Original Article

A novel preparation of visible light driven Durio zibethinus shell ash supported CuO nanocomposite for the photocatalytic degradation of acid dye

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ABSTRACT

In this work, a novel Durio zibethinus shell ash (DSA) supported copper (II) oxide (CuO) nanocomposite has been successfully synthesized via a single-step hydrothermal method. The resulting visible light responsive nanocomposite was subjected to the Scanning Electron Microscopy- Energy Dispersive X-Ray Spectroscopy (SEM-EDX), Photoluminescence (PL), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FT-IR), and nitrogen adsorption–desorption analysis. The major preparation and operational parameters, including the ash impregnation ratio, catalyst loadings, initial dye concentration, irradiation time and solution pH on the photoreaction were examined. Morphological study revealed that DSA served as an excellent supporting surface for the CuO nanoparticles to offer the synergistic adsorption–photodegradation reaction, verified by the rising porosity, and changing bandgap energy and surface functionalities. A complete degradation of Acid Red 88 with the high concentration of 500 mg/L was achieved within 2 h. Reusability test ascertained the high durability of the nanocomposite, with greater than 95% of decolourization efficiency even after five regeneration cycles. This study provides a new insight for the design of a low cost, eco-friendly and visible light driven photocatalyst, and innovative conversion of Durio zibethinus shell ash into a highly valuable nanocomposite for the effective purification of water contaminants.

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1. Introduction

Semiconductor metal oxides have gained considerable interests in the technological development, with specific applications in the electronic devices and sensor manufac-

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photocatalysis, also known as heterogeneous photocatalysis, is recognized as one of the best and “green” environmental friendly technology to confront with the challenges of environmental pollutants, owing to the excellent photocatalytic degradation capacity, non-destructive, lower energy consumption, relatively inexpensive, extremely stable, reproducible, and ease of operation for large-scale applications [3]. This technique involves predominantly advanced oxidation process (AOP), a reliable process that generates highly reactive and non-selective radicals in the presence of energy sources to completely mineralize noxious pollutants to carbon dioxide and water, and free from the generation of toxic intermediate products [4].

Among these transition metal oxides, CuO, a representative of p-type semiconductor oxide, also regarded as a visible light photocatalyst with a narrow bandgap 1.2 eV to 2.1 eV [5], has attracted enormous attention by the virtue of its non-toxicity, relatively low cost, excellent pigment properties, and unique photochemical and photoconductive characteristics [6]. Under the irradiation of visible light, CuO particles could get activated by the photons energy equal or greater than its band gap, and the transfer of photo-excited electron would take place from the valence band (VB) to the conduction band (CB). The excited electron from CB is further scavenged by an electron acceptor O₂ molecules to form superoxide (∗O₂⁻), and the holes from VB would react and split the H molecules to generate hydroxyl radicals (∗OH⁻). These highly reactive radicals are responsible for the oxidation of water contaminants expressed by:

\[
\begin{align*}
\text{CuO} + \text{hv} & \rightarrow \epsilon_{\text{CB}} + h_{\text{VB}} \\
\text{CuO}(e^-) + O_2 & \rightarrow \text{CuO} + \text{O}_2^- \\
\text{CuO}(e^-) + H_2O & \rightarrow \text{CuO} + H^+ + \text{OH}^-
\end{align*}
\]

2. Materials and methods

2.1. Model pollutant

Acid Red 88, an anionic azo dye, with the molecular structure of C₂₀H₁₃N₂O₄SNa, and molecular weight of 400.8 g/mole, was selected as the targeted model contaminant. A standard stock solution with the concentration of 500 mg/L was prepared in deionized water, and experimental working solutions were prepared by serial dilutions to the desired concentrations.

