Diffusion-controlled growth of CuAl$_2$O$_4$ nanoparticles: effect of sintering and photodegradation of methyl orange

Samvit G. Menon, Suresh D. Kulkarni, K. S. Choudhari and Santhosh C.

Department of Atomic and Molecular Physics, Manipal University, Manipal 576104, India

ABSTRACT
Facile synthesis of CuAl$_2$O$_4$ and sintering effects on the phase composition are reported. Annealing at 500 ºC showed only CuO phase and the spinel phase started evolving at 700 ºC with the concurrent decrease in the CuO phase. Diffusion-mediated growth of spinel phase was also observed at higher temperatures forming CuAl$_2$O$_4$ at 1000 ºC. The material was stoichiometric and the average particle size was 55 nm, as evidenced by EDS and FE-SEM studies, respectively. The zeta potential of +30 mV and lower (0.346) value of the poly dispersive index (PDI), confirmed the high dispersability of CuAl$_2$O$_4$ in water. The favourable band gap (2.2 eV) makes it suitable as visible light photocatalyst. Owing to its positive surface charge and conducive pH, material could adsorb anionic methyl orange dye. A total of 74% of the dye could be recovered by a simple methanolic extraction. The visible light photocatalysis of the same dye leads to 67% decolouration and the addition of H$_2$O$_2$ accelerated the photodegradation to completion. The catalyst displayed excellent reusability and stability even after five successive runs.

1. Introduction
Environmental pollution and the insufficiency of proper clean energy sources have resulted in the need for developing environmentally safe technologies and processes. Water pollution is one such environmental concern, which is the cause of 88% of 4 billion cases of diarrheal disease.[1] One of the major constituents of textile wastewater is azo dyes, which comprises ~70% of all commercial dyes. They are characterised by several substituted aromatic rings joined together by one or more azo bonds.[2] The presence of these rings make them highly toxic and carcinogenic and their toxicity increases with number of the aromatic groups.[3] These dyes are designed to make the molecules recalcitrant to conventional wastewater treatment methods and cannot be decomposed easily.[4] Thus, there is an imminent need to remove such dyes from wastewaters in order to conserve aquatic life.

Metal aluminate spinels are widely used as catalysts due to their high thermal and mechanical stability, hydrophobicity, and resistance to acids and alkalis.[5–8] They also
find a wide range of applications in magnetic materials,[9,10] paints, pigments,[11,12] refractory materials,[13] cements,[14] etc. Nanostructured metal aluminates have enhanced properties such as lower sintering temperatures, increased hardness, improved ductility,[15–17] etc. These properties make them suitable for catalytic applications.

Due to its ease of availability, chemical stability and strong redox potentials, TiO₂ is a widely used photocatalyst.[18–21] However, due to its bandgap of 3.2 eV, its optical absorption does not extend into the visible region and consequently fails as a visible light photocatalyst even with chemical modifications.[22–24] Photocatalysis is an advanced oxidation process that can be used for the degradation of stable organic dyes in the presence of suitable radiation. Several spinels such as ZnFe₂O₄ and AMn₂O₄ (A = Cu, Zn) have been successfully employed as visible light photocatalysts [25–28] CuAl₂O₄ spinels, with a low bandgap (1.77 – 2.3 eV) can also be used as a potential visible light photocatalyst in degrading toxic aqueous organic dyes.[29–31]

Stepwise development of spinel phase during solution-based synthesis of CuAl₂O₄ nanoparticles is rarely explained in the literature. Diffusion of intermediate oxides phases has been explained by some authors. For instance, Bondioli et al. propose a diffusion mechanism for the synthesis of a Cr₂O₃ – Al₂O₃ in which Al₂O₃ forms an immobile matrix into which mobile Cr₂O₃ diffuses and forms a solid solution.[32] In the current study, we propose the formation of single-phase CuAl₂O₄ spinel through a diffusion process involving an immobile Al₂O₃ matrix and investigate the effects of temperature on this diffusion mechanism.

For the removal of organic dyes from aqueous systems, several physical, chemical and biological methods have been employed successfully.[33–38] However, due to the presence of aromatic rings in these dyes and due to their stronger stability, biological treatment methods are ineffective for degradation or decolourisation. Among chemical processes, advance oxidative processes (AOP) such as photocatalysis are extensively used to degrade such organic dyes in their aqueous forms. In this study, CuAl₂O₄ nanoparticles were synthesised by co-precipitation and were used as adsorbent and photocatalyst for the removal of methyl orange, a commonly used organic dye and water pollutant.

