Migration Letters

Volume: 20, No: S13(2023), pp. 114-122

ISSN: 1741-8984 (Print) ISSN: 1741-8992 (Online)
www.migrationletters.com

Synthesis of CuO/CeO_2 Nanocomposites for Adsorption and Efficient Photocatalytic Degradation of Methylene Blue Dye

Dr. Vijayalaxmi Biradar[1] and Ravi Prakash Mahobia[2]

Abstract

Nanocomposites are composed of a wide range of systems, including 1-D, 2-D, 3-D, and unstructured substances, and are blended at nanometer sizes with very distinct constituents. Due to the presence of quantum confinement, surface Plasmon response, tunneling of electrons, and density of states, nanocomposites are superior materials that display unusual and distinctive features. Photocatalysts benefit from unique features offered by nanocomposites made of two or more semiconductors with differing band gaps. Due to their uses and possible threats to living things, dyes are considered the most significant water contaminants. Industrial effluent must be treated using powerful adsorbents and photocatalysts to remove dangerous chemical dyes from contaminated water sources. This paper employs a co-precipitation approach to create photocatalytic CeO_2 nanoparticles and a CuO/CeO_2 nanocomposite for the inexpensive removal of Methylene Blue (MB) from aqueous solution. In this approach, the dispersion of electrons and holes is induced by the absorption of visible light, leading to the breaking of water molecules into radicals. These radicals serve as agents for the degradation of dyes. Utilizing X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Ultra-Violet Visible spectroscopy (UV–Vis), and Fourier Transform Infrared spectroscopy (FTIR), the CuO/CeO_2 nanocomposite has been characterized. The peaks in XRD suggest that the nanocomposite is most likely made up of the crystalline phases of CuO and CeO_2. A sequence of smaller peaks and larger peaks are visible in the measured pattern, spanning the 20° to 40° 2θ range, indicating the presence of amorphous or loosely organized regions inside the material. The results of the FTIR study show that CuO and CeO_2 phases are present in the nanocomposite simultaneously. The results further suggest that the CuO/CeO2 nanocomposite exhibits notable photocatalytic activity, successfully facilitating the decomposition of the reactants under UV-Vis light exposure for a certain period.

Keywords: *Methylene blue dye, Nanocomposites, CuO, CeO2, Photocatalyst, Adsorbent, photodegradation.*

Introduction

The exponential advancement of technology and industry has significantly enhanced the quality of human existence. However, it has engendered an intricate network of environmental pollutants [1]. The textile, paper, and printing industries collectively manufacture a vast array of synthetic dyes regularly, including many distinct varieties. The wastewater these companies generate is considered troublesome due to its composition of various chemicals, suspensions, poisonous compounds, and colorants. The presence of

[1] Assistant Professor, Department of Electronics, Kalinga University, Naya Raipur, Chhattisgarh, India. ku.vijayalaxmibiradar@kalingauniversity.ac.in

[2] Assistant Professor, Department of Electrical, Kalinga University, Naya Raipur, Chhattisgarh, India. ku.raviprakashmahobia@kalingauniversity.ac.in

organic dyes in industrial effluents, which diminishes light penetration, significantly impacts the photosynthesis process of aquatic plants.

Additionally, the toxicity of metals, salts, and chlorides threatens aquatic organisms' survival. Hence, in the parliamentary process, it is imperative to employ efficient techniques for eliminating dye substances from wastewater to safeguard both human health and the surroundings. MB, a prominent dye, is important in several sectors, such as textiles, printing, and food. This aromatic aqueous solution, which contains sulphur, is utilized for coloring cotton, silk, and wool [2]. The electrostatic paint possesses the potential to pose a concern as a result of its adverse impacts on human health. The presence of these pigmented chemicals is significantly elevated in wastewater.

In recent years, there has been a notable rise in water pollution attributed to the rapid expansion and advancement of the industrial sector. The dyeing process leads to decreased water quality and reduced light penetration into the substrata. Additionally, these objects are regarded as having both aesthetic and sanitary qualities [3]. This particular hue can potentially induce allergic reactions and dermatological issues in individuals. Various technologies, including coagulation, membrane filtration, biological treatment, and adsorption, have been proposed to remove color contaminants from wastewater.

