

## An efficient synthesis of Biginelli Scaffolds using Ni multi-doped ZrO<sub>2</sub> nanocatalyst

Rajendra S. Patil, Sunil S Padavi, Narendra U. Chavan, Ganesh K. Kaharde, Jagdish U. Chavan, and Anil G. Beldar\*

<sup>a</sup>Department of Chemistry, PSGVPMandal's S.I.P Arts, GBP Science and STKV Sangh  
Commerce College, Nandurbar 425409, India  
\*e-mail: dragbeldar@gmail.com; phone: (+91) 94 20 134 233

### Abstract

This research article presents a green, efficient, and straightforward approach for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) and their corresponding thione analogues using a highly active Ni multi-doped ZrO<sub>2</sub> nanocatalyst. The target DHPM derivatives were prepared via the classical Biginelli multicomponent reaction. The developed methodology was evaluated under both microwave irradiation (MWI) and conventional heating conditions to compare catalytic performance. All synthesized compounds were thoroughly characterized by standard spectroscopic techniques along with melting point analysis to confirm their structures and purity. Notably, the Ni-doped ZrO<sub>2</sub> nanocatalyst exhibited superior catalytic efficiency under MWI, delivering significantly shorter reaction times and excellent product yields compared to traditional thermal conditions. This study highlights the potential of multi-doped metal oxide nanocatalysts in promoting sustainable, rapid, and high-yielding protocols for heterocyclic synthesis.

**Keywords:** Biginelli reaction, nanomaterial, multicomponent reaction, MWI,

### Introduction

Over the past decade, nanomaterials have attracted remarkable scientific interest owing to their exceptional physicochemical properties at the nanoscale, such as controlled morphology, tunable particle size, high surface area, and unique structural features. These characteristics make them particularly promising in catalysis, where enhanced surface reactivity and stability are essential. A wide range of nanostructured materials including nanoparticles (NPs), nanotubes (NTs), nanofibers, nanocages, nanowires, nanosheets, and nanoporous frameworks have been extensively investigated as efficient catalysts for the Biginelli multicomponent reaction. Literature reports demonstrate that nanoscale catalysts of diverse origins organic, inorganic, hybrid, and nanocomposite systems can effectively promote the synthesis of 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) and their thione analogues.

Among these catalytic systems, magnetic nanoparticles (MNPs) have garnered particular attention due to their straightforward magnetic recovery and reusability, which simplify workup

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and reduce operational costs.<sup>1</sup> In addition to metal-based nanocatalysts, several polymer-supported and heterogeneous catalytic materials have been successfully employed to accelerate the Biginelli reaction. These include heteropoly acids,<sup>3</sup> silica-based materials,<sup>4</sup> biocatalysts,<sup>5</sup> alumina,<sup>6</sup> clays and mineral-supported catalysts, cyclodextrins, heteropolyanions, and various organocatalysts.<sup>1</sup> Collectively, these systems highlight the versatility and efficiency of nanocatalysis in constructing chemically significant DHPM frameworks.<sup>2</sup>

Nanocatalysis particularly polymer-supported or surface-engineered catalytic systems has emerged as one of the most dynamic and rapidly advancing branches of modern catalysis. By tailoring size, shape, porosity, and surface chemistry, nanomaterials offer exceptional catalytic activity, enhanced reaction rates, improved substrate specificity, and superior selectivity. The growing emphasis on environmentally responsible chemical processes has further propelled the development of nanocatalyst-based methodologies. In alignment with the principles of green chemistry, nanocatalysts enable organic transformations under milder, safer, and more sustainable conditions, reducing energy consumption, minimizing waste, and often eliminating the need for hazardous solvents.<sup>7-8</sup> Consequently, nanoscale catalytic systems have become indispensable tools in designing eco-friendly synthetic protocols, particularly for multicomponent reactions like the Biginelli condensation. In light of the growing demand for efficient and environmentally benign catalytic systems, the present study explores the applicability of Ni multi-doped ZrO<sub>2</sub> nanocatalyst as a highly active catalyst for the synthesis of Biginelli-derived heterocycles. The successful synthesis of these DHPM scaffolds highlights the capability of the Ni multi-doped ZrO<sub>2</sub> hybrid material to accelerate the classical Biginelli reaction, thereby contributing to ongoing advancements in the development of greener and more sustainable routes for heterocycle construction. This work further underscores the potential of multi-doped metal oxide–carbon nitride nanocomposites as versatile catalytic platforms in modern organic synthesis.

