Indian Journal of Advances in Chemical Science

Research Article

Development of a Visible Light-Active Nanocatalyst Based on Barite $SrCrO_4$ for Efficient Methylene Blue Degradation

S. R. Patil[1], T. S. Shrirame[2]*

[1]Department of Chemistry, Science College, Pauni, Maharashtra, India, [2]Department of Chemistry, Shri Shivaji Science and Arts College, Chikhli, Maharashtra, India

ABSTRACT

Environmental pollutants and energy crises are a major global concern. Growing urbanization and rising living standards burden human as well as environmental health. Photocatalytic degradation of organic contaminants is an economically viable and efficient way to address these issues. Here, we are exploring the catalytic activity of $SrCrO_4$ nanoparticles as an eco-friendly and efficient catalyst in the degradation of methylene blue (MB) under visible light irradiation about wavelength range 655–660 nm. Strontium chromate is prepared by three different methods under various conditions from an application point of view. The degradation was monitored by measuring the change in concentration of substrate as a function of the irradiation period using spectroscopic techniques. The degradation of MB was studied using various factors including the type of photocatalyst, catalyst, and substrate concentration. The degradation rate was found to be strongly influenced by all the above parameters. In the current study, we will discuss the design and application of $SrCrO_4$ for the degradation of MB under visible light irradiation. $SrCrO_4$ prepared by the ultrasonic method was found to be more efficient as compared to the reflux method and solid-state methods.

Key words: Methylene blue, Nanocatalyst, Photocatalyst, Strontium chromate.

1. INTRODUCTION

In emerging countries, the textile industry is considered one of the key factors in the industrial revolution. However, during the past few decades, various organic and inorganic pollutants generated from such textile industries have caused tremendous deterioration of water resources [1,2]. The colored wastewater generated from textile industries contains high pH, chemical oxygen demand, biological oxygen demand, unpleasant odor, suspended solids such as heavy metals, inorganic salts, and hazardous chemicals [3,4]. However, the major portion of industrial effects carries a huge concentration of harmful and carcinogenic organic dyes. Consequently, it is essential to eliminate harmful dyes from water bodies.

Methylene blue (MB) is a principal class of synthetic azo dyes. Azo dyes are more than 50% of the dyes manufactured worldwide. Azo dye biodegradation in aerobic conditions is difficult and gives carcinogenic aromatic amines under anaerobic conditions [5]. Different conventional methods have been designed by researchers in the past several years [6].

This includes electrochemical, flocculation, coagulation, reverse osmosis; biodegradation, ultrafiltration, chemical oxidation, ion exchange, and adsorption are some conventional water treatment methods [7,8]. However, these techniques propose their limitations and threats to the environment due to excessive use of toxic chemical reagents, high cost, and disposal of sludge formed [9]. After applying these methods, pollutants are generated as secondary products. According to various studies, catalysis is one of the most efficient, economically feasible, and sustainable methods for the degradation of organic dyes [10,11]. Hence photocatalytic degradation serves as a substitute for wastewater treatment [12].

In recent years, the nanoparticles (NPs)-based semiconducting photocatalyst has been used frequently for the removal of organic dyestuff. In classical times the NP-based photocatalyst can be synthesized using surfactant, a chemical reducing agent with the least agglomeration [13]. During the past decades, researchers have focused on eco-friendly synthesis routes to minimize the generation of toxic and harmful byproducts [14]. Plants parts (roots, stems, leaves, flowers, fruits, etc.), microbes (bacteria, fungi, algae, yeast, etc.), protein, enzymes, amino acids, and biomolecules [15,16]. These dye compounds show very minimum absorption in the visible region and hence do not degrade easily by direct sun exposure. Extreme degradation can be achieved by combining semiconductors with oxide photocatalysts such as CdS, ZnO, and TiO_2. However, the majority of these oxide photocatalysts are effective only under UV light, they are restricted to use under direct sunlight as only 4% of UV light reaches to earth's surface [17,18]. A handful of photocatalysts that work under visible light have a fast recombination rate makes them less efficient [19]. Among these, $SrCrO_4$ performed as an active photocatalyst due to a band gap of 2.8 eV.

In our study, we focused on the fabrication and characterization of strontium chromate nanosized photocatalyst, for reduction and degradation of MB dye.