Nevertheless, these techniques include the transmission of color between phases without undergoing dye material degradation. Therefore, due to the generation of secondary pollutants, more treatment is required, wherein supplemental techniques such as advanced oxidation are recommended. Various techniques may be employed to eliminate colors from industrial effluents, including ion exchange, evaporation, inverse osmosis, chemical oxidization, ultrafiltration, microfiltration, and surface adsorption. Each of these processes possesses distinct objectives and constraints [4]. The photocatalyst is stimulated by light radiation, leading to the degradation of pollutants and their conversion into benign byproducts, such as water and CO_2. Photocatalysts assume a pivotal role in enhancing the process as mentioned above.

Furthermore, the semiconductor's Photocatalytic Activity (PA) can be augmented by introducing a certain concentration of oxygen vacancies via doping [5]. The successful construction of heterojunctions may be achieved by doping several Semiconductors (SC) that possess comparable band potentials, enhancing their charge separation efficiency. The heterojunction interfaces have the potential to function as a conduit for facilitating the passage of electron-hole pairs, hence promoting their effective separation. A limited body of research has specifically examined the enhancement of CeO_2 nanostructures by doping for ecological rehabilitation [6]. The PA characteristics of CeO_2 nanoparticles synthesized with various transition metal elements such as Mn, Ti, Fe, and Co were examined and documented. It was observed that introducing these dopants influenced the structure of the CeO_2 nanoparticles, increasing their surface area and absorption characteristics. Additionally, the presence of these transition metal moieties reduced the rate at which electron-hole pairs recombine [7].

Furthermore, MB, an aniline dye, is commonly employed to color various manufactured goods, particularly wool, silk, and cotton. Textile wastewater effluents exhibit a significant presence of the identified substance [8]. The potential risks of this phenomenon pose significant threats to humans and non-human organisms, including animals and plants. Hence, eliminating MB continues to be a paramount concern for industrialized countries.

In the current study, it has been demonstrated the effects of composite creation on CeO_2 nanostructures' structural, photosensitive, and PA properties. The Ce-Cu nanocomposites are synthesized using the co-precipitation technique. The materials created for this study have undergone analysis using several characterization techniques, and the findings have been extensively addressed. Furthermore, an investigation has been carried out to assess the PA efficiency of the subject under visible light irradiation, specifically targeting the breakdown of MB.

Related Works

The growing population and its needs have spurred industrial advances in recent years. This has increased land and groundwater contamination. Recent studies have used transition metal oxide nanoparticles in solitary or composite form due to their optical, electrical, magnetic, and catalytic properties. Photocatalysis, an emerging technique, uses microbes to break down chemical molecules and pigments. Photocatalysts produce fuel by removing CO_2 and splitting water [9].

SC photocatalysis can convert hazardous and non-biodegradable organic molecules into CO_2, water, and inorganic salts, purifying the environment. The fabric, paper, and polymer industries use water to dye their products. Companies that use color produce a lot of colored wastewater. MB is the most common industrial dye [10]. Cancer, cyanosis, nausea, increased heart rate, quadriplegic syndrome, and diarrhea are spreading due to pollution.

Therefore, wastewater degradation and purification should use a reliable and efficient treatment method. MB dye must be precisely broken down and purified to protect the environment. Several ways have been reported to remove methylene blue dye from polluted water. Adsorption and photocatalysts were crucial to water treatment. The main challenges of adsorption are adsorbent repair and hazardous sludge storage. Recently, several photocatalysts have removed hazardous wastewater effluents [11].

SC photocatalysis converts dyes into gaseous products instead of hazardous sludge buildup, a sustainable water filtration method. When a SC photocatalyst absorbs photons above its bandgap, electrons enter the Conduction Band (CB) and leave holes in the Valence Band (VB). These holes and electrons are strong oxidants and reductants that clean water of organic and inorganic contaminants [12]. It must overcome the large band gap, fast electron-hole recombination, and weak SC-pollutant interface to capture solar energy for various uses efficiently. CuO is a p-type SC used in field emitters, solar cells, rechargeable batteries, high-temperature superconductors, detectors, and catalysis.

