /ZrO <sub>2</sub>	MB	96	90	LS: UV light 40 W, D: 1.5 g/L, C <sub>0</sub> : 10 mg/L, V: 100ml	Qu X. et al.2007 [135]
3	PTA -TiO <sub>2</sub>	MB	100	15	LS: 400W lamp, D: 1 g/L, C <sub>0</sub> : 30 mg/L, V: 100mL	Zanjanchi M.A. et al. 2009 [125]
4	PTA /silicotungstic acid	MO	93.6	80	LS: metal halide lamp 400W, D: 8.89 gm/L, C <sub>0</sub> : 5.56mg/L, V: 45 mL	Wang-W. S. et al. 2010 [126]
5	PTA pillared Mg <sub>3</sub> Al-LDH	MO	96.39	30	LS: UV light, D: 0.4 g/L, C <sub>0</sub> : 0.02 M., V: 150mL	Zhang Y.H. et al.2010 [136]
6	PMA/MnO <sub>2</sub>	MB	>98	150	LS: 500W Xe light, D: 0.05 g/L, C <sub>0</sub> : 140 mg/L., V: 100mL	Kannan R. et al. 2011 [137]
7	PTA -yttrium-TiO <sub>2</sub>	MO	100	21	LS: 300 W (Xe light) (λ >365 nm). D:0.6 g/L, C <sub>0</sub> : 10mg/L., V: 50mL	Wang Y. et al. 2011 [138]
8	La- PTA/TiO <sub>2</sub>	MB	96	100	LS: A 125 W (mercury lamp), D:4g/L, C <sub>0</sub> : 40mg/L, V: 50mL	Shi H. et al. 2012 [139]
	Ce- PMA/TiO <sub>2</sub>		98			
9	PTA / SiO <sub>2</sub>	Rh- B	97.7	120	LS: Xe light 500W, D: 0.8 g/L, C <sub>0</sub> : 10 mg/L, V: 1L	Yang S. et al. 2012 [140]
10	PTA/ Activated clay	MO	78.9	60	LS: mercury light 50W, D: 200 g/L, C <sub>0</sub> : 0.065 mg/L, V: 500mL	Wei G. et al. 2012 [141]
11	PTA /BiVO <sub>4</sub>	MB	93	360	LS: 500 W Xe lamp, D: 0.6g/L, C <sub>0</sub> : 10mg/L, V: 50mL	Zhang J. et al. 2013 [142]
12	Ag/ AgPTA /Cu <sub>2</sub> O	MB	100	50	LS: 300 W halogen light, Area of catalyst 2*2 cm <sup>2</sup> , C <sub>0</sub> : 0.02 mg/L, V: 100ml	Zhou W. et al. 2013 [143]
13	PW <sub>12</sub> -APTES@MCF	MB	86	30	LS: mercury light 75 W, D: 0.5 g/L, C <sub>0</sub> : 50 mg/L, V: 20 mL	Fazaeli R. et al. 2014 [144]
		Rh-B	96			
14	PW <sub>12</sub> @g-C <sub>3</sub> N <sub>4</sub>	MB	90	180	LS: a metal halide lamp, D: 0.5 g/L, C <sub>0</sub> : 10 mg/L, V: 200mL	He J. et al. 2015 [145]
15	PTA (30%) on NH <sub>4</sub> ZSM <sub>5</sub> zeolite	MO	91	240	LS: 125 W (mercury light), D:1.875 g/L, C <sub>0</sub> : 2.62 mg/L, V: 400ml	Leal C. et al. 2015 [146]
16	PTA-TiO <sub>2</sub> /Bentonite	MO	82.7	120	LS: 2 lamps UV 15 W, D: 1 g/L, C <sub>0</sub> : 10 mg/L, V:1L	Zhang L. et al. 2015 [147]
17	LaFeO <sub>3</sub> @SiO <sub>2</sub> -NH <sub>2</sub> /PTA	MB	100	15	LS: 400W mercury light with a 420 nm cutoff filter, D: 0.5 g/L, C <sub>0</sub> : 25mg/L, V: 50 mL	Farhadi S. et al. 2016 [128]
18	PMA/Polymethylmethacrylate/ PA <sub>6</sub> nanofibrous membrane	MO	92.7	30	LS: mercury light 300 W, C <sub>0</sub> : 10 mg/L, V: 50mL	Li W. et al.2016 [148]
19	PTA / TiO <sub>2</sub> / SiO <sub>2</sub>	MB	81	150	LS: 500W Xe light, D: 2.9 g/L, C <sub>0</sub> : 10 mg/L, V: 150mL	Yang S. et al. 2016 [149]
		MO	99.9			
20	K <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> ·nH <sub>2</sub> O	Rh-B	100	90	LS: 500-W halogen lamp, D: 0.5 g/ L, C <sub>0</sub> : 0.2 × 10 <sup>-4</sup> M, H <sub>2</sub> O <sub>2</sub> =0.002 M, V:1 L	Li X. et al. 2017 [118]