2. Experimental

2.1. Synthesis and characterisation of CuAl₂O₄ nanoparticles

CuAl₂O₄ nanoparticles were synthesised by co-precipitation method using CuSO₄.5H₂O (Merck) and Al(NO₃)₃.9H₂O (Merck). Aqueous solutions of the corresponding salts taken in 1:2 mole ratio (Cu : Al) were mixed and precipitated using a 2M solution of NaOH at a pH of 9.5 under constant stirring for 30 min. The precipitate was vacuum-filtered, washed and dried in an oven at 60°C for 4h before sintering at temperatures between 150°C and 1000°C for 4 h. The structural properties of the nanoparticles and the formation of single-phase CuAl₂O₄ were investigated by X-ray diffraction (XRD) with CuKα radiation (λ = 0.154 nm) using a Rigaku Ultima-IV powder X-ray diffractometer. The particle size distribution and zeta potential were measured using Malvern Zetasizer (DTS Ver 5.10, Malvern Instruments Ltd., UK). The measurement was performed using a disposable zeta cell with ultrapure deionised Millipore water used as the dispersant (refractive index = 1.33, viscosity = 0.89 and dielectric constant = 78.5 at constant temperature of 25°C).
Scanning electron microscopy (SEM) images were obtained on a Zeiss Gemini Ultra 55 FE-SEM equipped with an energy dispersive X-ray spectrometer (EDS). The absorbance of the methyl orange solution was measured using a Jasco V-650 ultraviolet-visible (UV-Vis) spectrophotometer and the infrared (FT-IR) spectra of both methyl orange and the catalyst were collected using a Jasco FT/IR 6200 spectrometer. The optical bandgap of the sample was determined using diffuse reflectance UV-Vis spectra of the nanoparticles recorded on a Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer with a 150 mm integrating sphere attachment. Diffuse reflectance measurements were made between 1000 and 250 nm using BaSO$_4$ as a reflectance standard.

2.2. Photocatalytic studies

The point of zero charge (PZC) or the isoelectric point of CuAl$_2$O$_4$, i.e. the pH value at which surface charge on the catalyst is neutral was determined by the pH drift method. Methyl orange was used as a model organic dye to study the photocatalytic efficiency of CuAl$_2$O$_4$ nanoparticles. A 100 mL of 5.16 x 10$^{-5}$ M aqueous methyl orange with a catalyst concentration of 1.0 g/L were used for the experiments. Adsorption experiments were conducted in a dark chamber and the photocatalytic experiments were performed with a 125W high-pressure mercury vapour (HPMV) lamp as the visible light source at a distance of 10 cm. The pH of the resulting solution was 6 and all the experiments were conducted at this pH, and at same catalyst and dye concentrations unless otherwise stated. In a separate experiment, 0.5 mL of 9.2M aqueous H$_2$O$_2$ solution was added to 100 mL MO solution to accelerate the rate of degradation. The change in concentration of the dye was measured spectrophotometrically at $\lambda_{\text{max}} = 463$ nm. All measurements were conducted in triplicate at room temperature and the average values are reported.

The nanoparticles, after decolouration of the dye were separated by centrifugation and dried. The dye adsorbed on the catalyst surface was extracted using known quantities of methanol. To determine the concentration of dye extracted using methanol, the molar extinction coefficient ($\epsilon$) of methyl orange dissolved in methanol was calculated in the concentration range of 0.01–0.12 mM. This value of $\epsilon$ was used to calculate the concentration of the extracted dye.