Doping O_2 vacancies in the SC in a certain amount may improve PA. Doping several SCs with similar band potentials creates heterojunctions with improved charge separation efficiency. Using heterojunction layouts as transit channels can improve electron-hole pair dispersion. Few studies have focused on physically enhanced CeO_2 nanomaterials for environmental cleanup. PA properties of CeO_2 nanoparticles made with transition metal moieties like Mn, Ti, Fe, and Co were examined. This doping level changes the shape and structure of CeO_2 nanoparticles, increases their surface area and absorption, and reduces electron-hole pair recombination [13].

However, two or more SCs' complementary effects boost waste degradation. The energy-level systems in linked SC materials have distinct characteristics that show charge separation. Coupling several SC oxides narrows the band gap, raises the absorption spectrum to the visible area, and divides electron-hole pairs when exposed to light, increasing PA [14]. In this paper, photocatalytic CeO_2 nanoparticles and a CuO/CeO_2 nanocomposite have been generated using a co-precipitation method to remove MB from aqueous solution efficiently.

Materials and Methods

Materials

The chemical ingredients employed in the present experimental plan have been of analytical quality and utilized directly. SD Fine Chem. Limited was the source for the cerium nitrate hexahydrate and copper nitrate hexahydrate utilized as precursors for cerium and copper, respectively. The chemicals used have been of analytical quality and utilized without additional purification. Double distillation of water has been preferred for the creation of aqueous solutions.

Synthesis of CuO/CeO_2 Nanocomposites

The process of synthesizing cerium oxide (CeO_2) nanoparticles by the co-precipitation approach entails precipitation of cerium ions from aqueous solution, forming CeO_2 nanoparticles. A generalized chemical equation that serves to describe the synthesis process as follows:

$$Ce(NO_3)_3 + 3NaOH \rightarrow Ce(OH)_3\downarrow + 3NaNO_3 \quad (1)$$

In this equation:

The chemical formula $Ce(NO_3)_3$ denotes the compound cerium nitrate, which serves as the primary supplier of cerium ions in the form of Ce^{3+}. Sodium hydroxide (NaOH) is used as a precipitating agent to elevate the pH and commence precipitation. The chemical equation $Ce(OH)_3\downarrow$ denotes the production of cerium hydroxide as a solid residue. The chemical formula $3NaNO_3$ denotes the soluble compound sodium nitrate, which is produced as a byproduct in the process.

After the formation of cerium hydroxide [$Ce(OH)_3$] as a precipitate, it may undergo further processing to yield cerium oxide (CeO_2) nanoparticles. This is often achieved by calcination at elevated temperatures. It is important to acknowledge that the precise circumstances for synthesis, including the number of reactants, reaction temperature, and duration, may vary based on the particular laboratory's synthesis methodology.

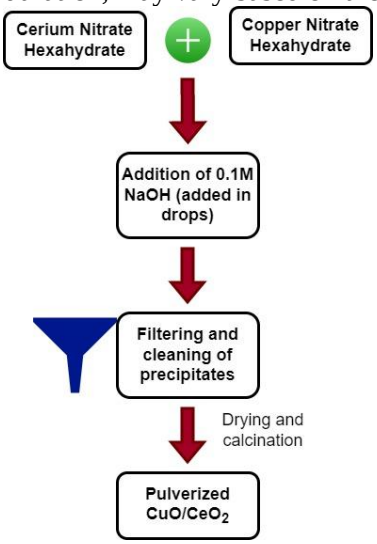

Figure 1: Synthesis of CuO/CeO_2 nanocomposites

In this synthesis scheme shown in Fig. 1, a precursor in the form of 10.9 g (0.1 M) of Cerium nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$] and 5% of 0.1M Copper nitrate hexahydrate has been dispersed in 250 mL of double distilled water. The combination has been subjected to heating and stirring, gradually increasing the solution's pH to 11 with the incremental addition of 0.1 M NaOH. Consequently, dispersion has been achieved. The growth solution underwent heating with continuous stirring at a temperature of 65℃ for 6.5 hours. The solid particles were then gathered, subjected to filtration, and rinsed with water and ethanol. Consequently, they were subjected to drying in an oven set at a temperature of 90℃ and underwent calcination at 650℃ for 6.5 hours.

