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# Nd doped $ZrO_2$ photocatalyst for organic pollutants degradation in wastewater

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## ABSTRACT

Wastewater management is the most discussed topic in this current era. To overcome the scarcity of water and wastewater treatment, reusage of water is the convenient way. By removing the organic pollutants, the water can be reused for domestic purposes. Pure and neodymium (Nd) doped $ZrO_2$ was produced using facile co-precipitation technique. Along with doping, surfactant was also included to enhance the morphology of the prepared samples. The nanoparticles morphology was formed with less agglomeration as investigated by TEM analysis. The photocatalytic action was further examined using annular photoreactor. Both methylene blue (MB) and Rhodamine B (RhB) dyes degradation was examined. Neodymium doped $ZrO_2$ was incorporated in the dye under visible light for 2 h. The light was irradiated for 20 min and sample solution was collected for every 20 min. The samples were analyzed for UV and degradation was confirmed. The enhancement of catalyst depended on the bandgap of the samples. The absorption peak for Rhodamine B and Methylene Blue dyes at 553 and 664 nm was decreased and confirmed the degradation of dyes. 2% Nd doped $ZrO_2$ catalyst added MB dye sample showed 90% efficiency and exhibited 77% efficiency on Rhodamine B pollutant. The "k" values of 2% Nd doped $ZrO_2$ was obtained as 0.0144 $\text{min}^{-1}$ and 0.00944 $\text{min}^{-1}$ for MB and RhB dyes. This candidate will be the potential one for futuristic water remediation process.

## 1. Introduction

By the abrupt escalation of people population, and increment of industries over past two decades with the emergence of new ideas in science and innovations, reflected a great impact on ecosystem and made consecutive effects on water, air and soil (Nasar and Mashkoor, 2019). The wastewater has obtained high proportion of toxic organic pollutants, heavy metals, dye products, pesticides etc., (Järup, 2003). For the adverse situation of water pollution and scarcity, textile industries have been recorded a high part on it (Yaseen and Scholz, 2019). Textile industries are the main components that have been draining out the colored dye products on to wastewater with no prior treatment. The water sources,

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land, soil located on industry sites have been completely demolished due to the mixing of all waste toxic effluents (Al-Mamun et al., 2019). Textile manufacturers are largely camped at south asian countries like India, Srilanka, China and Vietnam where these countries gross product is maximally based on textile industries. The raw materials utilized by those manufacturers are cotton, fibers, chemicals and dyes (Hossain et al., 2018). Dyes are the compounds used for inculcate colors on the materials. The dye compounds contains two main components as auxochrome and chromophore that are the reason for color absorbance and high intense reflection of colors that helps more attention on materials (Al-Kdasi et al., 2004). Auxochromes is a functional group with more intension by changing the wavelength of the light used (Azbar et al., 2004). On the basis of the parent material, dyes are differentiated into natural and synthetic dyes. In accordance to the behavior of chromophore and based on substrates the dyes are been classified and listed in Fig. S1. Synthetic dyes are the most popular one that is used in most of the industries and it has ability of exhibiting high intense color attractive to the materials. Totally 700000 tones of dyes are identified and among that 100,000 tones of dyes are easily used and produced every year (Kant, 2011). To overcome the disadvantages of natural dyes, synthetic dyes are introduced by W.H. Perkins in 1856, nevertheless this made another major environmental problem i.e. dye effluent wastewater is enclosed with environment created a large level of hazardous to environment, mankind and aquatic life (Gholami-Borujeni et al., 2011). These synthetic dyes have complicated structure which cannot be degraded by traditional methods. These compounds have high thermal stability and cannot break its bond even under high intense light source (Penha et al., 2005).

Methylene blue is a synthetic dye used for medical, analytical chemistry, food, textile industries etc. Though it has numerical uses, it also has adverse effects when it is loaded beyond limit (Mohammed et al., 2014). Rhodamine B dye is basic dye of xanthenes family. The dye is violet in color and has high solubility on water. Rhodamine B is employed in food industry, and textile industry as tracer. At the same time, it has evil effects on human health and on animals (Jain et al., 2007). Transition metal oxides are the potential candidates that have been replaced precious metals in variety of fields like sensing (Lee et al., 2018), energy-storage (Tan et al., 2016), catalytic activity, electrochemistry and environmental purification process (Lu et al., 2014). Nowadays fiber based photocatalyst were used for photocatalytic applications because by the replacement of fiber there is large reduce in secondary wastes (Xiong et al., 2020). By the superior behavior of metals such as their individual properties like large surface area, nanostructures, and good active sites have been attracted the research towards metal oxides. The ratio of surface to volume can be increased by various criteria and crystallite size can be decreased (Henglein, 1989). Other than surface area, morphology, crystallite size, band gap, and toxic behavior is also enhancing material efficiency (Li et al., 2015b).