3. Results and discussion

3.1. X-ray diffraction

The effect of sintering up to 1000 °C on the formation of CuAl$_2$O$_4$ nanoparticles as studied by XRD patterns is shown in Figure 1(a). Among the possible oxides, CuO is known to form at low temperatures.[39] However, the CuAl$_2$O$_4$ remains amorphous between 150 °C and 500 °C, and crystalline CuO peaks were observed at 500 °C. This observation is in agreement with the reported polymeric and solid state method of CuAl$_2$O$_4$ synthesis where CuO peaks were observed in the temperature between 500 and 600 °C.[40,41] Since the nucleation of spinel CuAl$_2$O$_4$ is slow at lower temperatures, the metal ions diffuse much slower into the bulk grain compared to the grain boundaries and pore surfaces. This implies that the diffusion of CuO into the Al$_2$O$_3$ matrix occurs slowly at low sintering temperatures.[42] The interaction between CuO and amorphous Al$_2$O$_3$ is known to
take place only on the surface, forming a CuAl₂O₄ monolayer. This thickness is too thin to be detected by XRD and hence no crystalline CuO was observed till 500 °C. However, at 700 °C, the crystallinity of the material significantly improves with the formation of CuAl₂O₄ in addition to the existing CuO, which is also in excellent agreement with the literature.[40–43] As the temperature was raised to 900 °C and 1000 °C the CuO phase diminished forming CuAl₂O₄ nanoparticles.

The diffraction patterns were assigned to cubic CuAl₂O₄ (JCPDS, 071-0966) and the additional peaks formed at temperatures below 1000 °C can be assigned to monoclinic CuO (JCPDS, 005-0661). The average crystallite size, calculated using the Debye–Scherrer formula, increased from 29 to 60 nm for CuAl₂O₄ while for CuO, the size increased from 2.2 nm at 500 °C to 31.4 nm at 700 °C. The relative composition of the CuO and CuAl₂O₄ phases were found from the relative intensity ratio method using the XRD patterns. At 700 °C, the material consisted of 47.5% CuAl₂O₄ which gradually increased to 97% at higher sintering temperatures (Table 1), supporting the proposed diffusion of CuO into the Al₂O₃ lattice. The increase in CuAl₂O₄ phase as a function of temperature is shown in Figure 1(b). All the results discussed below are for 1000 °C sample unless otherwise stated.

### 3.2. Scanning electron microscopy

The SEM images depicting the surface morphology of 1000 °C annealed CuAl₂O₄ nanoparticles are shown in Figure 2(a). The average particle size was found to be 55 nm, by

| Annealing temperature (°C) | Phase purity* | Crystallite size (nm) |
|----------------------------|---------------|-----------------------|
|                            | CuO           | CuAl₂O₄               | CuO      | CuAl₂O₄       |
| 500                        | 100           | 0                     | 2.2      | —              |
| 700                        | 52.5          | 47.5                  | 31.4     | 29             |
| 900                        | 20.7          | 79.3                  | 17.42    | 32             |
| 1000                       | 3             | 97                    | —        | 60.1           |

Note: *Calculated by RIR method using PDXL software provided by Rigaku.
measuring the size of about 300 nanoparticles using ImageJ software (see the inset of Figure 2(a)). This value is approximately the same as the crystallite size calculated from the Debye–Scherrer formula. The ratio of Al : Cu was found to be 2.07 from the EDS of CuAl$_2$O$_4$ nanoparticles (Figure 2(b)), in close agreement with expected stoichiometric ratio.

3.3. Bandgap measurements

The optical bandgap of CuAl$_2$O$_4$ nanoparticles annealed at 1000 °C was determined by diffuse reflectance spectroscopy. The diffuse reflectance is related to the Kubelka–Munk function, $F(R) = (1 - R)^2/2R$, where $R$ is the diffuse reflectance of the sample with infinite thickness. This spectrum gives direct band to band transitions which helps accurately determine the bandgap of the material. With the help of the Kubelka–Munk theory, the bandgap of the sample can be calculated by extrapolating the linear portion of the modified Kubelka–Munk function, $[F(R)hv]^2$ vs the photon energy ($hv$) curve on the zero ordinate (Figure 3). From this Kubelka–Munk plot, the optical bandgap of the CuAl$_2$O$_4$ nanoparticles annealed at 1000 °C was found to be 2.2 eV.

**Figure 2.** (a) SEM images of CuAl$_2$O$_4$ annealed at 1000 °C confirming an average particle size of ~55 nm (inset shows the particle size distribution) and (b) the EDS of CuAl$_2$O$_4$ nanoparticles confirming its stoichiometry.

**Figure 3.** Kubelka–Munk plot for bandgap determination of CuAl$_2$O$_4$ nanoparticles annealed to 1000 °C.
sample was determined as 2.2 eV, which suggests that it absorbs all wavelengths in the visible light region, making it suitable for visible light photocatalysis.