21	Ag/AgxH <sub>3</sub> -xPMA	MO	100	60	LS: 500 W Xe lamp, D: 1 g/L C <sub>0</sub> : 20mg/L, V: 20mL	Shi H. F. et al. 2017 [150]
22	PMA@MOG-Cr	MB	99	60	LS: 50 W Xe lamp, D: 0.2 g/L C <sub>0</sub> : 10 mg/L, V: 50mL	Zhou X.J. et al. 2018 [6]
		Rh-B	97			
		MO	91			
23	Exfoliated graphite-TiO <sub>2</sub> nanoparticle	Rh-B	100	60	LS: UV lamp 300 Watt, D: 0.025 g/L C <sub>0</sub> : 50 mg/L, V: 1 L	Guidetti G. et al 2019 [7]
24	NH <sub>4</sub> PW-GO	MB	96.86	150	LS: 20W UV light, D:1g. C <sub>0</sub> : 10 mg/L, V: 1 L	Li J. et al. 2019 [130]
25	PW <sub>12</sub> /Bi <sub>2</sub> WO <sub>6</sub>	MB	>99	240	LS: Xe light 300 W, D: 1 g/L C <sub>0</sub> : 10 mg/L, V: 200ml	Liu G. et al. 2019 [151]
26	(NH <sub>4</sub> ) <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> ·6H <sub>2</sub> O	MB	94.6	60	LS: 20W UV light, D: 5 g/L C <sub>0</sub> : 5 M, V: 25 mL	Joseph J. et al. 2020 [129]
27	PTA / SiC	Rh-B	77	180	LS: Xenon arc lamp (λ≥420 nm) D: 0.1 g/L, C <sub>0</sub> : 10 mg/L, V: 100 mL	Li P. et al. 2020 [123]
28	PTA /TiO <sub>2</sub>	Rh-B	98.5	240	LS: 300 W Xe light, D: 0.038 g/L C <sub>0</sub> : 25 mg/L, V: 120ml	Lu N. et al.2020 [152]
29	PMA-hexamine-nickel	MB	98.4	80	LS: sunlight, D: 0.5 g/L C <sub>0</sub> : 15 mg/L, V: 1 L	Taghdiri M. et al. 2021 [131]
30	PTA/SCN	Rh-B	74	60	LS: Xenon lamp, D: 0.1 g/L C <sub>0</sub> : 100 mg/L, V: 100 mL	Li P. [153]
31	TiO <sub>2</sub> doped with PMA	MB	99	180	LS: visible light /wavelength 460nm D: 0.05 M, C <sub>0</sub> : 50 mg/L, V:1 L	Praveendaniel M. et al. 2023 [133]

## 9. Conclusions and Expectations

It has become clear that the presence of dyes in water has environmental and health damages in various industries. Through studying the methods used to remove dyes, it has been shown that the best method is to use photocatalysts for their many benefits. The use of polyoxometalates for the two types of phosphomolybdic acid and phosphotungstic acid is considered one of the most common uses recently due to the high removal results, especially when loaded on other materials, which gives the possibility of reuse for many cycles. After comparing the results of previous studies, the following was concluded:

- The type of material used with polyoxometalates has a significant and important effect through its nature and the possibility of decomposition and electronic transfer between dyes and the photocatalyst, which speeds up the process of dye removal in less time and less quantity, and thus lower financial cost by completely removing the dye.

- The effect of light is considered one of the factors that have a direct effect on PMA and PTA in removing dyes, and it requires conducting tests for the photocatalyst to determine the appropriate wavelength, based on which the light source is used.

- Choosing the type of dye with the nature of the charge of the material that the polyoxometalate is loaded to ensure the greatest attraction between the surface charges of the catalyst and the dye to ensure the complete removal of the dye with a high concentration of the dye.

Therefore, expectations indicate an increase in the use of photocatalysts from polyoxometalate due to its distinctive properties in terms of electronic transfer with the dye and the ease of loading it without any conditions. As such, future ways to use polyoxometalates to achieve the highest removal rates with the least time, quantity and cost will undoubtedly stem from more experimental laboratory and industrial discoveries.

- Considering the possibility of improving the addition of the loaded material with phosphotungstic acid and phosphomolybdic acid, they will achieve greater industrial acceptance.

- There is still a lot to be done to fully exploit the structure and the distinctive electronic exchange of phosphotungstic acid and phosphomolybdic acid with other materials that increase their efficiency.

- The effect of dyes on water is a dangerous indicator for the environment, which calls for finding modern techniques to purify water at a lower cost and with low energy consumption.

## 10. References

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