$ZrO_2$ is a best n- type semiconductor and this material is newly investigated as a photocatalyst (Botta et al., 1999). $ZrO_2$ is non-toxic material and it has positive behaviors towards environmental applications. The synergic effect of $ZrO_2$ made this material a new emerging candidate in photo based researches (Bansal et al., 2015; Manoharan et al., 2015). Doping is a pragmatic way to enable the separation of changes present in semiconductor material. Rare earth metal doping exhibited drastic compliments on photocatalytic dye degradation (Chand et al., 2020; Zhou et al., 2009). Mostafa et al. synthesized Mn doped $ZrO_2$ by impregnation method. The catalyst was tested as oxidizing agent with the different effect on pH, catalyst composition and radical agents and showed efficient treatment on toxic pollutants. Hanggara Sudrajat et al. prepared *N* doped $ZrO_2$ by thermal decomposition route and investigated Amarnath and Methylene Blue (MB) dyes. Compared with pristine catalyst, *N* doped $ZrO_2$ showed high photocatalytic activity. Hadi Fallah Maofi et al. produced $TiO_2$ and $ZrO_2$ by sol- gel technique and it was grown on woolen fibers and showed good photocatalytic activity on toxic pollutants. Shar Zinataloo Ajabshir et al. prepared $Nd_2Zr_2O_7$-$ZrO_2$ nanocomposite by facile process with propylene glycol. Sachin Girdhar Shinde et al. synthesized $ZrO_2$ employing different dopants like Ni, C, *N* and S by ultrasound assisted hydrothermal method. Among different doping, 1% Ni doped $ZrO_2$ showed 96% degradation of Indigo Carmine dye on solar radiation. Jiangyan Tian et al. prepared $TiO_2$/ $ZrO_2$ nanocomposites with different ratios of $ZrO_2$:$TiO_2$ and 5% $TiO_2$:$ZrO_2$ possessed better photocatalytic property towards organic pollutant Rhodamine B dye. Turki Dawoud et al. produced Ag doped $ZrO_2$ by combustion route and exhibited 95% of efficiency on reducing the Rhodamine B dye. Renuka et al. prepared Mg doped $ZrO_2$ by green synthesis method and 2% Mg loaded $ZrO_2$ catalyst unveiled superior activity with 93%. Chiara Gionco et al. produced Ce and Er doped $ZrO_2$ by hydrothermal route and all doped catalysts showed higher efficiency on reduction of Rhodamine B dye. Venkata Reddy et al. prepared tetragonal $ZrO_2$ via hydrothermal method and reduced methyl orange (MO) and obtained 99% of efficiency (Khaksar et al., 2015; Sudrajat et al., 2016; Moafi et al., 2010; Zinatloo-Ajabshir et al., 2017; Shinde et al., 2020; Tian et al., 2019; Dawoud et al., 2020; Renuka et al., 2016; Gionco et al., 2019; Reddy et al., 2018). In this present work, the pristine and neodymium (Nd) doped $ZrO_2$ was synthesized employing co-precipitation technique. The powder was annealed at 600 °C for 6 h. The white powder was further analyzed. The catalyst loaded samples were investigated by annular reactor. The photocatalytic activity was investigated on both Methylene Blue and Rhodamine B dyes. The Nd doped $ZrO_2$ sample showed 90% on MB dye degradation and 77% on Rhodamine B dye degradation.

## 2. Experimental

### 2.1. Materials and methods

Zirconium (IV) nitrate ($ZrO(NO)_3)_2$, neodymium (III) nitrate hexahydrate ($Nd(NO_3)_2$), sodium hydroxide (NaOH), polyvinyl pyrrolidone were procured from Sigma Aldrich Pvt. Ltd. Distilled water, Whatmann filter paper, methanol and ethanol of analytical grade was procured from Thermo Fisher Scientific Pvt. Ltd. Methylene Blue dye and Rhodamine B dyes were purchased from ACS chemicals Pvt. Ltd with analytical grade. Acetophenone was bought from Isochem Laboratories Pvt. LTD with 99% purity. 0.1 M of $(ZrO(NO)_3)_2$ was first dissolved in 35 ml DI water. 1 M NaOH was dissolved in 35 ml DI water. After achieving complete dissolution, NaOH solution was added drop wise carefully on $(ZrO(NO)_3)_2$ solution and made to stirrer homogeneously. A separate solution of 15 ml of 0.5 g of PVP was subjected to magnetic stirrer and it was mixed drop wise to above solution and stirred for about 30 min. The light dusty white solution was covered with parafilm and kept undisturbed for 24 h for settling of precipitate. The second solution was prepared by adding neodymium as a dopant. 0.01 M of $(Nd(NO_3)_2)$ was dissolved and affixed to $(ZrO(NO)_3)_2$. For third solution, 0.02 M of $(Nd(NO_3)_2)$ was added to $ZrO_2$ solution. After getting precipitate, it was cleaned with DI water, ethanol and methanol for 6 times to eliminate foreign particles. The particle was dried at 80 °C for 12 h and collected and grind through mortal and the powder was saved for future use. The pristine, 1% Nd, 2% Nd doped $ZrO_2$ was annealed at 600 °C for 6 h. The pristine, 1% Nd, 2% Nd doped $ZrO_2$ samples were marked as Zr1, Zr2 and Zr3 in following sections.