3.4. Nature of surface charge

In order to understand the behaviour of adsorption or photocatalysis with respect to pH, it is important to determine the isoelectric point or PZC of the nanoparticles. The PZC value of CuAl₂O₄, was determined by the pH drift method.[44] In brief, the pH of a known concentration of NaCl solution was adjusted by adding HCl or NaOH and aged with the catalyst for 48h. After aging, the final pH of these solutions was plotted against initial pH. The PZC of the material is the point of intersection where a straight line representing initial pH = final pH crosses, which is 7.32 in our case (Figure 4).

Thus, the nanoparticles are positively charged as the experiments were carried out at pH of 6. The positive charge of nanoparticles was further supplemented by the positive value of Zeta potential (+30 mV). Therefore, the surface of the catalyst, being positively charged, favours adsorption of the anionic MO. Thus, all adsorption and photocatalytic studies were conducted at pH 6. A higher value of Zeta potential and lower (0.346) value of the poly dispersive index (PDI) suggest that the CuAl₂O₄ aqueous suspension was well dispersed. Generally, a PDI value of 1 suggests a very broad particle distribution which contain large particles or agglomerates that can settle down quickly and with this value approaching zero confers higher stability to the suspension.

3.5. Fourier transform infrared spectroscopy

In the FT-IR spectrum of the prepared CuAl₂O₄ nanoparticles (Figure 5(a)), the bands observed at 617 and 709 cm⁻¹ and the shoulder around 800 cm⁻¹ could be assigned to the vibrations of Cu—O, Al—O and the Cu—O—Al bonds. These peaks are in close agreement with other synthesis methods.[31,45,46] The band at 3200—3700 cm⁻¹ was attributed to
the longitudinal vibrations of the OH bond in water. The band at 1643 cm$^{-1}$ was due to the bending of the H—O—H bond of water.

### 3.6. Decolouration studies

The aqueous suspension of MO and CuAl$_2$O$_4$ was initially stirred in dark at a fixed speed. The change in concentration of MO was monitored spectrophotometrically at 463 nm. The decolouration was very fast up to first 2 h and was monitored up to 6 h. As much as 58% of the dye was adsorbed (Figure 6), which can be attributed to the conducive surface charge and pH. The material was separated at this stage and the adsorption of MO was analysed by FT-IR spectrum. The FT-IR spectrum of pure MO is shown in Figure 7(a) for comparison. FT-IR spectrum of CuAl$_2$O$_4$ with methyl orange adsorbed on to it is shown

![FT-IR spectra](image)

**Figure 5.** FT-IR spectra of (a) phase-pure CuAl$_2$O$_4$ and (b) CuAl$_2$O$_4$ after photocatalysis of methyl orange.

![Adsorption efficiency](image)

**Figure 6.** Adsorption efficiency of CuAl$_2$O$_4$ on the decolouration of MO in dark.
in Figure 7(b). The bands at 1067 and 1384 cm\(^{-1}\) can be attributed to the stretching of the \(\text{N} = \text{N} -\) bond and the vibrations of the \(-\text{C} - \text{N} -\) bond of MO, respectively. A shoulder at 1152 cm\(^{-1}\) and a weak band at 1078 cm\(^{-1}\) are attributed to the vibrations of \(-\text{N} - \text{CH}_3\) and the \(\text{S} = \text{O}\) bands, respectively, that are characteristic of MO. Thus, the FT-IR spectrum confirms adsorption of methyl orange on CuAl\(_2\)O\(_4\). It is to be noted that the concentration of adsorbed dye is substantially smaller than the amount of nanoparticles present in the KBr pellet used. Hence, the bands corresponding to adsorbed MO are expected to be of lower intensities as observed.

In order to quantify the extent of adsorption, the separated catalyst was re-dispersed in a known volume of methanol and kept in cyclomixer for 10 minutes. The solution slowly became coloured which suggested the probable dissolution of adsorbed MO into methanol. This step was repeated with known volumes of methanol until there was no visible colour change for methanol. The absorption spectrum of the separated methanolic solution was found to be matching with that of pure MO in methanol, as shown in Figure 8(a). It is to

![Figure 7. FT-IR spectra of (a) pure MO (b) CuAl\(_2\)O\(_4\) with adsorbed MO (inset shows the presence of MO on the surface of CuAl\(_2\)O\(_4\)) and (c) CuAl\(_2\)O\(_4\) after extraction of MO photocatalysis.](image)

**Figure 8.** (a) Overlaid absorption spectra of pure and extracted MO (b) verification of Beer's Law for methanolic solution of MO.
be noted that the absorption maxima for MO in methanol is observed at 420 nm, while it appears at 463 in water. This blue shift for the methanolic MO is attributed to difference in the specific solute — solvent interactions in both solvents.[47] The close match of the absorption spectra suggests that the MO has not undergone any chemical alteration. No characteristic MO peaks were observed in the FT-IR spectrum of the catalyst after extraction (Figure 7(c)).