2.2. Adsorbent

Durio zibethinus shell (DS), a major by-product abundantly available from the fruit processing industries was chosen as the initial raw precursor. The content of C, N, H, O and S elements analyzed using an elemental analyzer (Model CHN-O-RAPID) was identified to be 457.37 g/kg, 30.6 g/kg, 66.93 g/kg, 443.5 g/kg and 1.6 g/kg, respectively. The Durio zibethinus shell ash was prepared by controlled burning of DS in a muffle furnace at 700 °C under purified oxygen gas for 30 min. The as-prepared Durio zibethinus shell ash was washed extensively with deionized water to remove the adhering dirt particles from the surface, dried, screened through a sieve of 250–500 μm, and acid functionalized with 1 M of hydrochloric acid. The modified Durio zibethinus shell ash (DSA) was rinsed with deionized water till a constant pH was acquired in the washing solution. The estimated composition of the representative DSA was identified by the Energy Dispersive X-Ray Spectroscopy (EDX) analysis (Element Silicon Drift Detector (SDD)). DSA composed of mainly carbon (35.42 Wt%), 63.54 At%), sodium (0.06 Wt%; 0.05 At%), magnesium (7.57 Wt%; 6.71 At%), aluminum (0.47 Wt%; 0.37 At%), silicon (3.78 Wt%; 2.90 At%), phosphorus (12.37 Wt%; 8.61 At%), chloride (0.31 Wt%; 0.19 At%), calcium (14.35 Wt%; 7.72 At%), manganese (1.91 Wt%, 0.75 At%), and iron (23.78 Wt%; 9.18 At%).

2.3. Photocatalytic nanocomposite

The CuO/DSA derived nanocomposites were synthesized by a single-step hydrothermal method, by mixing the requisite amount of DSA in a dissolved Cu(NO₃)₂ solution with the impregnation ratio (CuO/DSA) of 1:1 to 1.5. The solution mixture was hydrothermally heated at 140 °C in a tightly sealed Teflon-lined autoclave for 10 h in an oven. The newly prepared nanocomposites were filtered, washed sequential with deionized water, dried at 80 °C, and kept in air tight bottles for further analysis.
2.4. **Physical and chemical characterizations**

The surface morphology was evaluated by using the Scanning Electron Microscopy (SEM, Zeiss Supra 35 VP, Germany). The crystalline phase composition was characterized with X-ray Diffraction (XRD) technique by using the Bruker AXS D8 Diffractometer with monochromatic Cu Kα radiation (λ = 1.5406 Å), while the High Resolution Transmission Electron Microscopy (HR-TEM) images were recorded by Bioinard's FEI Tecnai™ G2 20 S-TWIN microscope with an accelerating voltage of 200 kV. The surface functional groups were detected by Fourier Transform Infrared (FTIR) Spectroscopy (FTIR-2000, PerkinElmer) by using the KBr pellet method in the scanning range of 4000–400 cm⁻¹. The nitrogen adsorption–desorption isotherm was conducted at 77 K by using an automatic Micromeritics ASAP 2020 Volumetric Adsorption Analyzer. Prior to the measurement, the samples were degassed for 8 h at 573 K under a vacuum condition. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation, while the micropore surface area, external surface area and micropore volume were deduced using the t-plot method. The determination of point of zero charge (pH_{zpc}) was conducted by adjusting the pH of 50 cm³ of 0.01 M NaCl solution to a value between 2 and 12. 0.15 g of sample was added, and the final pH was measured after 48 h under agitation. The pH_{zpc} is the point where pH_{initial} – pH_{final} = 0. The photoluminescence (PL) spectra were obtained using a Raman & Photoluminescence Spectrophotometer (HR 800 UV), equipped with HeCd and Argon ion laser lamps with the excitation wavelength of 224–248 nm at room temperature.

2.5. **Photocatalytic analysis**

The photocatalytic analysis was examined by the photodegradation of AR 88 in a self-assembled photocatalytic reactor, equipped with four visible light sources (400 W metal halide lamps, λ = 380–780 nm), circulating water jackets, thermocouples and a cooling fan. The schematic diagram of the photocatalytic reactor is displayed in Supplemental Fig. 1. A prefixed amount of photocatalyst was added into 100 mL of AR 88 solution. Prior to the irradiation, the aqueous suspension was stirred in darkness for 30 min until the adsorption–desorption equilibrium was achieved. The aliquots of the reaction mixture were extracted at specific time intervals, filtered using a syringe filter (Nylon Millipore 0.25 μm) as to minimize the interference of catalyst fines with the analysis, and the concentration of AR 88 was measured using a UV–Vis Spectrophotometer (UV-1800 Shimadzu, Japan) at 506 nm. The degradation rate was defined as:

\[
\text{Degradation rate(%) } = \frac{C_0 - C_t}{C_0} \times 100% \tag{6}
\]

which C₀ and Cₜ are referred to the initial concentration of AR 88 and at time t (min), respectively.