### 2.2. *Characterization analysis*

The obtained samples were analyzed for its structural behavior with PANalytical/ X Pert Pro instrument. The SEM (Quanta FEG 250) and TEM characterization was performed in JEOL- 2100+ with resolution point of 0.194 nm. The BET analysis was performed under Quanta chrome Nova 2200e with nitrogen as analysis gas. The XPS analysis was analyzed by PHI- VERSAPROBE III X- ray Photoelectron spectroscopy instrument.

### 2.3. *Photocatalytic activity*

Methylene Blue and Rhodamine B dye stock was organized by suspending 0.1 M dye suspended in 100 ml of DI water and stirred under dark conditions for better absorption and desorption. For colorless organic pollutant, acetophenone was used. The stock solution was prepared as 1 M in 100 ml DI water. The stock solution was kept in dark conditions. For clean dye, 5 ml of stock solution was mixed in 45 ml DI water and made to stirrer under dark. In other catalyst added dye solution, 0.1 g of pristine, 1% Nd and 2% Nd doped $ZrO_2$ was appended to dye solution and made to stirrer for about 30 min in dark conditions to make better adsorption between dye and catalyst. 50 ml solution was dispensed into 90 ml glass tube and air purging was introduced into solution. 300 W lights were inserted into immersed glass reactor.

## 3. Results and discussions

For the prepared samples material confirmation, please see the supplementary information (Fig. S1–S10, Table S1). The photocatalytic activity was tested for both Methylene Blue and Rhodamine B dye with pH at 7 analyzed by UV-absorption spectra. The absorption band of Methylene Blue was examined at 660 nm and the peak intensity was reduced after light irradiation. The efficiency was estimated by $[A_0\text{- }A_t]/(A_0)\times 100$, where, $A_0$ - initial absorbance, $A_t$ - absorbance at $t = 20, 40$, etc. Fig. 1(a–b) shows the $C/C_0$ plot and kinetic pot of the pure and catalyst appended MB dye samples. The efficiency calculated for pure MB solution, $ZrO_2$ added MB solution, 1% Nd-$ZrO_2$ added MB solution, 2% Nd-$ZrO_2$ added MB solution was 42%, 44%, 67% and 90%. The dye sample without catalyst showed poor efficiency as it exhibited the presence of dye in water. As in catalyst added dye samples, the pure $ZrO_2$ sample by itself can make the degradation in a low concentration (Hanafi and Sapawe, 2019). While on comparing all the four samples, 2% Nd-$ZrO_2$ catalyst added sample showed higher efficiency. On doping neodymium, the efficiency on reducing toxic pollutants was increased to almost complete removal of pollutants. This enhanced efficiency is due to the reduced band gap, higher recombination rate and substantial number of reproduction of hydroxyl and oxide radicals (Akhtar et al., 2020). The kinetic plot was plotted as it was linear which showed pseudo first order kinetic reaction of degradation process. Rate constant k was calculated from formula, $-\ln\frac{c}{c0} = kt$. The rate constant 'k' for pure MB solution, $ZrO_2$ added MB solution, 1% Nd-$ZrO_2$ added MB solution, 2% Nd-$ZrO_2$ added MB solution was calculated as 0.0035, 0.00337, 0.00468, 0.0144 $\text{min}^{-1}$. The higher rate constant obtained for 2% Nd-$ZrO_2$ added MB solution revealed the higher degradation of toxic pollutants (Ahmed et al., 2020). The obtained SD value for $C/C_0$ plot is 0.20 and for kinetic plot the calculated SD is 0.22. The error percentage was ± 5%.