Adsorption of MB onto CeO2/CuO Nanocomposites

The process of adsorption may be depicted in the following manner:

$$CeO2/CuO + MB \text{ (in solution)} \rightleftharpoons CeO2/CuO\text{-}MB \text{ (adsorbed complex)} \quad (2)$$

The notation CeO2/CuO is used to denote the CeO2/CuO nanocomposites in the given equation. The abbreviation MB, when used in the context of a solution, denotes the presence of methylene blue molecules inside the solution. The CeO_2/CuO-MB (adsorbed

complex) refers to the nanocomposites of CeO_2/CuO where MB molecules are adsorbed onto the surface.

Several parameters, including temperature, concentration, and the nanocomposites' surface characteristics, influence the balance between the adsorbed complex and the unbound MB molecules. Adsorption is often used as a first treatment process to enhance the concentration of pollutants on the catalyst's surface before undergoing PA degradation.

Photocatalytic Degradation of Adsorbed MB

The PA has been assessed by using an aqueous solution of MB. A UV-Vis spectrophotometer assessed the degree of photodegradation caused by the photocatalysts when exposed to sunlight. The reaction solutions have been created by introducing the appropriate quantity of the developed nanocomposites into a 0.5L solution containing 0.04mM MB. The initial pH of the MB solution was measured to be 5. The aforementioned suspended combination was churning in a light-deprived environment for about 30 minutes until a state of equilibrium was attained.

The suspension was agitated in a lightless environment for 30 minutes to achieve adsorption-desorption equilibrium. The aqueous solution containing MB and the photocatalyst was exposed to direct sunshine while continuously stirred. The suspension was subjected to regular intervals, namely every 30 minutes, to obtain analytical samples. These samples were then centrifuged and cleaned to eliminate the presence of the photocatalyst. In addition, a UV-Vis spectrophotometer was used to assess the concentration of MB in the analyzed samples. Fig. 2 illustrates a suggested method for the breakdown of MB using catalysts that have been manufactured.

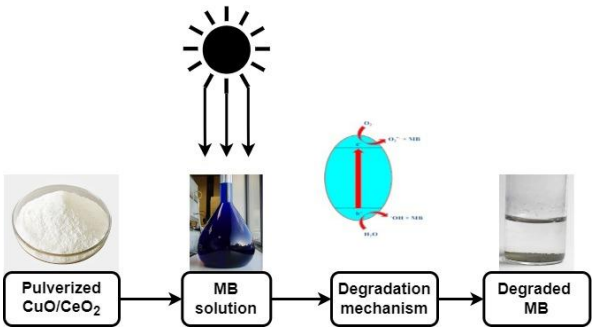

Figure 2: Suggested method for the degradation of MB using CuO/ CeO_2

One plausible method is the cooling or injection of electrons from photoexcited MB particles to CuO/ CeO_2. The solution combination underwent reduction of molecular O_2, which was then followed by the oxidative disintegration of MB, a process referred to as photosensitization. The degrading process primarily relies on the dispersion of electron-hole pairs, often known as an electron-hole charge. In this context, the power of visible light radiation is directly associated with the band gap energy of the catalytic substance. This energy prompts the movement of electrons from the VB to the CB. By creating a vacancy in the VB, the formation of a hole facilitates the breakdown (oxidation/reduction) of MB by generating unstable free radicals. The process begins with the collision of excited electrons with the closest O_2 atoms, forming superoxide anion radicals (O_2^-). These radicals then undergo further reactions with hydroxyl radicals and protons derived from H_2O, ultimately producing hydrogen peroxide (H_2O_2). In this particular system, the dispersion of electrons and holes is induced by the absorption of visible light, leading to the breaking of water molecules into radicals. These radicals serve as agents for the degradation of dyes.

The PA degradation of MB using the proposed method (CuO/CeO_2 nanocomposite) has been given as:

$$\text{PA degradation of MB } (\%) = [(A_0 - A_t)/A_0] \times 100 \quad (3)$$

The initial absorbance has been denoted as A_0. Absorbance at time 't' is A_t.

Results and Discussion

Nanocomposites' surface morphology has been evaluated using Field Emission Scanning Electron Microscopy (FESEM).