## Experimental

All chemical reagents were procured from Loba Chem Pvt. Ltd. and Thermo Fisher Scientific India Pvt. Ltd. Reaction progress and product purity were monitored using thin-layer chromatography (TLC) on silica gel 60 F<sub>254</sub> aluminum plates (0.25 mm, Merck, Darmstadt, Germany). Melting points were measured in open capillaries. The obtained melting point values, along with spectral data, were compared with literature reports, confirming that the synthesized compounds correspond to known structures.

## Preparation of catalyst system

The Ni, C, N, and S multi-doped ZrO<sub>2</sub> catalyst (NiZr) was prepared by dissolving ZrO(NO<sub>3</sub>)<sub>2</sub> (1.0 mM) in 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> (100 mL), followed by the slow addition of polyethylene glycol-200 (1.0 mL) under continuous stirring for 1 hour. A calculated amount of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was then introduced to achieve Ni:Zr doping ratios of 0.3%, 0.6%, or 1.0%, and the mixture was stirred for an additional hour. Thiourea (3 g) was added, and the solution was further stirred for 2 hours to ensure homogeneity. The mixture was dried at 100 °C for 12 hours to obtain a black residue, which was subsequently calcined at 500 °C for 3 hours to yield the final white Ni, C, N, S doped ZrO<sub>2</sub> catalyst. The synthesized nanocatalyst was characterized using XRD, TEM, SEM, EDS, FT-IR, and UV-DRS techniques.<sup>9</sup>

## Optimization of Ni multi-doped ZrO<sub>2</sub> nanocatalyst

The catalytic performance of the Ni multi-doped ZrO<sub>2</sub> nanocatalyst was systematically evaluated to determine the optimal conditions for the synthesis of Biginelli derivatives. Experiments revealed that using 0.1 g of the catalyst provided the best balance between efficiency, yield, and product purity, as summarized in Table 1. Increasing the catalyst quantity beyond 0.1 g did not result in significant improvements in either reaction time or product yield, indicating that this amount is sufficient to achieve complete conversion under the given reaction conditions. Comparative studies between conventional heating and microwave-assisted protocols highlighted the superior performance of the latter. The microwave-assisted method significantly accelerated the reaction, reducing the reaction time while maintaining or even improving the yield and purity of the synthesized 3,4-dihydropyrimidin-2(1H)-one and thione derivatives. These observations underscore the combined benefits of employing a highly active multi-doped nanocatalyst and microwave irradiation, providing an efficient, sustainable, and high-yielding approach for the preparation of Biginelli scaffolds.

**Table 1: Optimization of quantity of Ni multi-doped ZrO<sub>2</sub> nanocatalyst for Biginelli reaction.**

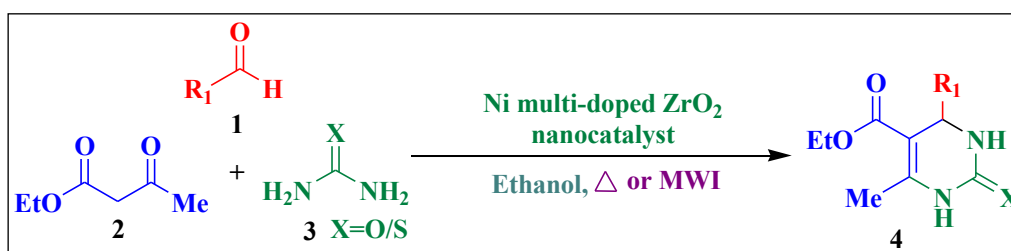
Entry	Catalyst, g	Conventional method		Microwave irradiation	
		Time, min	Yield, %	Time, min	Yield, %
1	0.02	90	78	13	88
2	0.04	80	82	10	90
3	0.06	70	86	8	92
4	0.08	60	88	6	94
5	<b>0.10</b>	<b>45</b>	<b>90</b>	<b>3</b>	<b>96</b>
6	0.12	45	90	3	96
7	0.14	45	90	3	96