***Corresponding author:**
T. S. Shrirame,
E-mail: truptishrirame111@gmail.com

ISSN NO: 2320-0898 (p); 2320-0928 (e)
DOI: 10.22607/IJACS.2024.1203007

Received: 09th July 2024;
Revised: 11th July 2024;
Accepted: 05th August 2024;
Published: 05th September 2024

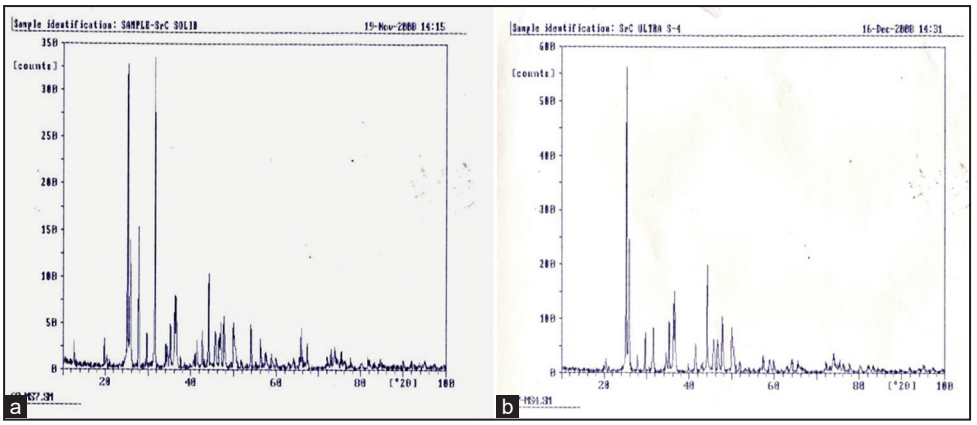

Figure 1: XRD patterns of SrC-SS (a) and SrC-US, SrC-RF (b).

1.2. HISTORICAL BACKGROUND

In the beginning of 21st century, the mankind has to face the problems of water as an important threat. According to WHO, 25% of the world population suffers health and hygienic problems related to water [20]. Therefore research field of water purification can be extensively studied in the last decades for the removal of organic pollutants from water.

TiO_2 and $SrTiO_3$ photocatalyst were used for water splitting during 1970s and first half of the 1980s [21]. In the beginning of second half of 1980s, new photocatalyst such as $K_2La_2Ti_3O_{10}$, ZrO_2, $K_4Nb_6O_{17}$, $BaTi_4O_9$, Ta_2O_5, etc were discovered [22]. Many cation containing oxide photocatalyst of Ga^{3+}, In^{3+}, Ge^{4+}, Sn^{4+}, and Sb^{5+} with d10 configuration were also been reported. As a result, there is now an abundance of information on photocatalyst for water splitting and degradation of harmful components from water. Nevertheless, these metal containing photocatalysts of d^0 and d^{10} configuration responds to only UV light due to their wide band gaps (Band gap > 3.0 eV) [23]. There aren't many materials available for photocatalysts driven by visible light. In 1990s, highly active photocatalyst which work under visible radiations even in the presence of sacrificial reagents, were only WO_3 and Pt/CdS [24]. However, it has been discovered that a variety of oxides, oxynitrides, and oxysulphides are active for the evolution of H_2 and O_2 when exposed to visible light even in the presence of sacrificial reagents [25].

2. MATERIALS AND METHODS

2.1. Materials

Potassium chromate (K_2CrO_4), Strontium carbonates ($SrCO_3$), and MB of analytical grade was purchased by S.d. fine-Chem Limited. The preparation of all aqueous solutions was done with double distilled water.

The strontium chromate ($SrCrO_4$) was prepared by three different methods viz reflux method, ultrasonic, and solid-state methods. The preparation procedures for the synthesis of strontium chromate are illustrated below.

2.2.1. Ultrasonic method

The aqueous solution of 100 mL of 0.1 N K_2CrO_4 was prepared for the synthesis of $SrCrO_4$ and kept in an ultrasonic bath for 20 min. Then, 100 mL of 0.1 N $SrCO_3$ was added dropwise into the above solution in an ultrasonic bath and both the solutions were allowed to react under ultrasonic conditions for about 1 h. The obtained solution was kept overnight. On the next day, lemon lemon-yellow colored precipitate of $SrCrO_4$ was obtained. The precipitate was washed repeatedly with double distilled water and maintained at 60°C in the oven for about 8 h to evaporate the solvent to obtain a dry precursor. Finally, dry precursors were crushed into lemon yellow colored powder of $SrCrO_4$.