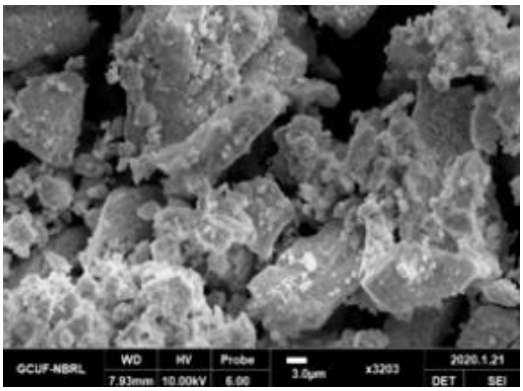

Figure 3: FESEM images of the CuO/CeO_2 nanocomposite

Fig. 3 shows the FESEM images of the CuO/CeO_2 nanocomposite. The results demonstrate that the nanoparticles have a homogeneous distribution, hence providing insights into the surface morphologies of the CuO/CeO_2 nanocomposites. This micrograph reveals the presence of sizable aggregates composed of tiny particles of CeO_2. The mean particle size is estimated to be about 20–25 nm. Despite the presence of aggregates in the images, it is evident that the nanocomposites have an irregular surface topology that facilitates catalytic activity.

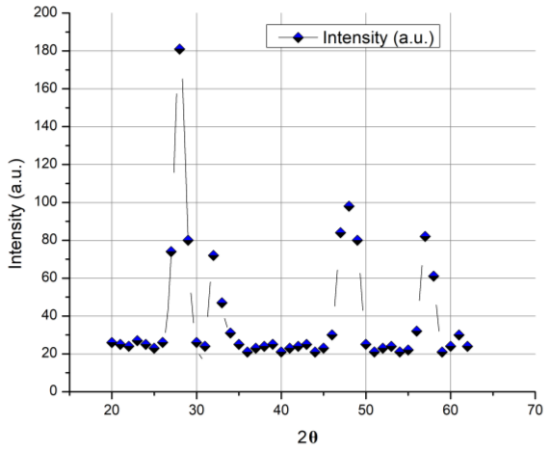

Figure 4: XRD pattern of CuO/CeO_2 nanocomposite

The structural characteristics of the CuO/CeO2 nanocomposite may be elucidated by analyzing its XRD pattern as shown in Fig. 4. The diffraction angles, denoted as 2θ values, provide valuable information on the crystalline phases that exist inside the nanocomposite. Within this arrangement, one may detect peaks occurring at different 2θ angles, accompanied by matching intensity levels denoted in arbitrary units (a.u.). The observed peaks at 2θ values about 27.3° (200), 28.4° (111), and 58.5° (311) have noticeably elevated intensities, suggesting the existence of distinct crystalline phases or favored orientations. The presence of these peaks indicates that it is probable that the nanocomposite is composed of crystalline phases of CuO and CeO_2. Furthermore, the observed pattern exhibits a sequence of minor peaks and wider peaks across the range of 20° to 40° 2θ, indicating the presence of amorphous or less structured areas inside the material. Additional investigation and evaluation of established reference patterns would be required to validate the precise crystalline phases and their respective proportions inside the CuO/CeO_2 nanocomposite.

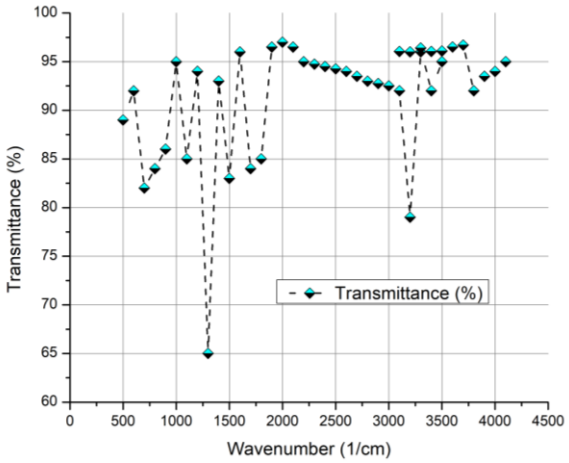

Figure 5: Spectral analysis of CuO/CeO_2 nanocomposite using FTIR

The FTIR spectrum study of the CuO/CeO_2 nanocomposite shown in Fig. 5 yields significant insights into its chemical composition and bonding properties. The wavenumber values, expressed in units of cm^{-1}, correspond to the vibrational frequencies associated with functional groups and chemical bonds in the nanocomposite. On the other hand, the transmittance percentages provide information on the extent to which infrared light can pass through the sample. The spectrum has several conspicuous peaks. The existence of distinct and robust chemical linkages, namely the metal-oxygen (M-O) vibrations in the CuO and CeO_2 components, is indicated by the high transmittance area between 1000 and 2000 cm^{-1}. Peaks within the lower wavenumber spectrum, namely within the region of 3200-3600 cm^{-1}, indicate the existence of hydroxyl (OH) or vibrations associated with water molecules.