The pristine, 1% Nd and 2% Nd doped $ZrO_2$ sample was also investigated on Rhodamine B dye under visible light exposure. Fig. 2(a–b) explored $C/C_0$ plot and kinetic study plot of the pure and catalyst added RhB dye samples. The liquid samples were collected for every 20 min and it was subjected to UV–Vis analysis. The peak of Rhodamine B dye at 550 nm was observed to reduce on its absorbance for every 20 min and efficiency was calculated. The degradation efficiency calculated was 32%, 46%, 64% and 77% for pure dye sample, $ZrO_2$ added dye sample, 1% Nd- $ZrO_2$ added dye sample and 2% Nd-$ZrO_2$ added dye sample. The efficiency of 2% Nd doped $ZrO_2$ catalyst added dye sample possess 3 times higher than pure dye sample. Doping of rare earth metal (Nd) performed an enthusiastic action on removing the toxic pollutants (Li et al., 2015a). Addition of neodymium showed good photocatalytic activity against organic effluents and it will make of reusability of water. The kinetic study was analyzed and the linear plot was in good agreement with Pseudo first order kinetic model. The rate constant was calculated by the formula used above. The rate constant 'k' for pure dye sample, $ZrO_2$ added dye sample, 1% Nd-$ZrO_2$ added dye sample and 2% Nd-$ZrO_2$ added dye sample was 0.00106,

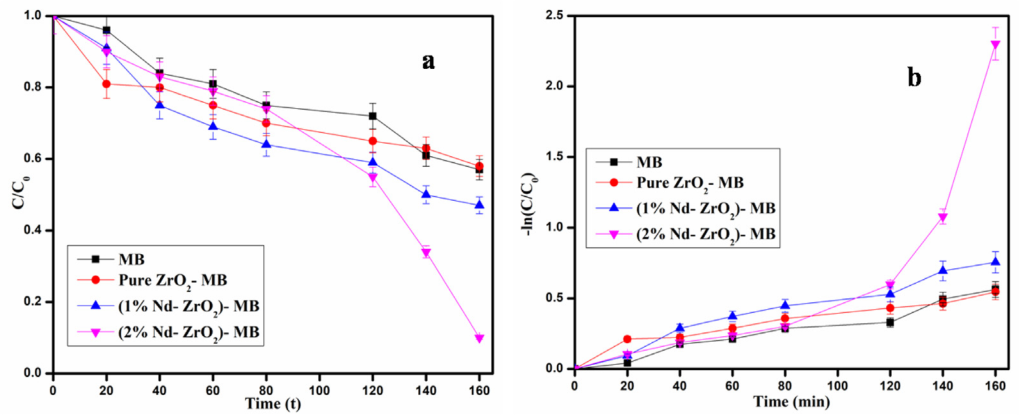

**Fig. 1.** (a) $C/C_0$ graph plot of MB dye with catalysts (b) Kinetic plot of MB dye with catalysts.

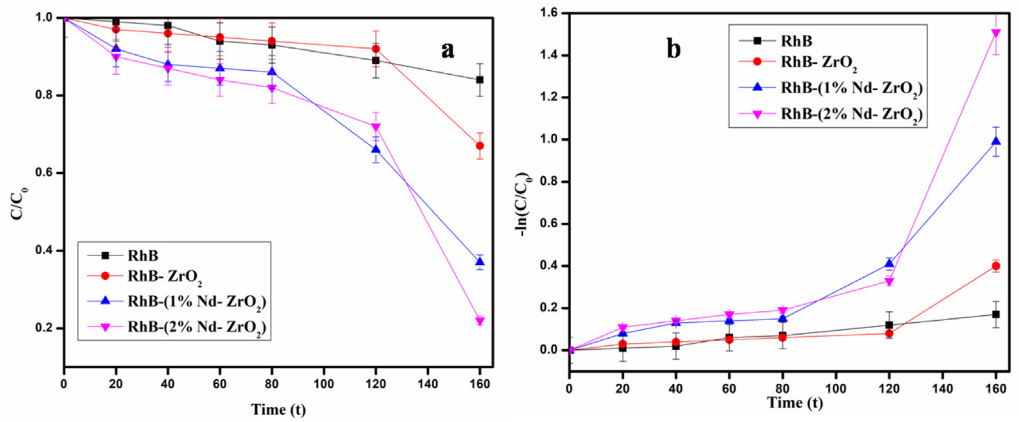

**Fig. 2.** (a) $C/C_0$ plot of pure and catalyst added RhB dye sample (b) Kinetic plot graph of pure and catalyst added RhB dye sample.

**Table 1**
Comparison of rate constant with previous literature.

| Sample | Dye | Rate constant “k” ($min^{-1}$) | Reference |
|---|---|---|---|
| Mesoporous $ZrO_2$ | Methyl Orange (MO) | 0.0046 | Sreethawong et al. (2013) |
| $ZrO_2$ nanoparticles | Victoria Blue (VB) | 0.14208 | Bansal et al. (2015) |
| Mn doped $ZrO_2$ | Methyl Orange | 0.019 | Reddy et al. (2019) |
| Eu doped C,N,S-$ZrO_2$ | Indigo Carmine | 0.010 | Agorku et al. (2015) |
| 2% Nd-$ZrO_2$ | Methylene Blue (MB) | 0.0144 | Present work |
| 2% Nd-$ZrO_2$ | Rhodamine B (RhB) | 0.0094 | Present work |

0.0025, 0.0062 and 0.00944 $min^{-1}$. For 2% Nd- $ZrO_2$ added dye sample, the rate constant was greater that acknowledge the higher degradation property of the sample. It was also confirmed from literatures that sample with greater value of ‘k’ explored better photocatalytic activity against toxic pollutants (Table 1) (Zhang et al., 2018; Nguyen et al., 2021). The mean SD value of the $C/C_0$ plot obtained is 0.184 and for kinetic plot the calculated SD is 0.325. The error percentage for the obtained plot is ±5%.