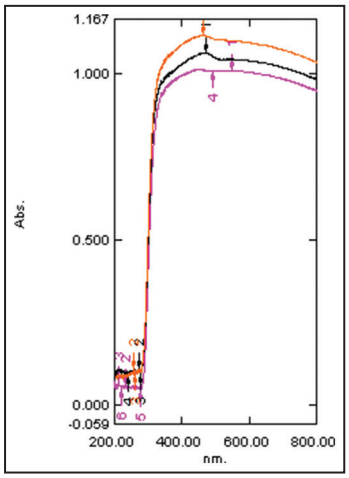

Figure 2: Absorption spectra of SrC-US (Red), SrC-RF (Black), and SrC-SS (Pink).

2.2.2. Reflux method

A mixture of 0.1 N $SrCO_3$ and 0.1 N K_2CrO_4 reflux was at 100°C for 1 h. Wash the reaction mixture with double distilled water. Powdered $SrCrO_4$ is obtained and placed in an oven for 8 h at 60°C. Lemon Yellow powder of $SrCrO_4$ is formed.

2.2.3. Solid state method

For the synthesis of strontium chromate NPs by solid-state method, a mixed powder of K_2CrO_4 (1.9419 g) and $SrCO_3$ (1.6987 g) was ground for 30 min in a mortar at room temperature. The mixture produced by grinding was then mixed with KOH powder, and grinding continued for a further 30 min at room temperature. The product obtained was then dried in an oven at 100°C for about 8 h. After drying, the lemon-yellow colored powder of $SrCrO_4$ was obtained.

3. STRONTIUM CHROMATE AS A PHOTOCATALYST

3.1. XRD Analysis

The X-ray diffraction analysis was performed to collect information regarding the crystalline nature of newly synthesized NPs. The XRD pattern of $SrCrO_4$ NPs synthesized by several techniques is shown in Figure 1 X-ray analysis and characteristics 2Θ values of different peak indexed barite strontium chromate structure. The XRD pattern shows that $SrCrO_4$ crystallizes in the monoclinic phase with the $P2_1/n$ space group. The recorded results matched well with JCPDS card #35-0743. The crystallite sizes (D) of $SrCrO_4$ NPs were calculated using the Debye-Scherrer formula given as [20],

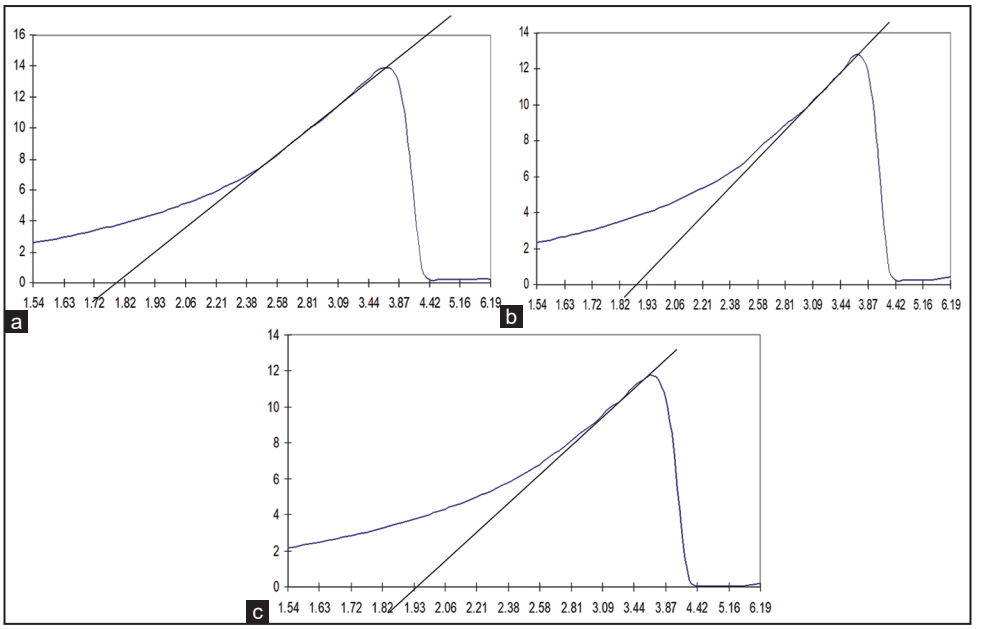

Figure 3: Band gap energy of SrC-US (a), SrC-RF (b) and SrC-SS (c).

