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Review on Adsorption and Photocatalysis of Dyes for Wastewater Treatment

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ABSTRACT

Managing wastewater from dyeing industries has become a significant challenging issue in the world. Various methods have been reported in the literature to treat these effluents with adsorption and photocatalysis emerging as popular methods due to their low cost, simplicity and effectiveness in reducing the quantity of pollutants before they enter water bodies. This review summarizes key findings of the recent few years on the application of metal oxide nanoparticles in wastewater treatment. Adsorption alone is effective for removing pollutants even in very trace amounts, but it does not break down into eco-friendly products. Photocatalysis, on the other side, needs the adsorption of contaminants onto the catalyst surface to initiate degradation. Thus, this review provides a discussion on the mechanism of adsorption, as well as photocatalysis.

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1. INTRODUCTION

Environmental issues are divided into three categories such as air pollution, water pollution, and solid water waste management. Regarding air pollution, the major contributor is CO_2, which causes global warming and is a serious threat to environmental sustainability. Scientists are working to reduce carbon emissions by replacing renewable energy sources such as hydrogen and other clear and renewable energy resources (Asif *et al*., 2021; Asif *et al*., 2023). CO_2 capture storage and hydrogenation are also one of the effective ways to reduce carbon emissions which can assisted by solar-powered water electrolysis and electrochemical CO_2 reduction (Ahmed *et al.,* 2024; Xie *et al*., 2021). Regarding solid waste management people are working to utilize it for energy production through several processes such as pyrolysis and thermochemical conversion processes (Raza & Abu-Jdayil, 2023; Hassan *et al*., 2023; Kareem *et al*., 2022; Zulqarnain *et al*., 2021). Recently people also working to convert biomass waste into biodigestate and biogas (Mushtaq *et al*., 2020) for small scale application which was previously synthesis from cola and other sources such as humic acid or other chemical compounds synthesis (Asif, 2022).

Water pollution is a global issue, with numerous hazardous contaminants surpassing the safe limits in water bodies (Donald *et al*., 2022). A considerable quantity of industrial wastewater includes heavy metals which are a serious threat to aquatic life and many challenges to detection and treatment process (Asif *et al*., 2020; Yousuf *et al*., 2022). Another main water pollutant is plastic waste which can be hazardous for fish and other aquatic animals, it should be treated carefully before the discharge of treated wastewater (Khan *et al*., 2024), leaked oil (Sun *et al*., 2022), and dyes which are the main concerning points in this article. Dyes are renowned as one of the major pollutants owing to their extensive utilization among different fields including cosmetics, pigment, ink, textiles, printing, electroplating, pigment manufacturing, mineral production, shoe polish manufacturing, etc (Elgarahy *et al*., 2021). Dyes primarily originate from biological sources that have not undergone any chemical treatment, such as plants, animals, minerals, or insects (Bello *et al*., 2015).

In aquatic situations, these colors impede light penetration, which can cause eutrophication by inhibiting photosynthesis and lowering oxygen concentrations (El-Sheekh *et al*., 2021). Aside from this, the health repercussions include respiratory and kidney failure, skin rashes, blindness, shock, cardiovascular collapse, bladder cancer, and asthma. However, untreated dye-containing wastewater puts both human health and the ecosystem in acute danger.

This review summarizes key findings of the recent few years on the application of metal oxide nanoparticles in wastewater treatment. Adsorption alone is effective for removing pollutants even in very trace amounts, but it does not break down into eco-friendly products. Photocatalysis, on the other side, needs the adsorption of contaminants onto the catalyst surface to initiate degradation. Thus, this review provides a discussion on the mechanism of adsorption, as well as photocatalysis.

2. METHODS

This study is a literature survey, obtaining data from internet sources, especially articles published in international journals. Data was then analyzed and compiled to comprehend the understanding the concept.

