

Development of the N-Doped Cu-Carbon Composite as a Novel Catalyst for the Removal Reactive Black 5

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How to cite this paper: Ara, N.J., Rahman, M.F., Hasan, Z., Islam, M.S. and Rahman, M.M. (2020) Development of the N-Doped Cu-Carbon Composite as a Novel Catalyst for the Removal Reactive Black 5. *Open Journal of Applied Sciences*, 10, 432-443.
<https://doi.org/10.4236/ojapps.2020.107030>

Received: February 3, 2020

Accepted: July 14, 2020

Published: July 17, 2020

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Abstract

In this study, two Cu-based catalysts with and without N doped carbon matrix, named N-Cu/CuO/C and Cu/CuO were synthesized via calcination of melamine-copper acetate complex and copper acetate at 500 °C under an inert atmosphere. The catalysts were characterized by X-ray powder diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), and CHNS elemental analyzer. The catalytic activity of both catalysts was evaluated through the NaBH₄ associated reduction of commercial textile dye named reactive black 5 (RB5). The kinetics of the reduction of reactive black 5 was also described by the pseudo-first-order kinetic equation. For the studied reduction, N-Cu/CuO/C exhibited enhanced catalytic activity both in conversion and kinetics (97% conv. in 315 sec) compared to that of by Cu/CuO/C (25% conv. in 1500 sec). Besides, N-Cu/CuO/C also demonstrated good reusability up to four consecutive cycles.

Keywords

Catalytic Reduction, Reactive Black 5, Non-Noble Metal Carbon Composites, Calcinations

1. Introduction

A huge amount of wastewaters having various synthetic dyes are generated worldwide because of their widespread use in the industry [1]. Every year approximately 8×10^5 tons of around 100,000 commercially available dyes are manufactured worldwide, which are widely used in various industries such as textile,

pharmaceutical, cosmetics, food, and so on [2]. Among various commercial dyes, azo dyes are widely used dyes that cover around 70% of the world dye production [3]. Around 70% of the aqueous wastes generated from textile industries are due to the use of azo dyes [4]. These textile waste water (concentrations between 10% - 15% w/v) should be discharged into different natural aquifers after proper treatment, however, many of the industries especially in third world country regularly discharge such wastewater without proper treatment [5].

Reactive Black 5 (RB5) is one of the most widely used azo dyes due to its high chemical stability along with enhanced water solubility [6] [7]. RB5 is a common reactive dye generally used to dye wool, nylon, cotton, and other cellulosic fiber [7]. In most cases, dyes do not completely fix the fabric which resulted in the generation of toxic aqueous waste [6]. These azo dyes are toxic and carcinogenic as a consequence, the wastewater with synthetic dyes can induce severe adverse effects such as carcinogenesis, mutagenesis in humans [8]. Moreover, the existence of a very small amount of dye in the water can alter the water transparency due to their high visibility that might adversely affect the aquatic life by sunlight to pass through the water [9].

At these circumstances, it is essential to develop methods and materials to remove these coloring contaminants from the aqueous media. So far, various methods have been applied to remove RB5 from water such as photo-catalytic degradation [10], Fenton/Fenton-like processes [11], biological treatments [12], electrochemical processes [13], electro-oxidation [14], ozonation [15], UV/H₂O₂ oxidation [16], etc. Nevertheless, many of these techniques suffer from several shortcomings such as extended operation time, lower efficiency, and high cost. To overcome such shortcomings, researchers have focused on the development of new methods. Recently, such as NaBH₄ assisted reductive decolorization using metal-based catalysts have drawn a great deal of attention [17]. In this method, so far, mostly noble metals based catalysts such as Au, Pd, Pt etc. have been widely used [17]. However, to reduce the cost, attempts to develop non-noble based catalysts such as Cu [18], Co [19], and Ni [20] were also encountered. Moreover, the catalytic activity of metals found to enhanced significantly when these metals were embedded in the N doped carbon matrix [21]. The presence of N atoms may enhance the electron density in the carbon architecture, which eventually improves the electrical properties as well as surface reactivity [21] [22] [23].