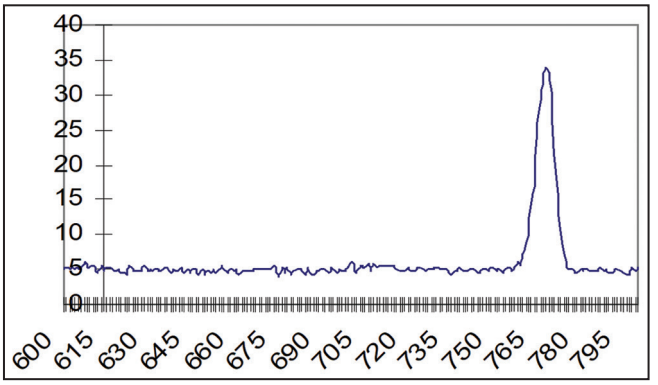

Figure 4: Photoluminescence spectra SrC-US.

$$D_{hkl} = \frac{k\lambda}{\beta cos\theta}$$

Here, D is the crystallite size of NPs, k is the shape factor (0.9), λ is the wavelength of X-ray, Θ diffraction angle, β is full width at half maximum (FWHM).

The crystallite size was calculated by taking the FWHM value for Sr-CR, $SrCrO_4$ synthesized by ultrasonic method (SrC-US), and $SrCrO_4$ synthesized by solid-state method (SrC-SS) estimating a size of 82 nm. This indicates that a low-temperature process decreases the rate of agglomeration and hence reduces particle size in the nanometer range.

3.2. Absorption Spectra

The absorption spectrum of SrCrO4 synthesized by ultrasonic method (Src-US), sol-gel method (Src-RF) and solid state method (Src-SS) are indistinguishable. The wavelength of light absorbed by SrCrO4 is dependent on different energy levels and electronic distributuion within the material. Absorption occurs between highest occupied molecular orbits (HOMO) and lowest unoccupied orbits (LUMO) in the range of 400-750 nm (visible range) as shown in Figure 2. The absorption spectra constitute a single absorption band validates chromium is a hexavalent not a trivalent.

3.3. Bandgap Energy

The photochemical and photophysical properties of semiconductors are based on band gap energy hence its precise determination is required. Tauc, in 1966 proposed a technique for band gap energy determination using absorption spectra. With the prepared sample, the UV/VIS diffuse reflectance spectroscopy method was used to estimate the band gap energy. The minimum wavelength required for the excitation of the electron relies on the band gap energy (E_{bg}) of the photocatalyst which is given as

$$E_{bg}=1240/\lambda \text{ eV}$$

λ=wavelength of light in nm

$(\alpha E_{bg})^2$ versus E_{bg} plot shows band gap transition as shown in Figure 3. Where α is the absorption coefficient and E_{bg} is the energy of the photon. The absorption energy, or 1.82 eV band gap energy, is obtained by extrapolating the energy of E_{bg} to α=0.

3.4. Photoluminescence Spectra (PL Spectra)

To learn more about the effectiveness of charge carrier immigration, transfer, and trapping as well as the destiny of electron-hole pairs in semiconductor particles, photoluminescence emission spectra have been used extensively. PL emission spectrum with an excitation wavelength at room temperature is shown in Figure 4. The direct recombination of a hole in the hybrid valence band (VB) of O 2p and Sr 4d and a conduction electron in the Cr 3d orbital was identified as the primary source of the emission peak.