The effect of catalyst loading on the photodegradation reaction was examined by varying the catalyst dosage from 0.01 g/100 mL to 0.06 g/100 mL in 500 mg/L of AR 88 solution at the irradiation time of 30 min. The effect of initial concentration and irradiation time was evaluated at the initial concentration from 100 mg/L to 500 mg/L at the optimum catalyst loading. The effect of solution pH on the removal efficiency was conducted at the pH range of 2 to 12, with the pH adjustment by using 0.1 M of HCl or NaOH under the optimized experimental conditions.

2.6. **Kinetic study**

To quantify the kinetic analysis of the photodegradation process, the photocatalytic reaction is assumed to obey the first order kinetics. At low initial concentration, the kinetic rate expression could be simplified as:

\[
\frac{d[C]}{dt} = K_{app}[C] \tag{7}
\]

where C is denoted to the concentration of AR 88, t is the time of reaction (min), and K_{app} is the apparent first order rate constant (min⁻¹). When the adsorption–desorption equilibrium was reached, the equilibrium concentration of AR 88 is defined as the initial concentration applied for the kinetic analysis. Eq. (7) can be integrated (the limit of C = C₀ at t = 0 when the equilibrium is achieved), and the simplified equation is given by:

\[
\ln \left( \frac{C_0}{C_t} \right) = K_{app}t \tag{8}
\]

2.7. **Reusability test**

The reusability test was conducted with respect to five successive degradation cycles of AR 88 at the initial concentration of 100 mg/L under the optimized experimental condition. For each experiment, the nanocomposites were regenerated through filtration, washed with deionized water till a constant pH was acquired in the washing solution, subsequently by drying at 120°C for 1 h. The regenerated nanocomposites were applied for the next consecutive degradation runs.

3. **Results and discussions**

3.1. **Preparation of DSA supported CuO photocatalyst**

The effect of ash impregnation ratio is an important prerequisite step for the preparation of photocatalysts with the highest activity. The variation of photocatalytic performance of the DSA supported nanocomposites at different ash impregnation ratio is presented in Fig. 1. Decreasing the ash impregnation ratio of CuO:DSA from 1:5 to 1:1 showed a drastically enhancement of the degradation efficiency from 54% to 80%, as compared with the degradation rate of 35% for the raw DSA. The result is mainly ascribed to the synergistic effect of the nanocomposites, which promotes the unique bi-functional properties of adsorption behavior and photocatalytic capability [11]. Similarly, the higher performance of the DSA supported CuO nanocomposite is well supported by a greater availability of the surface sites at the higher content of DSA, to accelerate the larger deposition of CuO as the catalytic center of the nanocomposite [12]. The representative structure of the nanocomposite is illustrated in Fig. 2 (a). Similarly, with a
larger surface area, the newly prepared nanocomposite would provide more adoptive sites for the targeted pollutants than the photocatalyst itself, to allow the migration of adsorbed AR 88 to the photoactive degradation center of CuO [13].

However, beyond the optimal impregnation ratio of 1:4, the degradation efficiency was gradually decreased. This phenomenon could be inferred to the excessive loading of DSA that turned to be unfavorable for the photodegradation process, due to the agglomeration of ash particles within the CuO nanoparticles [Fig. 2 (b)]. It could be an obstacle to confine the pathway of light from reaching to the CuO catalyst surface, and triggers to the lower generation of photo-induced electron-hole pairs, and eventually inhibits the photocatalytic efficiency of the nanocomposites [14]. Hence, the optimum impregnation ratio of 1:4 was applied for the further evaluations.