In order to quantify the extent of adsorption, the molar extinction coefficient (ε) of MO dissolved in methanol was determined as $26807 \pm 549 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$ from the slope of the absorbance vs. concentration plot (Figure 8(b)). This value of ε was used to quantify the amount of adsorbed MO in successive extractions. The quantification of adsorption was based on the absorbance value of MO at $\lambda_{\text{max}} = 420$ nm when extracted in methanol, as shown in Table 2. The extent of MO recovery was ~74% of the observed decolouration (43% of initial dye concentration). This type of extraction is beneficial for applications such as wastewater remediation as the adsorbent can be regenerated and reused. Attempts to extract remaining adsorbed dye using hot solvents were unsuccessful probably due to the chemisorption of MO.[48,49]

The spectral changes for the decolouration of MO under visible light are shown in Figure 9. The decrease in intensity of the peak at 463 nm with time suggests the gradual degradation of the azo group and the corresponding dye chromophore.[50–52] Under visible light, ~67% decolouration was observed in 6 h and 70% in 8 h and hence the

Table 2. Quantification of adsorption and photocatalysis of MO on CuAl$_2$O$_4$ nanoparticles extracted using methanol after 6 h of contact time at pH = 6.

|                         | Adsorption          | Photocatalysis         | Photocatalysis using H$_2$O$_2$ |
|-------------------------|---------------------|------------------------|---------------------------------|
| Initial dye concentration | $5.16 \times 10^{-3}$ M | $5.14 \times 10^{-3}$ M | $6.14 \times 10^{-3}$ M         |
| % Decolourised in 6 h (D) | 58%                | 67%                    | 99%                             |
| % Dye remaining in aqueous solution | 42%                | 33%                    | 1%                              |
| % Dye extracted (E)       | 43%                | 20%                    | 0%                              |
| % Unaccounted for = D – E | 15%                | 47%                    | 99%                             |

Figure 9. Spectral changes for the decolouration of MO using CuAl$_2$O$_4$ nanoparticles under visible light. Decolouration profiles of MO for 6 h and 8 h are shown in the inset.
experiments were restricted to 6 h. When quantified for adsorption, it was seen that only ~20% of the dye was extracted from the catalyst surface, inferring the photodegradation of ~47% dye.

H₂O₂ is known to enhance the photocatalytic rate as it contributes additional highly oxidising OH∙ and assists charge separation and hence its effect was studied. The corresponding spectral changes are shown in Figure 10(a). The stability of MO in Visible light was verified and the effect of H₂O₂ on the decolouration of MO was studied in the absence of the catalyst (Figure 10(b)) leading to ~42% decolouration. However, when CuAl₂O₄ was used as photocatalyst, complete decolourisation of MO was achieved in 6 h.

The following mechanism is proposed for the decolouration of MO under visible light. In the first step, CuAl₂O₄ semiconductor is photo-excited to generate electron (e⁻/C₀) – hole (h⁺/VB) pairs. Water molecules are then split into H⁺ and the oxidising OH∙ due to the presence of the valence band holes. Further, the hydroxyl ions also inject an electron into the valence band holes to form OH⁻. These highly oxidising OH⁻ are responsible for the degradation of the organic dye. An electron from the conduction band is scavenged by an O₂ molecule to generate superoxide radical O₂⁻; however, they have a minor role to play in the photocatalytic oxidation process [53,54]. Finally, the dye reacts with the hydroxyl radical to decompose into the mineralisation products. The mechanism is shown as follows:

\[
\begin{align*}
\text{CuAl}_2\text{O}_4 + h\nu &\rightarrow e_-\text{CB} + h^+\text{VB} & (1) \\
\text{CuAl}_2\text{O}_4(h^+\text{VB}) + \text{H}_2\text{O} &\rightarrow \text{CuAl}_2\text{O}_4 + \text{H}^+ + \text{OH}^- & (2) \\
\text{CuAl}_2\text{O}_4(h^+\text{VB}) + \text{OH}^- &\rightarrow \text{CuAl}_2\text{O}_4 + \text{OH}^- & (3) \\
(\text{O}_2)_{\text{ads}} + \text{CuAl}_2\text{O}_4(e_-\text{CB}) &\rightarrow \text{CuAl}_2\text{O}_4 + \text{O}_2^- & (4) \\
\text{OH}^- + \text{Dye} &\rightarrow \text{Organic Moiety.} & (5)
\end{align*}
\]

In low-bandgap photocatalysts the recombination of photoinduced electrons and holes decrease the availability of OH⁻ [55,56] consequently reducing the photocatalytic efficiency. Thus, it is desirable to suppress this recombination for increased photocatalytic efficiency, which can be achieved using electron acceptors such as H₂O₂. Under visible
light, the addition of H$_2$O$_2$ not only increases the number of reactive OH$^-$ radicals but also increases the amount of dissolved oxygen in the solution which facilitates charge separation.[57,58] This enhances the degradation rate significantly as can be seen from Figure 10 (b). There are also reports which suggest that the adsorbed dye absorbs a light photon to produce the dye in an excited state.[59,60] An electron from this excited state of MO is injected into the conduction band of CuAl$_2$O$_4$, leading to the formation of MO cationic radical which subsequently decomposes. This mechanism is shown as follows:

\[
\text{Dye} + h\nu \rightarrow \text{Dye}^* \\
\text{Dye}^* + \text{CuAl}_2\text{O}_4 \rightarrow \text{Dye}^- + \text{CuAl}_2\text{O}_4(e^-_{CB}).
\]

The nanoparticles after complete extraction of MO were dried and tested for further reusability. For a catalyst to be described as an effective photocatalyst, it is essential that its performance remains consistent over several runs. Despite several papers confirming the successful use of CuAl$_2$O$_4$ as a photocatalyst, there is a dearth of reports which confirms the reusability of CuAl$_2$O$_4$ as a photocatalyst. Figure 11 shows the decolouration profile of MO on successive reuse of the photocatalyst. The degradation efficiencies for each run were measured as 67%, 67%, 66%, 64%, and 59%, respectively, showing excellent reusability. There are no reports of reusability of CuAl$_2$O$_4$ nanoparticles as photocatalyst. The slight reduction in efficiencies from the second reuse could be attributed to leaching of the surface during successive adsorption and agglomeration of the CuAl$_2$O$_4$ nanoparticles, both of which reduce the surface area and, consequently, the sites available for adsorption.[61,62] To better understand the material stability, the XRD of the catalyst was collected after four successive reuses and compared with that of the fresh catalyst (Figure 12). The XRD patterns show no significant changes in the crystal structure of the catalyst implying that the catalyst remains stable even after four successive photocatalytic cycles attesting to its effective reusability.

![Figure 11. Decolouration profile of MO to assess the reusability of CuAl$_2$O$_4$ as a photocatalyst.](image)
4. Conclusions

Temperature-dependent diffusion of CuO into the alumina matrix was observed for the formation of CuAl₂O₄ nanoparticles by simple co-precipitation method. The formation of spinel phase increased with sintering temperature with the gradual disappearance of CuO. The stoichiometric nanoparticles of ~55 nm possessed positive surface charge suitable for the adsorption of anionic MO leading to 58% decolouration. A simple method was developed for the separation of adsorbed dye (~74%). The nanoparticles with band gap of 2.2 eV were employed as visible light photocatalyst for the decolouration of aqueous MO. The gradual disappearance of the absorption band at 463 nm inferred the decomposition of azo group and the amount of MO photodegraded was quantified. The addition of H₂O₂ enhanced the photocatalytic rate, leading to complete degradation of MO inferring the active participation of OH radicals in the process. The catalyst possessed excellent reusability with negligible reduction in efficiencies even after five consecutive runs. This process can be extended to solar wastewater remediation in textile and food industries that excessively use such harmful and toxic dyes.

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Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID

Suresh D. Kulkarni http://orcid.org/0000-0002-3004-2266
K. S. Choudhari http://orcid.org/0000-0001-7428-2678
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