3.5. Photocatalytic Degradation

The photocatalytic degradation activity of $SrCrO_4$ was evaluated by studying MB dye degradation under the influence of visible light; results are shown in Figure 5. The UV-visible absorption spectra of the solution sample after centrifugal treatment were measured and the characteristic peak at 655–660 nm was absorbed. At irradiation time t min, the MB dye degradation percentage was computed using the formula,

$$D.P.(t) = \frac{A_0 - A_t}{A_0} \times 100\%$$

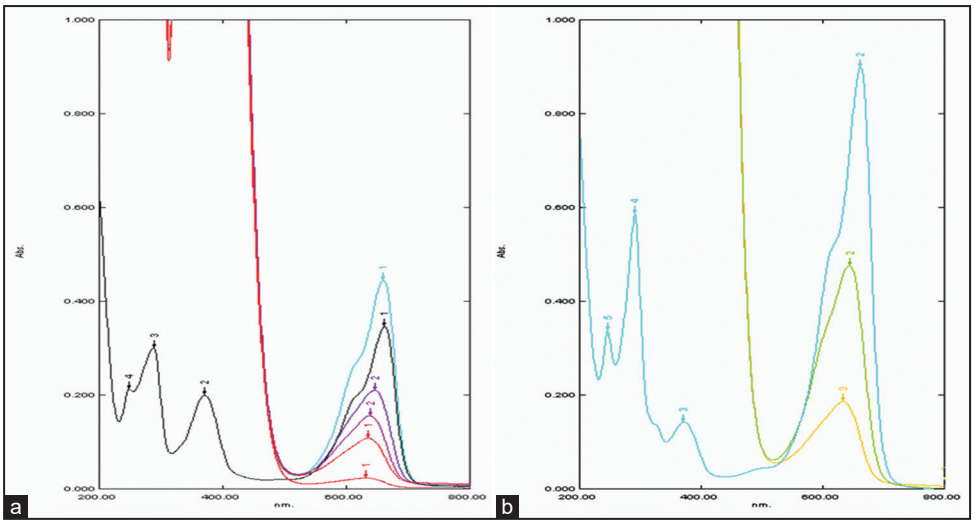

Figure 5: Temporal Spectral Changes during photocatalytic degradation of MB in the Presence of photocatalyst SrC-US and SrC-RF(a) and SrC-SS (b) under visible light.

The finding shows that MB dye degradation by SrC-RF and SrC-US is about 97% while SrC-SS is about 81% after 75 min of irradiation of visible light at 300 mg $SrCrO_4$ photocatalyst when MB concentration is 6 ppm. In the same experimental condition, the self-photocatalytic degradation of MB was reported to be 0%. The temporal evaluation of spectral changes happens on MB dye photodegradation as shown in Figure 5. Under visible light, the degradation of various concentrations of MB dye in an aqueous solution was used to measure the photocatalytic activity of SrCrO4.

3.6. Mechanism of Photocatalytic Degradation

Initially, MB absorbs visible radiation of the appropriate wavelength and gets excited to a singlet excited state. Across intersystem crossing (ISC) it further transfers to a triplet excited state. $SrCrO_4$ photocatalyst also absorbs radiation and electron excited from the conduction band (CB) to the VB which generates holes in VB. The electron from CB combines with dissolved oxygen and produces superoxide free radicals (O_2^-). These radicals degrade MB dye into leuco dye which further gives secondary harmless products such as Co_2 and H_2O. A proposed tentative mechanism for the degradation of MB dye in the presence of $SrCrO_4$ is

$$^1MB_0 \xrightarrow{\hbar} {}^1MB_1$$

$$^1MB_0 \xrightarrow{ISC} {}^3MB_1$$

$$SrCrO_4 \xrightarrow{\hbar} SrCrO_4h^+(VB) + e^-$$

$$O_2(\text{Dissolved Oxygen}) + e^-(CB) \rightarrow O_2^-$$

$$^3MB_1 + O_2^- \rightarrow \text{Leuco form of MB}$$

$$\text{Leuco form of MB} \rightarrow CO_2 + H_2O$$

4. CONCLUSION

In this study, we have successfully illustrated that the synthesis of barite $SrCrO_4$ NPs catalyzed the photodegradation of MB dye in the presence of visible light and contributed to remarkable enhancement in the degradation rate. The newly prepared NPs characterized by XRD show a crystalline size of 82 nm. Absorption spectroscopy revealed the visible light active nature of photocatalysts with characteristic peaks at 655-660 nm. The band gap energy was determined using UV/Vis DRS which corresponds to 1.82 eV. A photochemical property of NPs is evaluated by photoluminiscence spectroscopy which clarifies direct recombination of Cr 3d orbital with O 2p and Sr 4d orbital. The synthesized NPs proved to be extremely competent photocatalysts for the degradation of MB dye. It shows the maximum extent of degradation of MB after 75 min of irradiation. The finding of the present work indicates that $SrCrO_4$ NPs degrade MB dye efficiently.