3.2. Physical and chemical characterizations

The representative scanning electron micrographs (SEM) of DSA and CuO/DSA derived nanocomposite, with a magnification of 500 X, are depicted in Fig. 3. Generally, the raw DSA exhibited an irregular, rough and compact surface, with an uneven distribution of agglomerated flake particles. This morphological structure was highly porous, with the presence of different cavities over the surface, indicating good availability of surface area for the deposition of CuO. Conversely, the CuO anchored nanocomposite revealed a uniform configuration of spherical CuO nanocrystalline structure deposited over the entire surface of DSA, indicating the significant morphological transformation and size modification of the nanocomposite under hydrothermal treatment. Similar chemical restructuring process has been reported by Visa and Chelaru [15] and Yao et al. [16] under hydrothermal process within the ash and TiO2 nanoparticles. The surface morphological alteration ascertained the successive preparation of CuO/DSA nanocomposite, which would accelerate the photocatalytic activity by enhancing a greater availability to be activated by light, with the generation of the highly hydroxyl radicals as the foundation of the photodegradation process [17].

Nitrogen adsorption–desorption curve is a standard procedure elucidating qualitative information on the textural structure and surface properties of the composites. According to the classification of the International Union of Pure and Applied Chemistry (IUPAC), the nitrogen adsorption isotherm analysis (Fig. 4) resembles the type I-III hybrid isotherms, suggesting a combination of microporous–mesoporous structure. The initial part of isotherm curve showed a greater uptake of nitrogen at the relative pressure between 0 and 0.5, that may be correlated with micropore filling. However, further increase of the nitrogen adsorption found at the relative pressure higher than 0.5, illustrates the presence of mesoporous structure. The surface physical properties of DSA and the CuO/DSA derived nanocomposite are given in Table 1. The BET surface area, Langmuir surface area and total pore volume of the raw DSA were identified to be 5.59 m2/g, 7.96 m2/g, and 0.023 cm3/g, respectively. However, the BET surface area, Langmuir surface area and total pore volume of the CuO/DSA derived

![Fig. 1 – Effect of ash impregnation ratio (CuO:DSA) on the photodegradation of AR 88 (catalyst loading = 0.01 g/100 mL, C0 = 500 mg/L, t = 30 min).](image1)

![Table 1 – Surface physical characteristics of DSA and CuO/DSA derived nanocomposite.](image2)

![Fig. 2 – Schematic diagram of CuO/DSA derived nanocomposite at the (a) optimum impregnation ratio and (b) beyond the optimal impregnation ratio.](image3)
nanocomposite were found to be 36.41 m²/g, 53.52 m²/g, and 0.108 cm³/g, respectively, suggesting the positive development of surface porosity under hydrothermal treatment process. The findings were in the agreement with the results reported by Kim et al. [18] on the synthesis of multifunctional fly ash derived nanocomposites, which supported the vital role of DSA as a suitable backbone, and for the homogeneous and in-situ deposition of CuO nanoparticles, that in turn improved the overall surface area of the nanocomposite. Accordingly, Gao et al. [19] have suggested that hydrothermal treatment could promote crystalline nucleation and pore development, which has essentially improved the CuO/DSA framework.

The efficiency of the charge carrier trapping, immigration and transfer, and the fate of electron-hole pairs in semiconductor particles could be evaluated by the photoluminescence (PL) spectra of the DSA and CuO/DSA derived nanocomposite, as illustrated in Fig. 5. The two emission peaks are observed at 545 nm and 585 nm, which is generally attributed to the recombination of free excitons at the near-band edge. It is worth noting that the UV emission intensity of the CuO/DSA derived nanocomposite exhibits a distinct decrease.
as compared to the pure DSA. The PL emission was mainly resulted from the recombination of photogenerated electron-hole pairs, and a lower PL intensity may indicate a lower recombination rate of electron-hole pairs and better photocatalytic activity [20]. This PL analysis therefore suggested that the CuO/DSA derived nanocomposites would demonstrate a greater better photocatalytic activity as compared to the pure DSA. The optical bandgap energy for the strong intense blue light emission peaks in the PL spectra was within the range of 3.29 and 3.54 eV. The obtained higher values of the bandgap of CuO nanostructures as compared with that of bulk CuO (Eₚ = 1.39 eV) [21], could be ascribed to the quantum confinement effect, in which the nanocomposite with a smaller particle size demonstrated a higher bandgap value [22].