The radical species were the one which is responsible for enhancement of the photocatalytic activity and degradation of dyes. To find type of species present in the photocatalyst, radical test was undergone with scavenging agents like EDTA, isopropyl alcohol which are responsible for holes and hydroxyl species. The $C/C_0$ plot of scavenger test is included in Fig. 3. While in addition of EDTA, the efficiency obtained was 34% and in addition of IPA it exhibited the efficiency of 52%. When EDTA was added, the holes were completely suppressed and the efficiency was decreased. As in IPA added sample, efficiency was better as hydroxyl ions slightly helped the photocatalyst to be active under light irradiation. The holes were the main species to exhibit the efficient output. When $H_2O_2$was added, the photocatalytic activity was much better as the radicals helped the photocatalyst to be more active under light. The mean SD for the $C/C_0$ plot is 0.1747 and error percentage was ±5%.

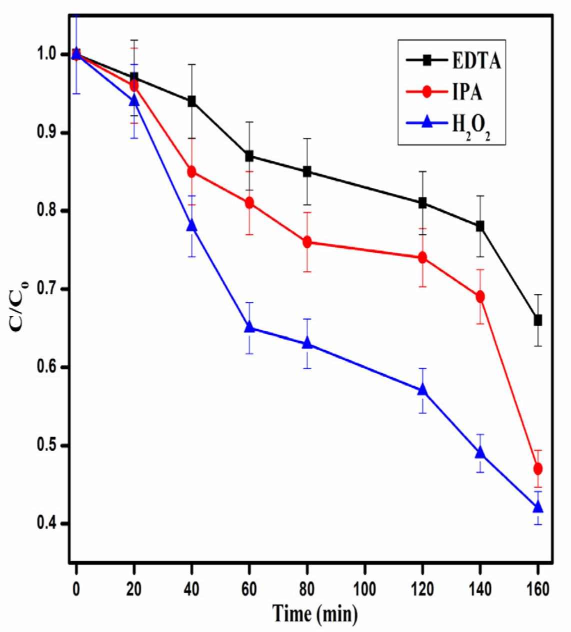

**Fig. 3.** $C/C_0$ plot of scavenger test.

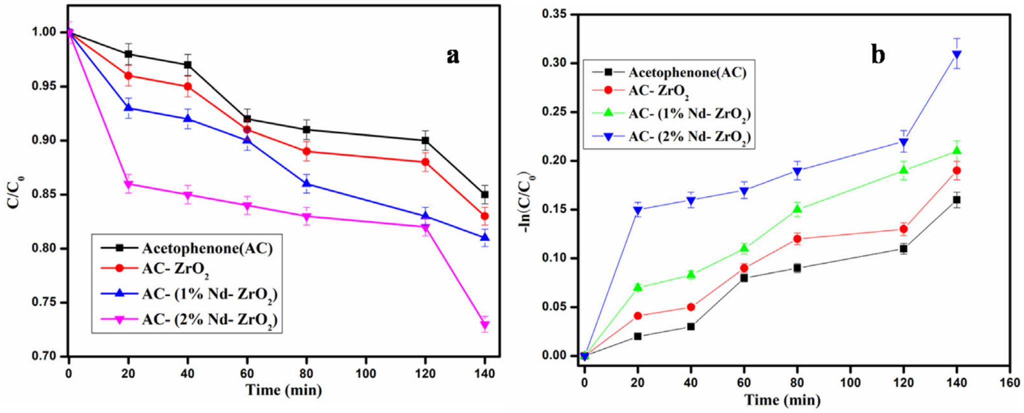

**Fig. 4.** (a) $C/C_0$ plot (b) kinetics plot of pure and photocatalyst added Acetophenone.

To establish the performance of photocatalyst, degradation of colorless organic pollutants were also investigated. Acetophenone was degraded under visible light. The absorption spectra around 200 to 300 nm were observed and it was decreased after irradiation. The $C/C_0$ plot and kinetics plot were depicted in Fig. 4(a, b). The $C/C_0$ plot reveals that the pure sample showed lesser efficiency. As in photocatalyst added samples the degradation was better. 2% Nd doped $ZrO_2$ sample exhibited higher efficiency than other samples. The efficiency was calculated using the above mentioned formula. The calculated efficiency were 12%, 25%, 49% and 60% for pure AC sample, $ZrO_2$ added AC sample, 1% Nd doped $ZrO_2$ added AC sample and 2% Nd doped $ZrO_2$ added AC sample. 2% Nd doped $ZrO_2$ sample possess the better efficiency on colored and colorless pollutants. The kinetics plot showed the rate constant "k" value for all the four samples. The obtained "k" values were 0.0011, 0.0014, 0.0015 and 0.0021 $\text{min}^{-1}$ for pure AC sample, $ZrO_2$ added AC sample, 1% Nd doped $ZrO_2$ added AC sample and 2% Nd doped $ZrO_2$ added AC sample. Higher the rate constant reveals that the photocatalyst has better efficiency (Iqbal et al., 2019). The calculated SD mean for the $C/C_0$ plot of AC dye was 0.069 and for the kinetic plot of AC the SD was 0.097. The error percentage calculated was ±5%.

To further analyze the separation of electron hole charge transfer the EIS and stability studies has been investigated and it was depicted in Fig. 5(a, b). The solution resistance (Rs) of pure $ZrO_2$, 1% Nd-$ZrO_2$ and 2% Nd-$ZrO_2$ was 1.28 Ω, 1.19 Ω, 1.04 Ω respectively. Lower the solution resistance improves the conductivity. The stability of the sample was tested under chronoamperometry studies. The stability of the pure $ZrO_2$ sample showed low current density. The stability of the 1%