In this study, a novel approach to prepare N doped copper carbon catalyst is investigated utilizing low-cost and readily available chemicals, copper acetate monohydrate, and melamine via heat treatment under an inert atmosphere. The catalytic performance of prepared catalysts was evaluated by the NaBH₄ assisted catalytic reduction of RB5.

2. Experimental

2.1. Materials

All reagents and solvents are commercially available and were used without fur-

ther purification. Copper (II) acetate monohydrate ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$, >98%), melamine ($\text{C}_3\text{H}_6\text{N}_6$, >98%) were purchased from Sigma Aldrich. Sodium borohydride (NaBH_4 , extra pure), methanol (CH_3OH , 99.5%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.9%) were purchased from Daejung chemical, South Korea. The dye, reactive black 5 ($\text{C}_{26}\text{H}_{21}\text{N}_5\text{Na}_4\text{O}_{19}\text{S}_6$) was supplied by Dye Star Ltd., Dhaka, Bangladesh.

2.2. Synthesis Cu-Mel Composites

25 ml water and 5.0 g of melamine were taken in a 200 ml round bottom flask and the solution are sonicated for 10 min at room temperature. The sonication resulted in the formation of white suspension where 1 mmol Copper (II) acetate monohydrate was added. The reaction mixture was further stirred using a magnetic hotplate stirrer at 100°C under reflux condition for 3 h. After that, the solids were filtered and kept in a conventional drying oven at 105°C for 12 h. After drying, the collected samples were stored for further heat treatment. The sample in this stage is denoted as Cu-Mel composites.

2.3. Synthesis of N-Doped Cu/CuO₂/Carbon Composites

1.0 g prepared Cu-Mel composites were taken in high temperature alumina crucible (14 H * 18 * 75 L mm), which as placed in a tubular furnace. A 700 mm long alumina tube with 40 mm outer diameter was used as a tubular reactor. The Cu-Mel composites were heated at 500°C under an inert atmosphere. The heating was set to $5^\circ\text{C}/\text{min}$ and the temperature was monitored using a K-type thermocouple. The inert atmosphere was maintained using a constant flow of N_2 gas at a rate of 30 mL/min throughout the reaction. After the reaction, when the temperature went down to room temperature, the black powder samples were collected, washed several times with methanol-water mixture and stored for next use in closed 20 mL vial. The synthesized composites were donated as N-doped Cu/CuO₂/Carbon (N-Cu/CuO/C) composites. A similar method was adopted for calcination of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ and the obtained black powder was named as Cu/CuO composites.

2.4. Characterization

X-ray powder diffraction (XRD) analysis was conducted with the Rigaku DMax-2500 diffract meter using $\text{CuK}\alpha$ radiation. The morphologies and composition of the samples were examined with a field emission scanning electron microscopy (FE-SEM, JEOL-JSM7401F). An elemental analyzer (Thermo Fisher, Flash-2000) equipped with a TCD detector was used to measure the nitrogen content of the catalysts.

2.5. Reduction of Reactive Black 5 (RB5)

The catalytic reduction of RB5 was carried out in a standard quartz cuvette with 1 cm path length in the presence of an excess amount of NaBH_4 at room temperature, and the progress of the reduction was monitored using a UV-vis spec-

troscopy (Shimadzu-1800). A 10 mg/mL aqueous dispersion of N-Cu/CuO/C was prepared to use as a catalyst. First, 0.2 mL of 80 ppm RB5 mixed with 2.5 mL DI water, and then, 0.2 mL of varying concentrations of the freshly prepared NaBH_4 solution was added to the cuvette. After that, 100 μL of the prepared dispersion was added to the cuvette, and the solution was quickly introduced to UV-vis measurements. The absorbance of the solutions was measured at different intervals within the scanning range of 400 - 750 nm. The kinetics data of RB5 reduction were obtained by monitoring the absorbance at 598 nm.