### Conventional method for the synthesis of DHPMs using nanocomposite catalyst

The reaction flask was charged with aldehyde (1) (10 mmol), ethyl acetoacetate (2) (10 mmol), urea or thiourea (3) (12 mmol), and 0.1 g of the Ni multi-doped ZrO<sub>2</sub> nanocatalyst, followed by the addition of 5 mL of ethanol. The reaction mixture was refluxed for the required duration, and the progress of the reaction was monitored periodically using thin-layer chromatography (TLC). Upon completion, the mixture was filtered while still warm to recover the catalyst for potential reuse. The filtrate was concentrated under reduced pressure using a rotary evaporator, and the crude product was purified by recrystallization from ethanol. This procedure afforded the desired 3,4-dihydropyrimidin-2(1H)-one and thione derivatives in good to excellent yields.<sup>10</sup>

### Microwave irradiation method for the synthesis DHPMs using nanocomposite catalyst.

In a typical microwave-assisted procedure, a reaction flask containing aldehyde (10 mmol), ethyl acetoacetate (10 mmol), and urea or thiourea (12 mmol) in 5 mL of ethanol was added with 0.1 g of Ni multi-doped ZrO<sub>2</sub> nanocatalyst. The mixture was subjected to microwave irradiation for the time indicated in Table 1, with the reaction monitored at 1-minute intervals using thin-layer chromatography (TLC). Upon completion, the reaction mixture was worked up following the same procedure as described for the conventional method to isolate the desired 3,4-dihydropyrimidin-2(1H)-one and thione derivatives.



**Scheme 1: Ni multi-doped ZrO<sub>2</sub> nanocatalyst nanocomposites catalyzed Biginelli reaction. Results and discussion**

The synthesized Ni multi-doped ZrO<sub>2</sub> composite nanocatalyst was thoroughly characterized using a series of advanced spectrochemical and microscopic techniques to evaluate its structural, morphological, and surface properties. X-ray diffraction (XRD) analysis confirmed the crystalline phases present in the catalyst and enabled the calculation of average crystallite sizes, indicating the successful incorporation of Ni dopants into the ZrO<sub>2</sub> lattice. Transmission electron microscopy (TEM) further revealed the morphological features of the nanocomposite, showing well-defined nanoscale particles with uniform size distribution and high crystallinity.

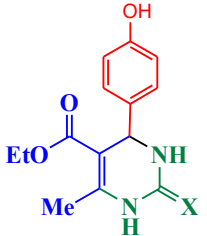
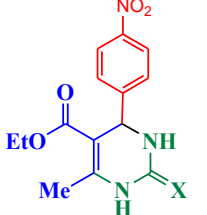
To obtain information about elemental composition, surface texture, and porosity, the material was examined using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). These analyses validated the homogeneous dispersion of nickel species within the zirconia matrix and indicated a porous surface conducive to catalytic activity. Overall, the multi-doped Ni–ZrO<sub>2</sub> nanocomposite exhibited favorable surface characteristics, particle uniformity, and structural stability, making it a promising heterogeneous catalyst for the synthesis of various heterocyclic scaffolds.

Following characterization, the Ni multi-doped ZrO<sub>2</sub> nanocatalyst was employed for the synthesis of dihydropyrimidinones (DHPMs) and their thione analogues via the multicomponent Biginelli reaction. Substituted aromatic aldehydes, ethyl acetoacetate, and urea or thiourea were reacted in the presence of the catalyst to generate the corresponding DHPM and thione derivatives. To evaluate the catalytic efficiency of the nanocomposite, reactions were carried out under both microwave-assisted conditions and conventional reflux methods.

In both approaches, the catalyst facilitated smooth conversion to the desired products; however, microwave irradiation significantly enhanced performance. Under microwave conditions, reaction times were drastically reduced, and the products were obtained in higher yields (80–96%), highlighting the synergistic effect between microwave energy and the engineered surface properties of the nanocatalyst. In comparison, the traditional reflux method afforded slightly lower yields (76–92%) with longer reaction times, as summarized in Table 2. These results clearly demonstrate the superior catalytic activity and operational advantage of the Ni multi-doped ZrO<sub>2</sub> composite nanocatalyst, particularly in microwave-assisted synthetic protocols.