The XRD patterns of the pure CuO (JCPDS File No. 41-0254), DSA and CuO/DSA derived nanocomposite are given in Fig. 6. All of the diffraction peaks for the pure CuO are corresponded to the monoclinic structure of CuO, which is in good agreement with the standard JCPDS data. The absence of diffraction peaks related to Cu(OH)₂ or Cu₂O indicated the high purity of the as-synthesized samples. The CuO diffraction peaks were located at 2θ = 32.5°, 35.6°, 38.8°, 48.7°, 53.4°, 58.3°, 61.5°, 66.2°, 67.8°, 72.4° and 75.0°, mainly ascribed to the (110), (002), (111), (020), (022), (113), (220), (311) and (2 2 2) planes, respectively. This pattern has been indexed as the monoclinic phase of CuO, with the lattice constants a = 4.84°, b = 3.47°, and c = 5.33°, which is consistent with the standard values for bulk CuO. Conversely, the crystalline peaks of the CuO/DSA derived nanocomposite corresponding to (101), (211), (002), (111), (110), (040), (002), (222), (111), (020), (020), (113), (3 1 1), (2 2 0), (100), (311) and (2 2 2) planes diffraction planes at 2θ angles of 14.9°, 21.2°, 26.7°, 28.4°, 32.5°, 34.8°, 35.6°, 36.1°, 38.8°, 48.7°, 53.4°, 58.3°, 61.5°, 66.2°, 67.8°, 69.8°, 72.4° and 75.0°, respectively, were recorded.

The TEM patterns of the DSA and CuO/DSA derived nanocomposite are illustrated in Fig. 7. Generally, the HR-TEM image of the pure DSA consisted of an agglomeration of spherical and oral nanoparticles [Fig. 7(a)], whereas CuO/DSA derived nanocomposite showed a flower-shaped hierarchical architecture consisting of interpenetrating CuO thin nanosheets [Fig. 7(b)]. The particle size distribution depicted in Fig. 7(c) revealed that the diameter of the nanoparticles ranged from 2.77 to 69.0 nm, with an average diameter of 35.89 nm. The fringe spacing, also known as the difference between the two atomic layers, as indicated in Fig. 7(d) has been measured to be 0.25 nm, which is related to the (002) crystal plane of monoclinic structure of the CuO phase (JCPDS File No. 41-0254).

The representative FT-IR spectra of DSA and CuO/DSA nanocomposite are presented in Fig. 8. The broad band at 3411 cm⁻¹ is assigned to the stretching of the hydroxyl group. The vibration at 2968/2962 cm⁻¹ is identical to the C–H stretch-
Fig. 7 – HR-TEM images of (a) DSA and the (b) CuO/DSA derived nanocomposite; (c) Histogram of particle size distribution of CuO nanostructures; and (d) d-spacing.

Fig. 8 – Fourier-Transform Infrared spectra of DSA and CuO/DSA derived nanocomposite.
ing of alkane group, while the transmittance at 2355 cm\(^{-1}\) is related to the stretching of C=CC in alkene group. The IR peak at 1608/1602 cm\(^{-1}\) is corresponded to the bending vibration of hydroxyl group. The region between 1495–1409 cm\(^{-1}\) is ascribed to the symmetrical stretching of Si–O–Si bond, while the signals at 1063/1031 cm\(^{-1}\), and 692–559 cm\(^{-1}\) are attributed to the bending vibration of Si–O bonds, and representative of the C–H stretching in aromatic compounds, respectively. The presence of extra bond at 867 cm\(^{-1}\) for the FTIR spectrum verified the formation hydrogen bonding of Cu–OH generated by the Cu(NO\(_3\))\(_2\) of the CuO/DSA derived nanocomposite. Additionally, the lower peak intensity and peak deconvolution at 2962/2928, 2355 and 867 cm\(^{-1}\) justified the homogeneous deposition of CuO onto DSA through the matrix via Van der Waals interaction, which renders the pattern interpretation of the spectra. Such interactions have been reported in the TiO\(_2\)-deposited fly ash derived composite [23].