Furthermore, the observation of peaks within the spectral region of 3300-3400 cm^{-1} indicates the existence of O-H stretching vibrations. In general, the findings from the FTIR study indicate the simultaneous presence of CuO and CeO2 phases within the nanocomposite. Additionally, the FTIR analysis reveals the presence of hydroxyl groups, which contribute to the nanocomposite's distinctive chemical composition and features. Additional investigations using peak assignments and spectrum comparisons have the potential to provide a more comprehensive understanding of the composition and functional groups present in the nanocomposite.

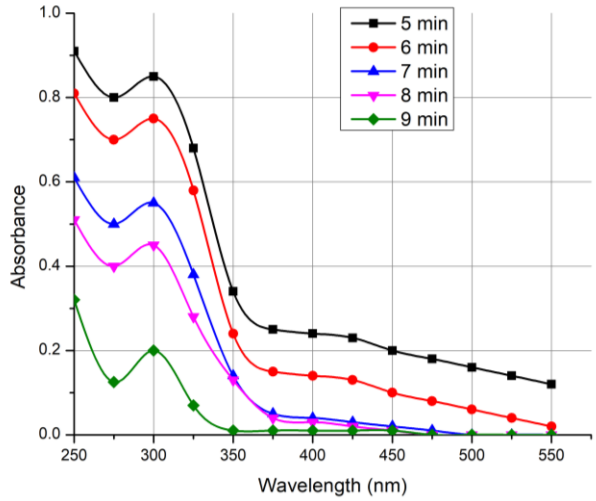

Figure 6: UV-Vis spectra of CuO/CeO_2 nanocomposite during the irradiation of the reaction mix.

The UV-Vis spectra in Fig. 6 of the CuO/CeO2 nanocomposite, obtained while irradiating the reaction mixture, offer valuable information on the PA performance of the material at various time intervals. The spectral data illustrates the variation in absorbance at different wavelengths as the process proceeds. During the initial stage (5 minutes), there is observable absorption within the UV wavelength range (about 250-350 nm), indicating the existence of photoactive components produced by the nanocomposite when exposed to radiation. A rise in response time is accompanied by a progressive decline in absorbance throughout the UV-Vis spectrum, suggesting the degradation or alteration of these entities. The observed reduction in absorbance is notably significant within the UV spectrum, indicating the successful PA degradation of the reaction mixture. As mentioned above, the pattern persists as the duration of irradiation increases, as seen by absorbance values that approach almost zero at longer wavelengths, suggesting effective degradation. The findings indicate that the CuO/CeO2 nanocomposite has significant PA efficacy, effectively decomposing the reactants over time when exposed to UV-Vis light.

Conclusion

This paper produced photocatalytic CeO2 nanoparticles and a CuO/CeO2 nanocomposite using a co-precipitation method to remove MB from aqueous solution efficiently. The CuO/CeO_2 nanocomposite has been studied using XRD, FESEM, UV-Vis, and FTIR. The nanocomposite is most likely composed of the crystalline phases of CuO and CeO_2, according to the peaks in the XRD analysis. The observed pattern, spanning the 20° to 40° 2θ range, shows a series of smaller peaks and larger peaks, indicating the presence of amorphous or loosely organized regions inside the material. The FTIR study's findings demonstrate that the CuO and CeO_2 phases are both present in the nanocomposite simultaneously. The findings also point to the CuO/CeO_2 nanocomposite's noteworthy PA, which successfully speeds up the reactant's degradation when exposed to UV-Vis light over some time. Therefore, by removing dangerous MB dye, CuO/CeO_2 nanocomposite could help treat industry wastewater.

References

Poorsajadi, F., Sayadi, M. H., Hajiani, M., & Rezaei, M. R. (2022). Synthesis of CuO/Bi2O3 nanocomposite for efficient and recycling photodegradation of methylene blue dye. *International journal of environmental Analytical Chemistry*, *102*(18), 7165-7178.