**Table 2: Ni multi-doped ZrO<sub>2</sub> nanocomposites catalyzed synthesis of Biginelli derivatives under conventional as well as microwave irradiation conditions.**

Entry	Product	R1	X	Conventional heating		Microwave irradiation		Melting point, °C	
				Time, min	Yield, %	Time, min	Yield, %	Observed	Reported
1.	4a		O	45	92	3	96	200-202	200-202 <sup>11</sup>
2.	4b		O	130	76	8	82	196-198	196-198 <sup>11</sup>
3.	4c		O	60	79	5	86	228-230	228-230 <sup>11</sup>
4.	4d		O	50	89	3	94	212-214	210-212 <sup>12</sup>
5.	4e		S	60	86	4	94	204-206	205-207 <sup>11</sup>
6	4f		S	140	76	8	80	154-156	154-156 <sup>11</sup>

7.	4g		S	130	80	6	87	206-208	206-208 <sup>12</sup>
8.	4h		S	60	83	5	89	180-182	180-182 <sup>11,13</sup>

Both electron-donating and electron-withdrawing substituted aromatic aldehydes participated efficiently in the Biginelli reaction under traditional reflux as well as microwave-assisted conditions. Aldehydes bearing activating groups facilitated slightly faster conversions, while those containing deactivating substituents also underwent smooth cyclocondensation, delivering the corresponding DHPM and thione derivatives in good to excellent yields.

The evaluation of the Ni multi-doped ZrO<sub>2</sub> nanocatalyst in the Biginelli multicomponent cyclo-condensation is particularly noteworthy, as it showcases the catalyst's ability to promote complex organic transformations efficiently. Its high surface area, improved acidity, and synergistic effects arising from nickel incorporation into the zirconia framework collectively contribute to enhanced catalytic activity. These features facilitate the activation of key functional groups during the reaction, promoting rapid formation of the dihydropyrimidinone nucleus.

Overall, the catalyst's strong performance across a wide substrate scope and under diverse reaction conditions underscores its potential as a highly effective and reusable heterogeneous catalyst for the synthesis of biologically important heterocycles.

## Conclusions

The catalytic performance of the Ni multi-doped ZrO<sub>2</sub> composite nanocatalyst was effectively demonstrated in the Biginelli multicomponent cyclocondensation reaction. The catalyst exhibited excellent efficiency, particularly under microwave irradiation, where it provided superior yields within significantly shorter reaction times, offering notable improvements in reaction economy. Its broad substrate tolerance was also evident, as it promoted smooth conversions with a wide range of aldehydes, including variously substituted aromatic aldehydes as well as aliphatic aldehydes.

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Both dihydropyrimidinones (DHPMs) and their corresponding thione analogues were successfully synthesized using urea and thiourea, respectively. In both cases, the Ni multi-doped ZrO<sub>2</sub> composite nanocatalyst delivered consistently high performance, further confirming its effectiveness and versatility as a robust heterogeneous catalyst.

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### Characterization Data

5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (4a)

IR (KBr, cm<sup>-1</sup>): 3480, 3247, 2980, 1728, 1705, 1646, 1466, 1222, 1090. <sup>1</sup>H NMR (400 MHz, δ, ppm) (DMSO-d<sub>6</sub>): δ 9.17 (s, 1H), 7.75 – 7.69 (m, 1H), 7.37 – 7.27 (m, 2H), 7.24 (ddt, J= 6.9, 3.3, 1.5 Hz, 3H), 5.15 (d, J= 3.4 Hz, 1H), 3.99 (q, J= 7.0 Hz, 2H), 2.25 (s, 3H), 2.09 (s, 2H), 1.10 (t, J= 7.1 Hz, 3H). MS (m/z): 261 (M+1)

5-(Ethoxycarbonyl)-4-(4-methoxyphenyl)-6-methyl-3,4 dihydropyrimidin- 2(1H)-one (4b)

IR (KBr, cm<sup>-1</sup>): 3479, 3413, 3246, 2928, 1724, 1705, 1651, 1513, 1224, 1220. <sup>1</sup>H NMR (400 MHz, δ, ppm) (DMSO-d<sub>6</sub>): δ 9.13 (s, 1H), 8.25 – 8.17 (m, 2H), 7.91(dd, J= 3.5, 2.0 Hz, 1H), 7.54 – 7.47 (m, 2H), 5.27 (d, J= 3.3 Hz, 1H), 3.98 (q, J= 7.1 Hz, 2H), 2.26 (s, 3H), 1.09 (t, J= 7.1 Hz, 3H).