5. REFERENCES

1. W. U. Khan, S. Ahmed, Y. Dhoble, S. Madhav, (2023) A critical review of hazardous waste generation from textile industries and associated ecological impacts, ***Journal of the Indian Chemical Society***, **100(1)**: 100829.
2. P. Chowdhary, R. N. Bharagava, S. Mishra, N. Khan, (2020) Role of industries in water scarcity and its adverse effects on environment and human health. In: ***Environmental Concerns and Sustainable Development: Volume 1: Air, Water and Energy Resources***, Berlin: Springer, p235-256.
3. R. Kishor, D. Purchase, G. D. Saratale, R. G. Saratale, L. F. R. Ferreira, M. Bilal, R. Chandra, R. N. Bharagava, (2021) Ecotoxicological and health concerns of persistent coloring pollutants of textile industry wastewater and treatment approaches for environmental safety, ***Journal of Environmental Chemical Engineering***, **9(2)**: 105012.
4. M. Mostafa, (2015) Wastewater treatment in textile Industries-the concept and current removal technologies, ***Journal of Biodiversity and Environmental Sciences***, **7(1)**: 501-525.
5. K. T. Chung, (2016) Azo dyes and human health: A review. ***Journal of Environmental Science and Health, Part C***, **34(4)**: 233-261.
6. I. Zinicovscaia, (2016) Conventional methods of wastewater treatment. In: ***Cyanobacteria for Bioremediation of Wastewaters***, Berlin: Springer, p17-25.
7. A. Saravanan, P. S. Kumar, S. Jeevanantham, S. Karishma, B. Tajsabreen, P. R. Yaashikaa, B. Reshma, (2021) Effective water/wastewater treatment methodologies for toxic pollutants removal: Processes and applications towards sustainable development, ***Chemosphere***, **280:** 130595.