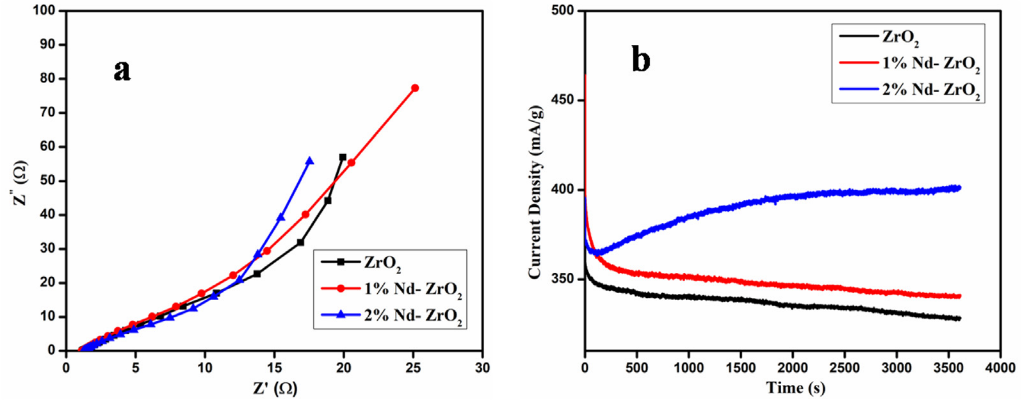

**Fig. 5.** (a) EIS spectra (b) Chronoamperometry study of the fabricated electrodes.

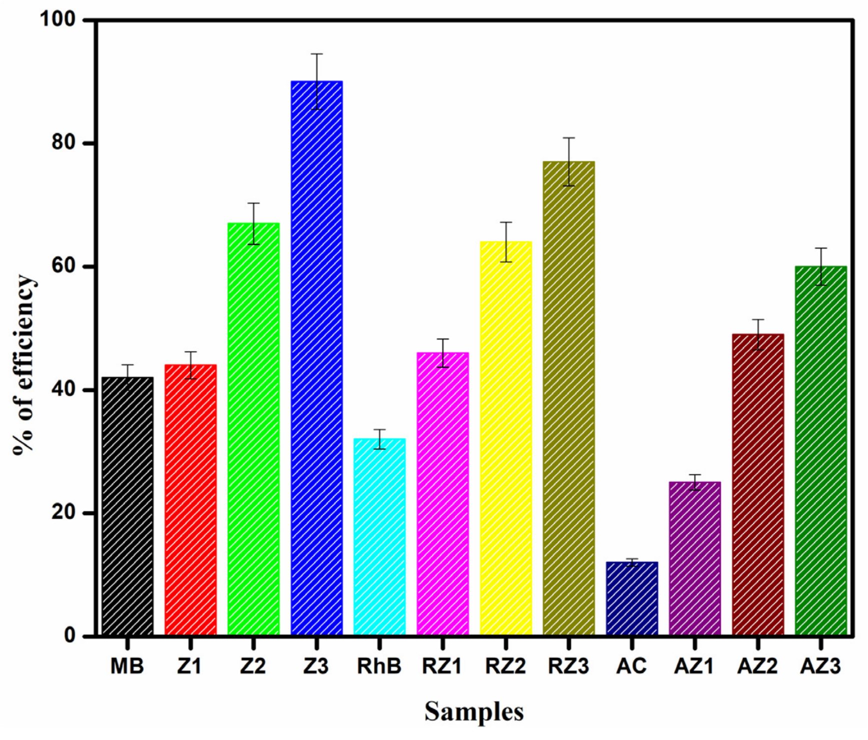

**Fig. 6.** Bar chart of efficiency of the samples.

Nd-$ZrO_2$ sample showed higher current density at 359 mA/g. The 2% Nd doped $ZrO_2$ sample showed 362 mA/g. The lower solution resistance was attributed by 2% Nd doped $ZrO_2$. This is attributed to the doping of Nd doping. The effect of electron hole separation is better attributed to the best sample (Kim et al., 2018).

The efficiency of pure and catalyst added MB and RhB dye sample was plotted in bar chart as given in Fig. 6. The 2% Nd doped $ZrO_2$ sample exhibited almost complete efficiency on MB dye and above average efficiency on RhB dye sample. The sample proved excellent photocatalytic activity against toxic pollutants and good candidate for future practical applications.

MB and RhB dye solution were tested for its before and after photocatalytic degradation for water parameters. The parameters like absorbance, pH value were calculated for water quality parameters (Table 2). The water quality parameters

**Table 2**
Mineralization analyzes of water quality parameters.

| Parameters | WHO accepted value | Before degradation | | After degradation | |
|---|---|---|---|---|---|
| | | MB | RhB | MB | RhB |
| Absorbance | – | 0.95 | 1.02 | 0.2 | 0.6 |
| pH | 6.5–8.5 | 5.0 | 6.0 | 6.7 | 6.8 |

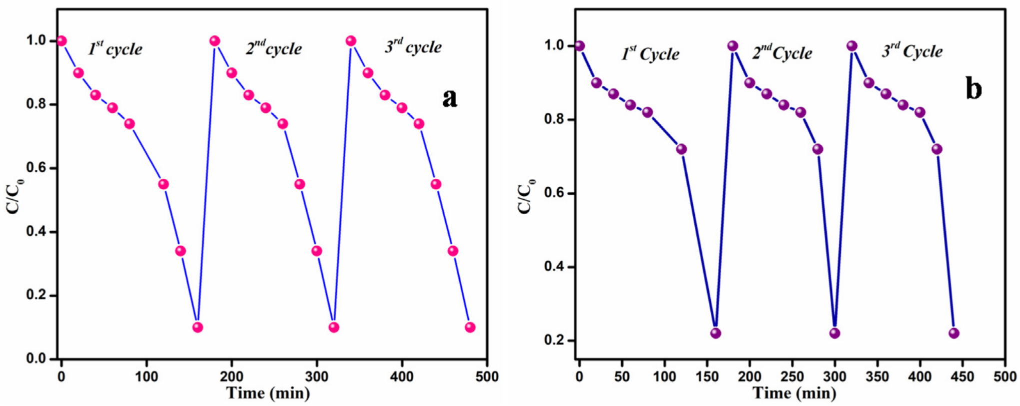