5-Ethoxycarbonyl-6-methyl-4-(4-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (4c)

IR (KBr, cm<sup>-1</sup>): 3520, 3362, 2991, 1737, 1705, 1652, 1566, 1250. <sup>1</sup>H NMR (400 MHz, δ, ppm) (DMSO-d<sub>6</sub>): δ 9.33 (s, 1H), 9.08 (d, J= 2.2 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.07 – 6.99 (m, 3H), 6.83 (s, 1H), 6.73 – 6.65 (m, 3H), 5.05 (d, J= 3.3 Hz, 2H), 3.98 (q, J= 7.1 Hz, 3H), 2.23 (s, 5H), 2.09 (s, 1H), 1.10 (t, J= 7.1 Hz, 5H), 1.06 (s, 1H).

5-(Ethoxycarbonyl)-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one (4d)

IR (KBr, cm<sup>-1</sup>): 3343, 3107, 2981, 1704, 1651, 1520, 1347, 1213. <sup>1</sup>H NMR (400 MHz, δ, ppm) (DMSO-d<sub>6</sub>): δ 9.37 (s, 1H), 8.25 – 8.17 (m, 2H), 7.91(dd, J= 3.5, 2.0 Hz, 1H), 7.54 – 7.47 (m, 2H), 5.27 (d, J= 3.3 Hz, 1H), 3.98 (q, J= 7.1 Hz, 2H), 2.26 (s, 3H), 1.09 (t, J= 7.1 Hz, 3H).

5-(Ethoxycarbonyl)-4-(n-propyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-one (4e)

IR (KBr, cm<sup>-1</sup>): 3237, 3015, 1735, 1712, 1666, 1599, 1287. <sup>1</sup>H NMR (400 MHz, δ, ppm) (CDCl<sub>3</sub>): δ 8.04 (s, 1H), 5.85 (s, 1H), 4.33 (dt, J= 7.6, 3.5 Hz, 1H), 4.28 – 4.12 (m, 2H), 2.30 (s, 3H), 2.19 (s, 2H), 1.67 – 1.39 (m, 2H), 1.30 (t, J= 7.1 Hz, 4H), 0.93 (t, J= 7.1 Hz, 3H).

5-Ethoxycarbonyl-4-(phenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-thione (4f)

IR (KBr, cm<sup>-1</sup>): 3380, 3186, 2986, 1720, 1703, 1660, 1586, 1270. <sup>1</sup>H NMR (400 MHz, δ, ppm) (DMSO-d<sub>6</sub>): δ 9.81 (s, 1H), 9.65 (s, 1H), 7.37–7.21 (m, 5H), 5.17 (d, J= 3.4 Hz, 1H), 4.00 (q, J= 7.1 Hz, 2H), 2.29 (s, 3H), 1.10 (s, 3H). MS (m/z): 277 (M+1).

5-Ethoxycarbonyl-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-thione (4g)

IR (KBr, cm<sup>-1</sup>): 3463, 3192, 2889, 1737, 1708, 1653, 1573, 1243. <sup>1</sup>H NMR (400 MHz, δ, ppm) (DMSO-d<sub>6</sub>): δ 9.9 (s, 1H), 9.60 (s, 1H), 7.13 (d, J= 8.7 Hz, 2H), 6.89 (d, J= 8.7 Hz, 2H), 5.11 (d, J= 3.4 Hz, 1H), 4.01 (q, J= 7.1 Hz, 2H), 3.72 (s, 3H), 2.28 (s, 3H), 1.11 (t, J= 7.0 Hz, 3H).