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3. RESULTS AND DISCUSSION

3.1. Dye Removal Techniques

Several methods have been investigated and examined for the extraction of dye from water, which mainly include advanced techniques such as membrane separation, ozonation, coagulation, biological treatments, and chemical oxidation, and have been thoroughly examined for the decontamination of dyes from the wastewater (Piaskowski *et al*., 2018; Shah *et al*., 2020). All these approaches, meanwhile, have significant drawbacks. For instance, because dyes are usually soluble, coagulation and flocculation are less effective, and biological therapies are unsuccessful because the dye is not biodegradable. Among the various approaches, adsorption and photocatalysis are considered more cost-effective and efficient as compared to chemical and physical methods (Gusain *et al*., 2019). These methods are ideal due to their simple operating conditions, cost-effectiveness, simple procedure, and energy saving over other methods (Zango *et al*., 2020; Hussain *et al*., 2025).

Numerous substances and materials have been effectively and efficiently utilized to eliminate the colored impurities or pollutants from the water including clays, composites clay-alginate, and polydopamine microspheres (Xiong *et al*., 2023), chitosan (Bhatt *et al*., 2023), activated carbon, metal oxides (Kim *et al*., 2023), etc. Besides this nanocomposites (Kk & Gangadharan, 2022), magnetic porous carbon (Chen *et al*., 2017), natural dolomite (Shah *et al*., 2023), hybrid iron cobalt metal oxide nanoparticles (Hussain *et al*., 2023), activated biocarbon (Bazan-Wozniak & Pietrzak, 2020; Mirza, 2024), magnetic Fe_3O_4 nanoparticles (Iconaru *et al*., 2016), alginate-based nano adsorbent (Qamar *et al*., 2022), magnetic chitosan nano adsorbent (Karimi *et al*., 2022), orange peel (Castañeda-Figueredo *et al*., 2022). Metal oxides such as oxide of titanium cerium, zinc, zirconium (Kumar *et al*., 2014; Hassan *et al*., 2023), manganese, and tin (Hassan *et al*., 2023) are regarded as super useful photocatalysts due to their pronounced stability across a wide pH range, superior efficiency and effectiveness, very cost-effective, affordability, least toxic, and extremely oxidizing photo-generated holes.

This review thoroughly analyses and highlights the mechanisms of adsorption and photocatalytic process along with adsorption isotherm models, kinetic models, and degradation via photocatalytic methods.

3.2. Adsorption: A Promising Approach for Dye Removal

Adsorption is one of numerous treatment techniques that is mostly popular due to its simplicity and easiness of use, high efficacy, environmental friendliness, and low emission of toxic byproducts. Different adsorbents used for the removal of dyes in literature are listed in **Table 1**.

Table 1. Type of adsorbents used and percentage of removal.

Adsorbent	Removal (%)	References
Hematite iron oxide nanoparticles (α-Fe_2O_3)	83%	(Dehbi *et al*., 2020)
GO@Zn-$NiFe_2O_4$-αAl_2O_3 nanocomposite	73	(Hojjati-Najafabadi et al., 2023)
Cobalt Iron Oxide Doped by Chromium	88	(Alwan *et al*., 2021)
TiO_2 nanoparticles	80	(Abou-Gamra & Ahmed, 2015)
Fe_2O_3/MWCNTs/Cellulose	92	(Khalatbary *et al*., 2024)

3.3. Mechanism of Adsorption

Based on the strength of engagement between the adsorbate and the adsorbent, adsorption is normally classified as either physical or chemical as shown in **Figure 1**. It involves a variety of processes, including electrostatic contact, π-π interaction, hydrogen bonding, complexation, and cation bridge. The features of the adsorbent molecules and the pollutant have an impact on the mechanism that is involved in the process. Furthermore, the adsorption may consist of more than one adsorption mechanism. According to a study, colors from wastewater can be effectively adsorbed using the unintended reverse osmosis post-carbon, and there may be interactions between the adsorbent and the adsorbate (Saini *et al*., 2023).