3. Results and Discussion

3.1. Characterization of the Composites

Figure 1 presents the XRD pattern of the composites prepared from Cu-melamine and copper acetate monohydrate, respectively. After calcination at 500°C , both of the precursors resulted in the formation of composites having metallic Cu and cubic CuO phases.

Both of the composites, N-Cu/CuO/C and Cu/CuO, exhibited three peaks evolved at 43.3° , 50.3° and 74.1° , which might be ascribed to the (111), (200) and (220) planes of metallic copper (JCPDS No: 4-0836), respectively [24] [25]. On the other hand, peaks exist at 38.9° and 66° might be attributed to the (111) and (31-1) phase of the monoclinic CuO phase (JCPDS card No. 48-1548) [26]. No diffraction peaks of any Cu_2O phases were observed in the diffraction pattern of both composites.

SEM images of the prepared composites were used for the further illustration of the morphology of N-Cu/CuO/C and Cu/CuO/C composites. As depicted in **Figure 2(a)**, the Cu/CuO/C seemed to be many aggregated particles comprising of a great amount of irregular small crystals. This agglomeration might be due to the high-temperature calcination of the solid precursors. However, agglomeration was more prone in N-Cu/CuO/C composites as shown in **Figure 2(b)**. Besides, a little bit of layered type morphology was noticed in N-Cu/CuO/C which might be the presence of melamine in the precursor as the thermal condensation of melamine generally occurred during the heat treatment that usually resulted in the formation of the layered structure [27].

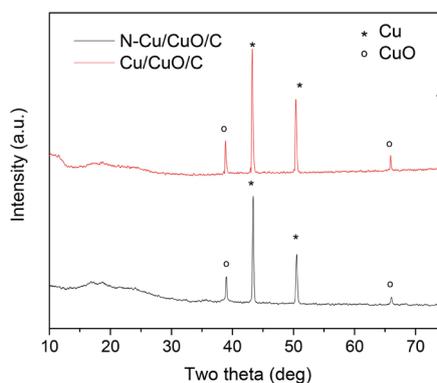


Figure 1. XRD patterns of N-Cu/CuO/C and Cu/CuO composites.

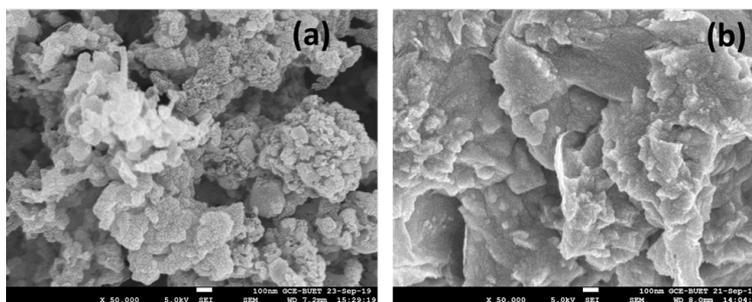


Figure 2. FE-SEM images of (a) Cu/CuO; (b) N-Cu/Cu/CuO.

In both synthesis, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ was as the source of metal or metal oxide. However, melamine has been used during the synthesis of the precursor of N-Cu/CuO/C composites, where melamine served as a source of carbon as well as nitrogen when heat treatment was conducted under inert atmosphere [28] [29] [30] [31]. The elemental analysis (CHNS) of N-Cu/CuO/C revealed the presence of 4.12% nitrogen and 5.15%, respectively.

3.2. Catalytic Reduction of RB5

Figure 3 represents the UV-vis spectra of RB5 and the change of this spectra in the presence of NaBH_4 along with/without catalyst (N-Cu/CuO/C). As seen in **Figure 3**, the pure RB 5 exhibited typical characteristic UV-absorbance peak (λ_{max}) at 598 nm. However, in presence of NaBH_4 , the position of the characteristic UV-absorbance peak did not undergo significant change, however, the absorbance reduced to 2.2 (80 ppm) to 1.9 (70 ppm) after 3600 Seconds. However, in the presence of N-Cu/CuO/C along with NaBH_4 , the concentration of RB5 reduced to 2.5 ppm.