**Fig. 7.** (a) Stability cycle – MB dye (b) Stability cycle- RhB dye.

deliberated by WHO was also given. The water quality parameters were on limit that water is opted for domestic purposes (Shinde et al., 2021). The wastewater treatment is based on reducing the toxic pollutant content and to reuse the water for domestic purposes. For making the treated water for reuse, there are some parameters that must be analyzed. Mineralization analyzes will reveal the characteristics of the treated water and its quality on reuse. The mineralization includes pH, absorbance etc. The pH and absorbance were calculated and it was tabulated (Table 2).

The stability of the best sample was illustrated in Fig. 7(a, b). The 2% Nd doped $ZrO_2$ sample was tested for about three cycles. The efficiency was same for all the three cycles. The efficiency was investigated for RhB dye with the 2% Nd doped $ZrO_2$ sample. The efficiency remains same for about three cycles. This is one of the advantages of the prepared photocatalyst to be used in practical applications.

The possible degradation mechanism of the photocatalytic activity is depicted in Fig. 8. When light was irradiated, valence electrons move to conduction by absorbing light energy. While electrons moves to conduction, there creates holes in valence band and recombination process will be continued. The electrons were trapped by oxygen vacancies and it migrates towards the surface of the photocatalyst. On the same way, holes are trapped by $H_2O$ molecules and these trapped electrons and holes form the superoxide and hydroxyl radicals. Finally these produced active species will degrade the organic pollutant in the enthusiastic way.