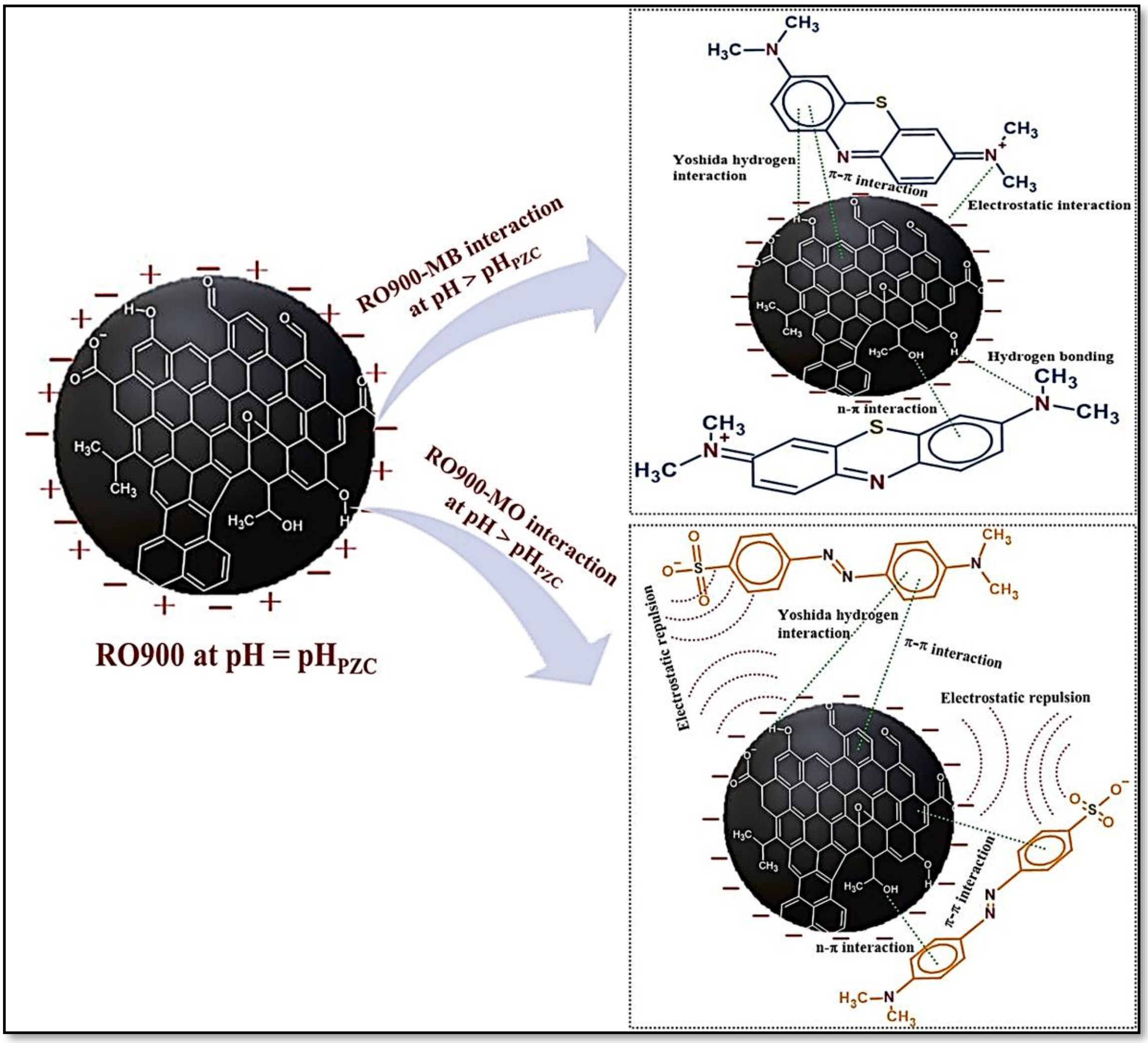

Figure 1. Possible interaction between adsorbent and adsorbate (Saini *et al*., 2023).