### 3.3. Photodegradation process

#### 3.3.1. Effect of catalyst loading

Catalyst loading is the major influencing parameter to determine the operation cost, and the feasibility for large-scale practical applications. The effect of catalyst loading on the photocatalytic degradation of AR 88 was examined by varying the catalyst loading from 0.01 g/100 mL to 0.06 g/100 mL under the irradiation of visible light for 30 min, as illustrated in Fig. 9. An increase of catalyst loading showed a superior improvement on the degradation efficacy of AR 88. The degradation efficacy increased linearly from 80% to 93%, with an increase of catalyst loading from 0.01 g/100 mL to 0.03 g/100 mL. The finding could be ascribed to the larger availability of surface active sites at higher catalyst loading for the greater exposure and adsorption of AR 88 molecules [24]. Meanwhile, higher number of surface catalytic sites at higher catalyst loading would contribute to the higher light absorption by the photocatalyst, to promote a greater formation of photo-induced hydroxyl radicals [25], which in turn enhanced the rate of photocatalytic decomposition reaction.

Beyond the catalyst loading of 0.03 g/100 mL, no appreciable enhancement of the degradation efficacy was observed, in which the removal efficacy increased only slightly from 93% to 96%. This finding could be rationalized in terms of further increase of catalyst slurry dosage above the saturation limit, that might induce the excessive agglomeration of catalyst particles, with some part of the catalyst surface that has been blocked for the photon absorption [26]. Additionally, the aggregation of catalyst may cripple the transparency of the tested solution, which in turn reduced the light penetration into the solution, and affected the incidence of photons striking from the catalyst surface [3]. These obstacles could directly reduce the number of photo-generated hydroxyl or superoxide radicals, and consequently decline the degradation rate of AR 88 [27]. According to Ameta et al. [28], an excessive catalyst loading may trigger to the collision among catalyst particles, and induce a further impact on the deactivation of catalyst. Hence, a lower collision rate between the catalyst with the dyes pollutants would retard the overall photocatalytic process. This finding suggested a good balance between the catalyst loading with the tested pollutants should be well optimized for a better performance.

#### 3.3.2. Effect of initial concentration and irradiation time

The variation of AR 88 removal as a function of initial concentration and irradiation time, under the optimized experimental conditions is depicted in Fig. 10. In the present work, increasing the initial concentration of AR 88 from 100 mg/L to 500 mg/L showed a rising irradiation time from 8 min to 105 min for the complete degradation of dye pollutant. Similar observation has been reported for the photodegradation of AR 88 over the TiO\(_2\)-SiO\(_2\) derived nanocomposite by Balachandran et al. [29]. The findings could be ascribed to the saturation of surface active sites and ineffective action of hydroxyl radicals, as additional dye molecules were adsorbed.
onto the surface of the photocatalysts at the higher initial concentrations with the constant catalyst loading [30]. Similarly, the rising concentration would lead to a collision, or blockage of the overloaded adsorbed dye molecules, and longer contact and irradiation time is required to accomplish the successive degradation of these dye molecules. The finding was in agreement with the research outputs concluded by Gao et al. [19] on the adsorption–photocatalytic degradation of AR 88 by activated carbon supported TiO$_2$.

Meanwhile, according to Ahmed et al. [30], the generated intermediate products from the photocatalytic process might diffuse slowly to the catalyst surface, and deactivate the surface binding sites when the pollutants were overloaded. Similarly, a higher initial concentration would enhance the opacity of the solution, to induce a light scattering effect, that subsequently reduced the light utilization and the photocatalytic activity of the photocatalyst, owing to the lesser photons activation limit, and formation of reactive species radicals throughout the photodegradation process. At this stage, the photolysis of dye molecules rather than the photocatalysis of dye molecules might take place [31]. As a result, the removal rate of AR 88 would be rapidly retarded as the initial concentration increased.