## 4. Conclusions

Nd doped $ZrO_2$ sample was synthesized and analyzed fundamental properties like structure, phase, crystallite size, optical properties, semiconducting, vibrational and morphology properties. The band gap obtained was 1.48 eV, 1.4 eV and 1.23 eV for pristine, 1% Nd and 2% Nd doped $ZrO_2$. The narrow band gap of 2% Nd doped $ZrO_2$ will make the catalyst highly active during photocatalysis. With the help of dopant, the agglomeration was reduced which is evident from the morphological studies. The photocatalytic activity was tested against MB and RhB dye and Acetophenone pollutant. 2% Nd doped $ZrO_2$ catalyst added dye sample showed 90% of efficiency on reducing MB dye and 77% on reducing RhB dye and 60% on degrading Acetophenone dye. All the dye sample system showed pseudo first order kinetics. The rate constant of 2% Nd doped $ZrO_2$ catalyst added MB dye sample was 0.0144 $min^{-1}$ and for 2% Nd doped $ZrO_2$ catalyst added RhB dye sample was 0.00944 $min^{-1}$ and 2% Nd doped $ZrO_2$ catalyst added AC dye sample was 0.0021 $min^{-1}$. Optimum level of doping rare earth metal Nd on $ZrO_2$ showed excellent photocatalytic activity against all the three dyes. The prepared photocatalyst is more efficient and stable on degrading the toxic pollutant. This candidate will be the promising one to give out enthusiastic output on removal of colored and colorless toxic pollutants from wastewater. In future, the photocatalyst with improved performance will be prepared to attain complete efficiency.

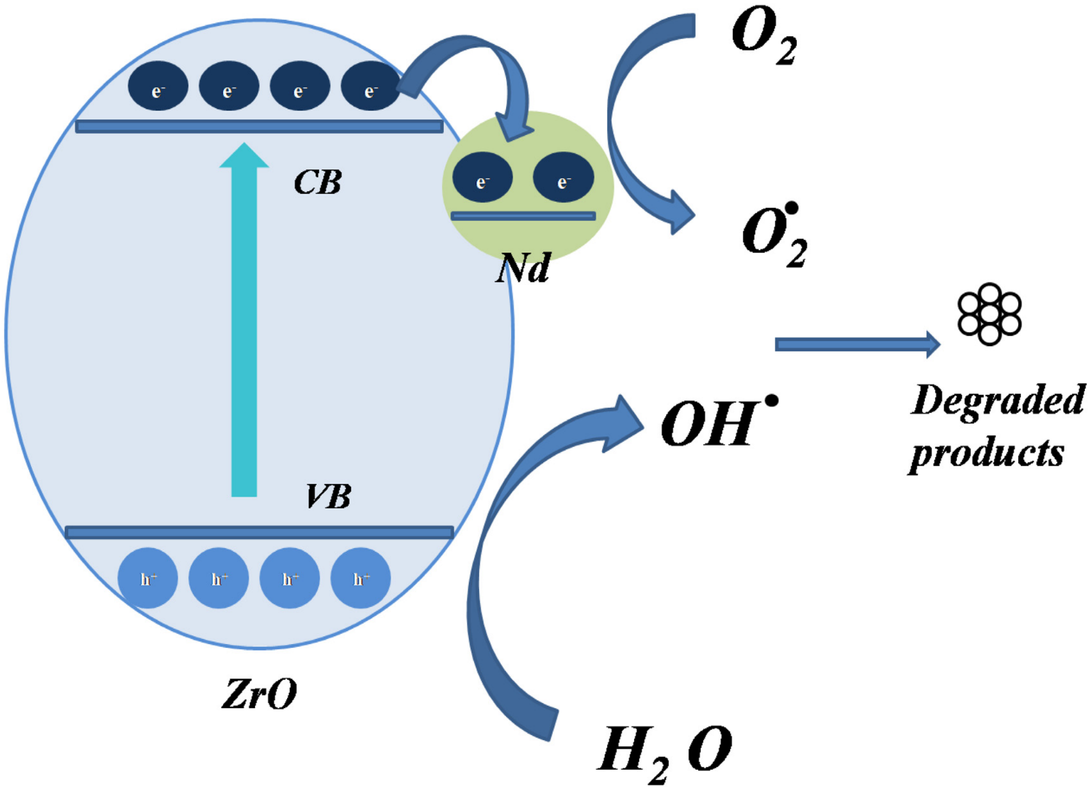

**Fig. 8.** Proposed degradation mechanism.

## CRediT authorship contribution statement

**S.P. Keerthana:** Investigation, Data curation, Resources, Writing – original draft. **R. Yuvakkumar:** Conceptualization, Methodology, Validation, Supervision. **P. Senthil Kumar:** Conceptualization, Methodology, Validation, Supervision. **G. Ravi:** Data curation, Formal analysis, Resources. **Dhayalan Velauthapillai:** Formal analysis, Resources, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.eti.2022.102851.

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