Optimization of the concentration of NaBH_4 during catalytic reduction is an important issue as it governs total reaction efficiency. As it is observed from **Figure 3**, NaBH_4 itself could reduce the concentration of RB5 to a certain level as it could produce hydrogen via hydrolysis of NaBH_4 [22] [32]. To study the effect of concentration of NaBH_4 on the reduction of RB5, several kinetic experiments where the concentration of RB5 and catalyst amount were kept constant and the concentration of NaBH_4 was varied. It was reported earlier that the reaction kinetics of the NaBH_4 assisted catalytic reduction of organic contaminants could be well represented by pseudo first-order kinetics [22] [33] [34] [35]. As a consequence similar methods have adopted to determine the rate constant.

Figure 4 represents the time courses of RB5 reduction with the variation of the concentrations of NaBH_4 . The corresponding pseudo-first-order rate constants (k_{app}) retrieved from **Figure 4** for the reduction of RB5 using 0.2, 0.3 and 0.3 M NaBH_4 are 0.059, 0.087, and 0.087 s^{-1} , respectively. The values of k_{app} increase with an increase of concentration of NaBH_4 to 0.3 M, however, more increase of NaBH_4 concentration did not exhibit higher reduction kinetics. The higher value of RB5 reduction kinetics at higher NaBH_4 concentration up to 0.3 M might be ascribed to higher availability of BH_4^- that worked as a reductant while bonded

to the catalyst [22] [36]. In the present study, when the NaBH_4 concentration exceeded 0.3 M, the catalytic surface might be saturated and no more increase in the reduction kinetics of RB5 was witnessed. Consequently, 0.3 M NaBH_4 was taken as an optimum concentration for the present study.

Catalytic conversion of RB5 by N-Cu/CuO/C and Cu/CuO in the presence of NaBH_4 is presented in **Figure 5(a)**. When N-Cu/CuO/C catalyst was used, about 97% conversion was attained within 315 s, whereas for Cu/CuO catalyst, around 25% conversion was found after 1500 s reaction. The calculated k_{app} value of RB5 reduction by N-Cu/CuO/C was 0.058 S^{-1} which was much higher than that by Cu/CuO (0.023 S^{-1} , See **Figure 5(b)**). The enhanced catalytic activity by N-Cu/CuO/C over Cu/CuO might be due to the presence of carbon matrix as well as for the presence of N moiety which will be discussed in more detail in the next sections.

3.3. Plausible Mechanisms

As observed in **Figure 6**, at the beginning (when $t = 0$), the UV-Vis Spectra of RB5 is shown with two main characteristic peaks at 597 nm and 313 nm within the visible range along with a small peak at 255 nm within the UV range which is in good agreement with the previous report [34]. The peaks at 597 nm, 312 nm, and 254 nm represent chromophoric ($-\text{N}=\text{N}-$) group, naphthalene, and benzene rings,

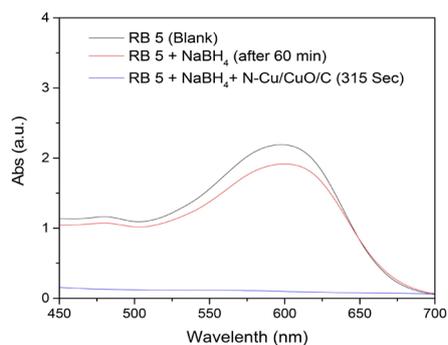


Figure 3. UV-vis spectrum of RB5 (blank); before and after the addition of NaBH_4 along with and without the catalyst.

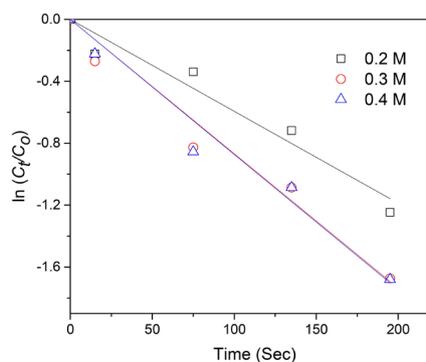


Figure 4. Effect of the concentration of NaBH_4 on catalytic reduction of RB5 by N-Cu/CuO/C catalyst.