Esmaeili, H., & Foroutan, R. (2018). Adsorptive behavior of methylene blue onto sawdust of sour lemon, date palm, and eucalyptus as agricultural wastes. *Journal of Dispersion Science and Technology*.

Rangreez, T. A., Mobin, R., & Chisti, H. T. (2022). Potentiometric Determination of Mercury Ions by Sol-gel Synthesized Multi-walled Carbon Nanotubes Zr (IV) Phosphate Composite Fabricated Membrane Electrode. *Current Analytical Chemistry*, *18*(4), 466-474.

Azanaw, A., Birlie, B., Teshome, B., & Jemberie, M. (2022). Textile effluent treatment methods and eco-friendly resolution of textile wastewater. *Case Studies in Chemical and Environmental Engineering*, 100230.

Kumar, S., Kumar, A., Navakoteswara Rao, V., Kumar, A., Shankar, M. V., & Krishnan, V. (2019). Defect-rich MoS2 ultrathin nanosheets-coated nitrogen-doped ZnO nanorod heterostructures: an insight into in-situ-generated ZnS for enhanced photocatalytic hydrogen evolution. *ACS Applied Energy Materials*, *2*(8), 5622-5634.

Killivalavan, G., Sathyaseelan, B., Kavitha, G., Baskarann, I., Senthilnathan, K., Sivakumar, D., ... & Maaza, M. (2020). Cobalt Metal Ion Doped Cerium Oxide (Co-CeO 2) Nanoparticles Effect Enhanced Photocatalytic Activity. *MRS Advances*, *5*, 2503-2515.

Zhang, W., You, Q., Shu, J., Wang, A., Lin, H., & Yan, X. (2023). Photocatalytic degradation of glyphosate using Ce/N co-doped TiO2 with oyster shell powder as carrier under the simulated fluorescent lamp. *Frontiers in Environmental Science*, *11*, 61.

Singha, K., Pandit, P., Maity, S., & Sharma, S. R. (2021). Harmful environmental effects for textile chemical dyeing practice. In *Green Chemistry for Sustainable Textiles* (pp. 153-164). Woodhead Publishing.

Koe, W. S., Lee, J. W., Chong, W. C., Pang, Y. L., & Sim, L. C. (2020). An overview of photocatalytic degradation: photocatalysts, mechanisms, and development of photocatalytic membrane. *Environmental Science and Pollution Research*, *27*, 2522-2565.

Zhang, F., Wang, X., Liu, H., Liu, C., Wan, Y., Long, Y., & Cai, Z. (2019). Recent advances and applications of semiconductor photocatalytic technology. *Applied Sciences*, *9*(12), 2489.

Fanourakis, S. K., Peña-Bahamonde, J., Bandara, P. C., & Rodrigues, D. F. (2020). Nano-based adsorbent and photocatalyst use for pharmaceutical contaminant removal during indirect potable water reuse. *NPJ Clean Water*, *3*(1), 1.

Maraj, M., Anwar, H., Saba, A., Nabi, G., Shaheen, N., Ansar, N., ... & Sun, W. (2023). Synergistic effect of nanostructured CdO/Ag3PO4 composite for excellent electrochemical and photocatalytic applications. *Arabian Journal of Chemistry*, *16*(8), 104906.

Hamidian, K., Najafidoust, A., Miri, A., & Sarani, M. (2021). Photocatalytic performance on degradation of Acid Orange 7 dye using biosynthesized un-doped and Co doped CeO2 nanoparticles. *Materials Research Bulletin*, *138*, 111206.

Mansoori, S. M., Yamgar, R. S., & Rathod, S. V. (2021). Photocatalytic Degradation of Methylene Blue Dye Using Synthesized CuO: CdO Nanocomposite. *Journal of Scientific Research*, *65*(6).

Jamil, M.N., Hossain, M.S., Islam, R.U., & Andersson, K. (2020). Technological innovation capability evaluation of high-tech firms using conjunctive and disjunctive belief rule-based expert system: a comparative study. Journal of Wireless Mobile Networks, Ubiquitous Computing, and Dependable Applications, 11(3), 29-49.

Alizadeh, M., Andersson, K., & Schelen, O. (2020). A survey of secure internet of things in relation to blockchain. Journal of Internet Services and Information Security (JISIS), 10(3), 47-75.