8. P. Senthil Kumar, A. Saravanan, (2018) Sustainable wastewater treatment technologies. In: ***Detox Fashion: Waste Water Treatment***, Berlin: Springer, p1-25.
9. F. Younas, A. Mustafa, Z. U. R. Farooqi, X. Wang, S. Younas, W. Mohy-Ud-Din, M. A. Hameed, M. M. Abrar. A. A. Maitlo, S. Noreen, M. M. Hussain, (2021) Current and emerging adsorbent technologies for wastewater treatment: Trends, limitations, and environmental implications, ***Water***, **13(2)**: 215.
10. M. Hasanpour, M. Hatami, (2020) Photocatalytic performance of aerogels for organic dyes removal from wastewaters: Review study, ***Journal of Molecular Liquids***, **309:** 113094.
11. A. Rafiq, M. Ikram, S. Ali, F. Niaz, M. Khan, Q. Khan, M. Maqbool, (2021) Photocatalytic degradation of dyes using semiconductor photocatalysts to clean industrial water pollution, ***Journal of Industrial and Engineering Chemistry***, **97:** 111-128.
12. D. Chen, Y. Cheng, N. Zhou, P. Chen, Y. Wang, K. Li, S. Huo, P. Cheng, P. Peng, R. Zhang, L. Wang, H. Liu, Y. Liu, R. Ruan, (2020) Photocatalytic degradation of organic pollutants using TiO2-based photocatalysts: A review, ***Journal of Cleaner Production***, **268:** 121725.
13. Q. Liang, X. Liu, G. Zeng, Z. Liu, L. Tang, B. Shao, Z. Zeng, W. Zhang, Y. Liu, M. Cheng, W. Tang, S. Gong, (2019) Surfactant-assisted synthesis of photocatalysts: Mechanism, synthesis, recent advances and environmental application, ***Chemical Engineering Journal***, **372:** 429-451.
14. S. Shamaila, A. K. L. Sajjad, S. A. Farooqi, N. Jabeen, S. Majeed, I. Farooq, (2016) Advancements in nanoparticle fabrication by hazard free eco-friendly green routes, ***Applied Materials Today***, **5:** 150-199.
15. A. Rana, K. Yadav, S. Jagadevan, (2020) A comprehensive review on green synthesis of nature-inspired metal nanoparticles: Mechanism, application and toxicity, ***Journal of Cleaner Production***, **272:** 122880.
16. G. Pal, P. Rai, A. Pandey, (2019) Green synthesis of nanoparticles: A greener approach for a cleaner future**.** In: ***Green synthesis, characterization and applications of nanoparticles***, Amsterdam: Elsevier, p1-26.
17. S. G Kumar, K. K. Rao, (2017) Comparison of modification strategies towards enhanced charge carrier separation and photocatalytic degradation activity of metal oxide semiconductors (TiO2, WO3 and ZnO), ***Applied Surface Science***, **391:** 124-148.
18. K. Mondal, A. Sharma, (2014) Photocatalytic oxidation of pollutant dyes in wastewater by TiO2 and ZnO nano-materials-a mini-review. In: ***Nanoscience and Technology for Mankind***, Allahabad, India: The Academy of Sciences India (NASI), p36-72.
19. D. Kong, Y. Zheng, M. Kobielusz, Y. Wang, Z. Bai, W. Macyk, X. Wang, J. Tang, (2018) Recent advances in visible light-driven water oxidation and reduction in suspension systems, ***Materials Today***, **21(8)**: 897-924.
20. Z. Bekturganov, K. Tussupova, R. Berndtsson, N. Sharapatova, K. Aryngazin, M. Zhanasova, (2016) Water related health problems in Central Asia-A review, ***Water***, **8**(6): 219.
21. N. A. R. Che Mohamad, F. Marques Mota, D. H. Kim, (2021) Photocatalytic and photoelectrochemical overall water splitting. ***In: Solar-to-Chemical Conversion: Photocatalytic and Photoelectrochemcial Processes***, United States: John Wiley and Sons, Inc., p189-242.
22. N. Nuraje, R. Asmatulu, S. Kudaibergenov, (2012) Metal oxide-based functional materials for solar energy conversion: A review, ***Current Inorganic Chemistry (Discontinued)***, **2**(2): 124-146.
23. G. Hautier, A. Miglio, D. Waroquiers, G. M. Rignanese, X. Gonze, (2014) How does chemistry influence electron effective mass in oxides? A high-throughput computational analysis, ***Chemistry of Materials***, **26**(19): 5447-5458.
24. A. Kudo, (2007) Photocatalysis and solar hydrogen production, ***Pure and Applied Chemistry***, **79**(11): 1917-1927.
25. K. Maeda, T. Takata, K. Domen, (2011) (Oxy) nitrides and oxysulfides as visible-light-driven photocatalysts for overall water splitting. ***In: Energy Efficiency and Renewable Energy Through Nanotechnology***, London: Springer, p487-529.
26. L. K. Bharat, L. S. Reddy, J. S., Yu, (2015) Sol-gel synthesis, characterization and photocatalytic properties of SrCrO4 particles, ***Materials Letters***, 144: 85-89.

****Bibliographical Sketch***

Dr. Subhashchandra Ramraoji Patil is working as an Assistant Professor, Department of chemistry, Science college, pawani, Dist. Bhandara, Maharastra. He holds Ph. D. degree from Rastrasant Tukdoji Maharaj Nagpur University, Nagpur, Maharashtra.His research interests are in the area of photocatalysis, Nanoscience and Technology. He has four (4) research articles in National and International Journals of repute and attended many National and International conferences. He had experience of teaching in college for 24 years.

Ms. Trupti Shrikrishn Shrirame is working as an Assistant Professor, Department of chemistry, Shri Shivaji Science and Arts College, Chikhli Dist. Buldhana, Maharastra. She is perusing her Ph. D. degree at Set Kesriwal Porwal College, Kamptee, Dist. Nagpur Maharashtra. Her research an interest is in topic Graphene based photocatalyst. She has four 1 research articles, 5 chapters in books and attended National and International conferences. She had experience of teaching in college for 4 years.