3.3.3. Effect of solution pH
Solution pH is the key factor affecting the degradation reaction by the generation of hydroxyl radicals, catalyst surface properties, surface charge, ionization and the adsorption ability of the dye molecules. The degradation efficacy of AR 88 with the changing solution pH from 2 to 12 is presented in Fig. 11. The photocatalytic efficacy was decreased remarkably from 98% to 20% with an increase of solution pH from 2 to 12. Higher degradation efficiency was attained at pH 2 to 4, as similar to the observation reported by Song et al. [32]. The effect of solution pH on the photodegradation process could be explained by the acid–base property of the dye molecules, in term of pKa value [33]. At the solution pH lower than the pKa value of AR 88 (10.7), the dye molecules would predominant in the molecular state, with a hydrophobic behavior, which they are readily to be degraded by the hydroxyl radicals, due to the higher accessibility to the solid-water interface. In the basic medium, the dye molecules would undergo ionization by the hydrogen loss from the protonated sites, and turned hydrophilic in the bulk solution [34]. The condition of this bulk solution may reduce the concentration of hydroxyl radicals, and further retard the degradation efficiency of AR 88.

The changing degradation rate with the rising solution pH could also be explained according to the theory of point of zero charge (pH$_{pzc}$) of the photocatalysts. The point of zero charge (pH$_{pzc}$) of the newly prepared CuO/DSA derived nanocomposite was identified to be 4.5. Hence, at the acidic condition (pH < pH$_{pzc}$), a higher formation of H$^+$ radicals would protonate the surface of the photocatalytic nanocomposites, to enhance the electrostatic attraction between AR 88 with the protonated nanocomposites, which favoring the adsorption of the negatively charged AR 88. This phenomenon resulted in a higher degradation efficacy of AR 88, as reported by Saharan et al. [34]. Conversely, as the solution pH increased beyond 4.5 (>pH$_{pzc}$), the functional groups of the nanocomposites turned less protonated, and unfavorable to the uptake of anionic AR 88, mainly ascribed to the formation of electrostatic repulsive force. Consequently, a lower removal efficacy of AR 88 was observed in the basic medium.

4. Kinetic analysis
Kinetic analysis provides an invaluable insight into the controlling mechanism of the degradation process, which in turn governs mass transfer and the residence time. A kinetic plot of ln (C$_0$/C) versus irradiation time (t), with respect to different initial concentrations of AR88 is displayed in Fig. 12. From Fig. 12, the linear relationship of the stimulation curve, with the determination coefficient, R$^2$ greater than 0.97 for all of the tested concentrations, ascertained the great configuration to the first order kinetics model. The kinetic parameters, in terms
of apparent rate constant, \( K_{\text{app}} \) (min\(^{-1}\)), yielded from the slope of the plots, together with the determination of coefficient, \( R^2 \) for the photodegradation process are given in Table 2. From the presented findings, the kinetic rate constants for the degradation reactions revealed a decreasing \( K_{\text{app}} \) from 0.841 min\(^{-1}\) to 0.094 min\(^{-1}\), as the initial concentration of dye increased from 100 mg/L to 500 mg/L. The obtained results illustrated a proportional relationship between the kinetic rate constant with the changing initial dye concentration.

Accordingly, this degradation process appeared to be driven primarily by the lower kinetic order. By following the first-order kinetics, it could be suggested that the photocatalytic degradation of AR 88 was more inclined towards physisorption, which involved intermolecular forces between the catalyst with AR 88, and the diffusion of photogenerated hydroxyl radicals were inferred to be the major rate-limiting factors in the photocatalytic system, specifically at the higher initial concentrations of dye pollutants [35]. With the aforementioned statement, a similar conclusion has been drawn by Dimitrakopoulos et al. [36] in the activity evaluation of TiO\(_2\) for the photocatalytic treatment of amoxicillin, who indicated the transition from the kinetic controlled reaction at the lower solute concentration to mass transfer controlled at the higher solute concentrations. Few recent studies pertaining to the photocatalytic performance of different photocatalyst for the decolourization of AR 88 are summarized in Table 3 [19,31,37,38]. As a comparison, the CuO/DSA derived nanocomposite prepared in this work showed a comparable and higher photocatalytic degradation efficacy for the complete mineralization of AR 88, even at the higher initial concentration of 100 mg/L.