3.4. Adsorption Isotherms

Adsorption isotherm models serve as important mathematical models for characterizing various parameters, including uniformity or variability of the adsorbent surface, molecular coverage, binding energies, physical or chemical types of interactions, and adsorption temperature. Equationuationuilibrium data were evaluated with isotherms such as Freundlich, Halsey, Langmuir, Temkin, and DR, with the relevant parameters and constants being calculated. Langmuir isotherm (Birniwa *et al*., 2022) indicates that molecules are

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adsorbed as a monolayer onto the adsorbent surface, primarily by chemical bonds (see equation (1-2)). The application of the Freundlich isotherm describes effectively the surface heterogeneity in addition to the imbalanced allocation of energy and active sites on the adsorbent surface. Compounds with higher K_f values exhibit a stronger affinity for the adsorbent as compared to those with lower K_f values. Moreover, excellent correlation coefficients completely ensured and revealed the fact that the available experimental data closely matches and well fitted with the Freundlich isotherm model (see equation (3)) (Othman *et al.*, 2023; Ajibade & Nnadozie, 2023). The Halsey model (equation (4)) is utilized to access multilayer adsorption, where dye molecules are located at a significant distance from the adsorbent surface. To demonstrate the chemisorption of heterogeneous surfaces, the Temkin model is employed (see equation (5)).

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}}\right)\frac{1}{C_e} + \frac{1}{q_{max}} \quad (1)$$

$$R_L = \frac{1}{1+K_L C_e} \quad (2)$$

The Langmuir constant K_L determines the maximal adsorption energy based on the adsorbent's area. Additionally, R_L is a dimensionless separation factor, where its values determine the shape of the isotherms (Kumar *et al.*, 2013; McKay *et al.*, 2011; Ashour *et al.*, 2022).

The Freundlich equationuationuation is shown in equation (3).

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \quad (3)$$

Where C_e, K_f, and $1/n$ are Freundlich constants (Qin *et al.*, 2023).

Halsey's linearized equationuationuation is shown in equation (4).

$$lnq_e = \frac{lnK_{HA}}{n_{HA}} - \frac{lnC_e}{n_{HA}} \quad (4)$$

Where n_H and K_H are Halsey's isotherm model constant (Amin *et al.*, 2015; Taher *et al.*, 2023).

The equation for Temkin isotherm is shown in equation (5).

$$q_e = \frac{RT}{B_T}\ln(A_T C_e) \quad (5)$$

3.5. Kinetic Modelling

Adsorption kinetic studies are crucial for optimizing conditions that govern pollutant adsorption. In literature kinetic data have been analyzed using several models including pseudo 1st order (PFO), pseudo 2nd order (PSO), intraparticle diffusion model (IPD), and Elovich model which can be expressed in equation (6-9). Each of these models provides insight into the adsorption process.

$$\log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q^2}_e} + \frac{t}{q_t} \quad (7)$$

$$q_t = k_p t^{1/2} + C \quad (8)$$

Where k_p is the IPD rate constant (min^{-1}) which can be determined from the plot of q_t vs t ^{½} and C is the intercept.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta} lnt \quad (9)$$

3.6. Photocatalysis for Dye Degradation

Adsorption is established on the physical or chemical bond of dye molecules to the surface of a solid substance, whereas photocatalysis encompasses the use of light to stimulate a catalyst, typically a semiconductor, which then degrades the dye. This technique is very valuable in environmental cleanup like water purification, air treatment, and self-cleaning surfaces. The semiconductor absorbs photons and moves an electron (e^-) from the valence band (VB) to the conduction band (CB), resulting in a positively charged hole (h^+). These electron-hole pairs move towards the surface, where they are easily able to take part in redox reactions holes (h^+) oxidize water molecules, producing hydroxyl radicals (•OH) (Ajmal *et al.*, 2014; Yang & Wang; 2018; Mohamadpour & Amani, 2024). Both species are tremendously reactive and are involved in breaking down organic pollutants, making photocatalysis an effective technique for dye degradation, insecticides, and other harmful substances. **Figure 2** depicts the mechanism of photocatalysis.