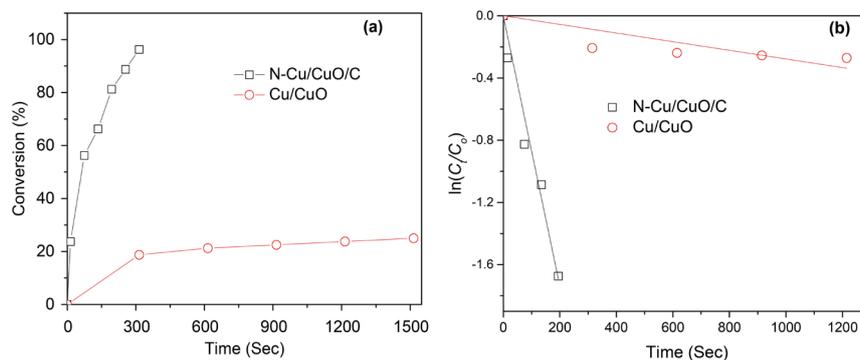


Figure 5. (a) Catalytic conversion of RB5 by N-Cu/CuO/C and Cu/CuO catalysts; (b) The relationship between $\ln(A_t/A_0)$ and reaction time (t) for the reduction of RB5 in presence of 0.2 M NaBH_4 by N-Cu/CuO/C and Cu/CuO catalysts.

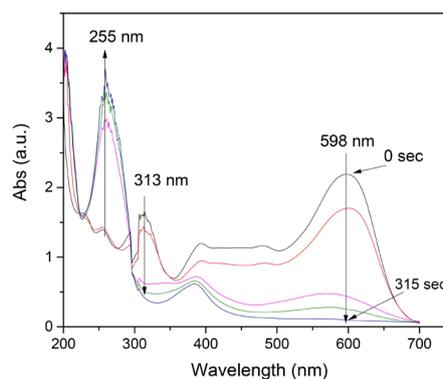


Figure 6. UV-Vis Spectra at various time points during NaBH_4 assisted catalytic reduction of RB5 by N-Cu/CuO/C.

respectively [34] [37]. In electrocatalytic reduction, Popli *et al.* demonstrated that the reductive decomposition of RB5 proceeded via cleavage of azo ($-\text{N}=\text{N}-$) bond to produce aromatic amines ($-\text{NH}_2$ groups), such as Sodium 1, 2, 7-triamino-8-hydroxynaphthalene-3,6-disulfonate and Sodium 2-[(4-aminophenyl) sulfonyl] ethyl sulphate [34]. So during the progression of the reduction, the azo bond diminished which resulted in the disappearance peak at 597 nm (corresponding to azo bond in Figure 6). Sodium borohydride is a well-known strong reducing agent (with standard redox potential $-1.24 \text{ E}^\circ/\text{V}$ at pH 14) that has been used to reducing a wide range of redox-active pollutants [18] [38]. However, due to the negative charge on BH_4^- , it exhibited inadequate applicability to the anionic substance. In aqueous media, NaBH_4 hydrolyze ($\text{NaBH}_4 + 4\text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_3\text{BO}_3 + 4\text{H}_2$) to produce H_2 that can increase the pH of the solution [32] [38]. As a consequence, the addition of NaBH_4 in RB5 might increase the pH over the pK_a value of RB5 (6.9) [39]. The higher pH of the solution (over the pK_a value of the RB5) might induce speciation which ultimately reduces the probability for the direct reduction due to the development of electronic repulsion between BH_4^- and anion part of RB5.