### 5. Stability test

Photochemical stability is an essential key issue concerning the cost-effectiveness and long-term photocatalytic application of the nanocatalysts. The reusability of the newly-synthesized bio-ash supported nanocomposites was accessed by performing five sequential cyclic experiments by using AR 88, under the optimized experimental conditions, as depicted in Fig. 13. From the figure, it could be clearly revealed that the nanocomposite could retain a relatively high photocatalytic activity, with the removal efficacy for AR 88 of exceeding 95% even after five successive cycles. An inconspicuous decrease of the removal efficiency suggested that the present nanocomposite demonstrated excellent and stable photocatalytic activity. This result can be attributed to the fact that the structural integrity of the heterostructure of nanocomposite was well maintained, and it was not easily photo corroded and deactivated against the photodegradation process [39]. It could be deduced that DSA could serve as the adsorptive support to anchor or immobilize the dispersion of CuO onto the adsorbent surface, to protect against the destruction of the surface binding catalytic sites. This hybrid adsorptive and degradation surface active sites have contributed to both adsorptive force and the generation of photoinduced reactive species for the effective photodegradation reaction [40]. However, further recovery resulted in a slight decrease of the photocatalytic activity, mainly related to the changes in the mesoporous–microporous structures, or blockage of the surface binding active sites of this nanocomposite, and the possible leaching of the surface fragment of the catalyst after several successive adsorption and photocatalytic reactions.

Table 4 provides a comparison of the photocatalytic performance of different regenerated photocatalysts for the decolourization of different dye pollutants. The CuO/DSA derived nanocomposite synthesized in this work showed a

### Table 2 – The apparent kinetic rate constants for the photodegradation of AR 88 at different initial concentrations.

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>( K_{\text{app}} ) (min(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.841</td>
<td>0.995</td>
</tr>
<tr>
<td>200</td>
<td>0.300</td>
<td>0.977</td>
</tr>
<tr>
<td>300</td>
<td>0.143</td>
<td>0.984</td>
</tr>
<tr>
<td>400</td>
<td>0.108</td>
<td>0.992</td>
</tr>
<tr>
<td>500</td>
<td>0.094</td>
<td>0.997</td>
</tr>
</tbody>
</table>

### Table 3 – A comparison of the photocatalytic performance of different photocatalysts for the degradation of AR 88.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Initial concentration (mg/L)</th>
<th>Irradiation time (min)</th>
<th>Removal (%)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>CuO/DSA nanocomposite</td>
<td>100</td>
<td>8</td>
<td>100</td>
<td>Present study</td>
</tr>
<tr>
<td>ZnO/biosilica nanocomposite</td>
<td>20</td>
<td>30</td>
<td>96</td>
<td>[31]</td>
</tr>
<tr>
<td>TiO(_2)/Activated carbon-Darco-G60</td>
<td>40</td>
<td>180</td>
<td>93</td>
<td>[19]</td>
</tr>
<tr>
<td>Ni–TiO(_2)</td>
<td>50</td>
<td>35</td>
<td>97</td>
<td>[37]</td>
</tr>
<tr>
<td>TiO(_2) on glass plate</td>
<td>20</td>
<td>90</td>
<td>93</td>
<td>[38]</td>
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</tbody>
</table>
comparable excellent reusability potential to maintain the degradation efficiency at above 95% even after the fifth regeneration cycles, at the initial concentration of 100 mg/L. The result justified the great photostability of the newly prepared photocatalyst, with high capability to extend the lifespan for the photocatalytic degradation of different organic water pollutants.

6. Conclusion

A novel CuO/DSA derived nanocomposite has been successfully prepared using a simple one step hydrothermal synthesis method. This newly prepared CuO/DSA derived nanocomposite demonstrated a synergistic function of adsorption and photodegradation, with the enhanced photocatalytic performance for the complete removal of AR 88 from a lower concentration of 100 mg/L to the higher concentration of 500 mg/L, within a short duration of 8 to 105 min. Morphological evaluation verified structural transformation, supported by the BET surface area and total pore volume of 36.41 m²/g and 0.108 cm³/g. Stability analysis revealed the great photostability of the nanocomposite, even after five regeneration cycles. This study suggested an alternative pathway of Durio zibethinus shell derived ash as a renewable resource for preparation of high quality photocatalyst for the decontamination of water pollutants.

Conflicts of interest

The author declares no conflicts of interest.

Uncited References

[36,40].

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.10.042.

References