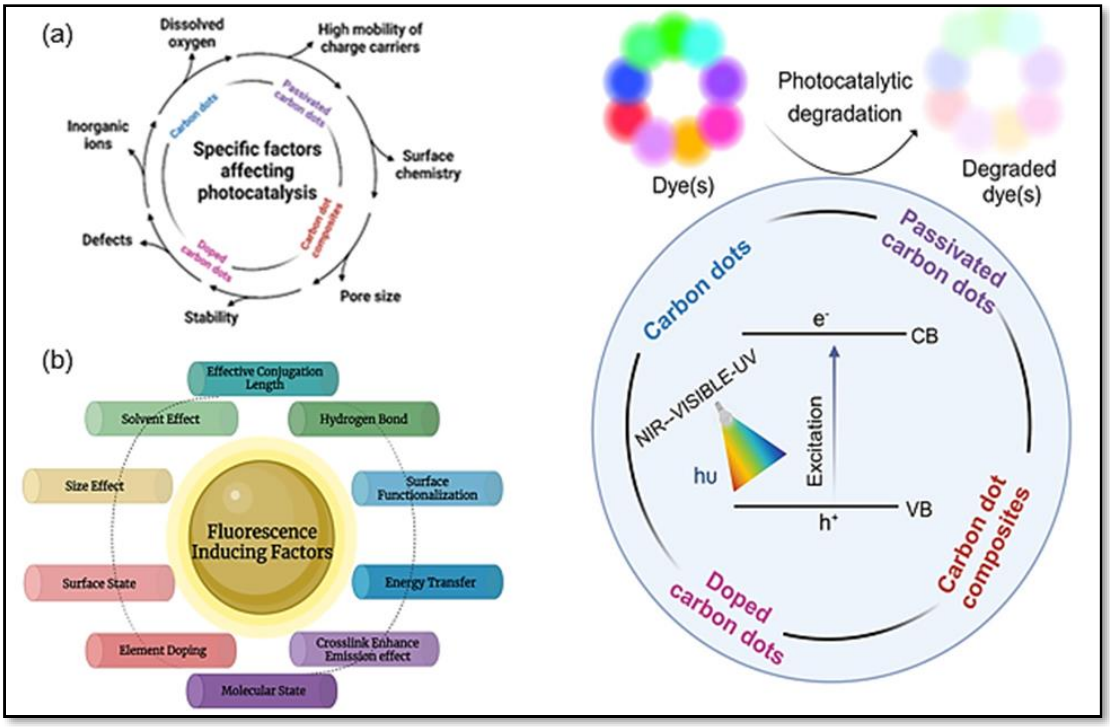

Figure 2. Specific factors affecting photocatalysis (b) fluorescence inducing factors (c) Mechanism of photocatalysis (Kaur *et al.*, 2024).

The effectiveness of photocatalysis is determined by various parameters, including the semiconductor's bandgap, charge carrier recombination, and light absorption capabilities. (Lettieri *et al.*, 2021). The key problem is to minimize the electron-hole pairs recombination, which limits total efficiency. Advanced tactics such as doping with metals or nonmetals and establishing heterojunctions between different materials are used to improve charge separation and broaden light absorption (Chen *et al.*, 2021). Continued research in optimizing photocatalyst material holds potential for addressing environmental pollution and advancing clean energy technologies. In literature. Different materials were employed by the researchers in photocatalysis such as TiO_2 (Lee & Park, 2013). Hybrid BiOBr–TiO_2 nanocomposites (Wei *et al.*, 2013), ZnO nanoparticles (Mohd Adnan *et al.*, 2016), carbon nitride supramolecular hybrid (Asif *et al.*, 2024) for wastewater treatment.

4. CONCLUSION

Both adsorption and photocatalysis offer effective solutions for removing contaminants from water, particularly organic dyes. Adsorption is economical and possesses a basic and simple design considered an efficient method for pollutant removal, while photocatalysis aids

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in pollutant degradation under light exposure. Another fact is that due to the large surface area to volume ratio of nanoparticles, they have a greater capacity and tendency for enhanced adsorption and photocatalytic degradation. To understand the in-depth and detailed mechanism of adsorption and photocatalysis, additional comprehensive computational approaches such as DFT or machine learning could be applied. Understanding the basic mechanism of dye adsorption and its subsequationuationuent degradation into final products, ideally which could be CO_2 and H_2O, can be investigated, and used to design a suitable catalytic surface for the effective degradation of dyes. There are several studies published to discover new photocatalytic active materials for dye degradation but there is a lack of in-depth understanding of the degradation process over the surface of these materials.

5. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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