5-Ethoxycarbonyl-6-methyl-4-(2-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-thione (4h)

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IR (KBr,  $\text{cm}^{-1}$ ): 3487, 3290, 2857, 1750, 1698, 1634, 1534, 1232.  $^1\text{H}$  NMR (400 MHz,  $\delta$ , ppm) (DMSO- $d_6$ ):  $\delta$  1.07 (t,  $J=7.6$  Hz, 3H), 2.4 (s, 3H), 4.1 (q,  $J=7.6$  Hz, 2H), 5.68 (s, 1H), 6.91-7.15 (m, 4H), 7.72 (s, 1H), 9.65 (s, 1H), 9.95 (s, 1H). MS ( $m/z$ ): 293 (M+1).

5-(Ethoxycarbonyl)-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-thione (4i)

IR (KBr,  $\text{cm}^{-1}$ ): 3410, 3269, 2897, 1755, 1631, 1575, 1365, 1268.  $^1\text{H}$  NMR (400 MHz,  $\delta$ , ppm) ( $\text{CDCl}_3$ ):  $\delta$  7.52 (d,  $J=8.7$  Hz, 1H), 6.92 – 6.81 (m, 2H), 6.16 (q,  $J=1.3$  Hz, 1H), 4.14 (t,  $J=5.9$  Hz, 2H), 3.56 (t,  $J=6.5$  Hz, 2H), 2.42 (d,  $J=1.2$  Hz, 3H), 2.17 – 2.06 (m, 2H).

5-Ethoxycarbonyl-4-(n-propyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-thione (4j)

IR (KBr,  $\text{cm}^{-1}$ ): 3337, 3019, 1745, 1705, 1651, 1520, 1320.  $^1\text{H}$  NMR (400 MHz,  $\delta$ , ppm) ( $\text{CDCl}_3$ ):  $\delta$  8.41 (s, 1H), 7.94 (s, 1H), 4.37 (dt,  $J=7.7, 3.7$  Hz, 1H), 4.28 – 4.09 (m, 2H), 2.32 (s, 3H), 2.18 (s, 1H), 1.69 – 1.55 (m, 1H), 1.55 – 1.43 (m, 1H), 1.46 (s, 1H), 1.47 – 1.30 (m, 1H), 1.30 (s, 1H), 1.28 (d,  $J=7.1$  Hz, 2H), 0.92 (t,  $J=7.0$  Hz, 3H).

## References

1. Patil, R. V.; Chavan, J. U.; Dalal, D. S.; Shinde, V. S.; Beldar, A. G. *ACS combinatorial science* **2019**, 21, (3), 105-148.
2. Patil, R.; Chavan, J.; Beldar, A. *World Journal of Pharmacy and Pharmaceutical Sciences* **2016**, 5, (11), 419-432.
3. Chopda, L. V.; Dave, P. N. *ChemistrySelect* **2020**, 5, (19), 5552-5572.
4. Chopda, L. V.; Dave, P. N. *Arabian Journal of Chemistry* **2020**, 13, (6), 5911-5921.
5. Zanin, L. L.; Brito Matos, T. K.; Leitão, A.; Ellena, J.; Porto, A. L. M. *European Journal of Organic Chemistry* **2022**, 2022, (38), e202200331.
6. Zanin, L. L.; Porto, A. L. *ChemistrySelect* **2020**, 5, (28), 8604-8608.
7. Patel, S. R.; Patil, R. V.; Chavan, J. U.; Beldar, A. G. *ChemistrySelect* **2023**, 8, (35), e202301972.
8. Patil, R.; Chavan, J.; Beldar, A. *RSC advances* **2017**, 7, (38), 23765-23778.
9. Shinde, S. G.; Patil, M. P.; Kim, G.-D.; Shrivastava, V. S., *Journal of Environmental Chemical Engineering* 2020, 8 (3), 103769..
10. Liu, J.; Zhang, T.; Wang, Z.; Dawson, G.; Chen, W. *Journal of Materials Chemistry* **2011**, 21, (38), 14398-14401.
11. Dilmaghani, K. A.; Zeynizadeh, B.; Parasajam, H. *Phosphorus, Sulfur, and Silicon and the Related Elements* **2012**, 187, (4), 544-553.
12. Heirati, S. Z. D.; Shirini, F.; Shojaei, A. F. *RSC advances* **2016**, 6, (71), 67072-67085.
13. Darehkordi, A.; Hosseini, M. S. *Iranian Journal of Materials Science and Engineering* **2012**, 9, (3), 49-57.