It was evident from the previous study that novel metals such as Ag, Pt, Pd, etc. played an important role in the enhanced reduction of different pollutants in

association with NaBH_4 [17]. Later, some non-novel metals such Co, Ni, Cu, etc. have also demonstrated similar activities. Both for the novel or non-novel metal catalyst, the reduction process seemed to follow the same mechanism [18] [22] [32]. In the first step, the accumulation of BH_4^- and binding SO_3^- groups of the dye via anchoring the two oxygens (exist in SO_3^- groups) onto surface Cu catalyst. In the next step, the electrical reaction between BH_4^- and RB5 on the catalyst surface. The surface of the synthesized might play a vital role to establish an electrical connection between BH_4^- and RB5 and consequently allowing the electrons to travel from the oxidation site to the reduction site [40]. In the case of the N-Cu/CuO/C catalyst, the active Cu or CuO sites are distributed throughout the carbon matrix that might enhance electron travel from the oxidation site to the reduction site. As a consequence, higher conversion RB5 was occurred by N-Cu/CuO/C (97%) compared to that by Cu/CuO (23%) catalyst. Additionally, different studies revealed that the presence of N doping in the carbon matrix may enhance the chemical reactivity and electronic density [21]. Consequently, the presence of these supplementary active sites resulted in the improved catalytic activity of N-Cu/CuO/C composite compared to Cu/CuO.

3.4. Reusability

In consideration of economic as well as environmental aspects, the reusability of a catalyst is an important parameter. As a result, the reusability of best-synthesized catalyst *i.e.* N-Cu/CuO/C was assessed by conducting repetitive reduction cycles. After every consecutive cycle, the samples were carefully filtered, washed with ethanol and water, and finally dried to use for the next cycle. After each run, Co-NCC was separated using a magnet and washed with ethanol for regeneration. **Figure 7(a)** demonstrated the result of RB5 by N-Cu/CuO/C. As observed in the figure, the N-Cu/CuO/C catalyst showed superb reusability, steadily keeping more than 96% conversion up to the last cycle. However, the time needed to complete each cycle increased from 315 s in the first cycle to 555 s in the fourth cycle (**Figure 7(b)**), showing a slight decrease in catalytic efficiency. This decrease in catalytic efficiency might be attributed to the leaching of a small amount of active species, along with the blocking of the active sites.

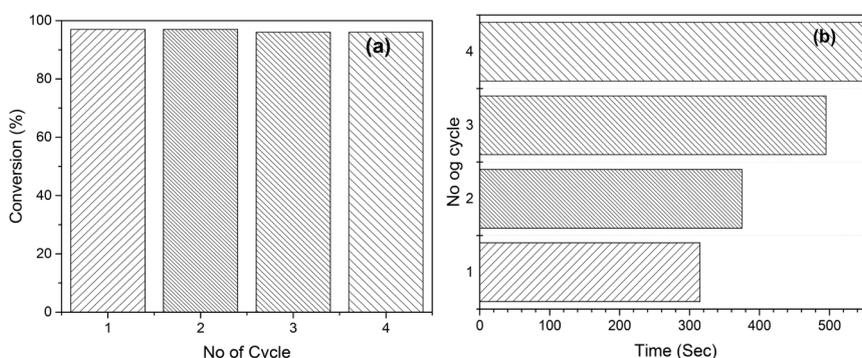


Figure 7. (a) Reusability of N-Cu/CuO/C catalyst during the reduction of RB5; (b) Time required to accomplish each complete cycle for the reduction of RB5 by N-Cu/CuO/C.

4. Conclusion

Two Cu-based catalysts were successfully synthesized and their catalytic activity was evaluated via the reduction of RB5 in the presence of NaBH₄. Between the two catalysts, N-Cu/CuO/C exhibited 97% conversion which is around 4.21 times higher than that of by compared to that of by Cu/CuO. The apparent reaction rate for RB5 reduction by N-Cu/CuO/C was 2.5 times higher than that by Cu/CuO. The greater catalytic activity of N-Cu/CuO/C probably originates from the presence of carbon matrix as well as N moiety. The carbon might boost the electron travel from oxidation to reduction site and the N moiety might work as an additional active site for the reduction. Besides, N-Cu/CuO/C also demonstrated good reusability up to four consecutive cycles.

Acknowledgements

Authors like thank the University of Textile, Bangladesh (BUTEX) for funding the project.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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