

Effects of Inorganic Anions on Methylene Blue Degradation by Heterogeneous Fenton-Like Reaction using Cobalt Doped Carbon Aerogel Catalyst

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In this study, novel cobalt-doped carbon aerogels (Co-CA) are synthesized from jackfruit core via sequential steps of hydrothermal, impregnation, and pyrolysis. The aerogels show a uniform distribution of cobalt particles on the aerogel surface without any bunching regions. The large surface area of 160 m²/g and pore diameter of 10.5 nm are determined for the Co-CA by the Brunauer-Emmett-Teller equation and Barrett-Joyner-Halenda model. The as-fabricated Co-CA exhibit an excellent methylene blue (MB) degradation efficiency via a heterogeneous Fenton-like reaction in the presence of H₂O₂ and carbonate ions. While chloride (Cl⁻) and sulfate (SO₄²⁻) ions show insignificant changes in the MB degradation efficiency, the presence of carbonate (CO₃²⁻) and phosphate (PO₄³⁻) ions causes a great impact on the MB removal efficiency with the highest value of up to 90% when CO₃²⁻ concentration is considerably low at 1 mM. Compared with the condition of only H₂O₂ in the environment, the addition of CO₃²⁻ extensively increases the rate of MB degradation by recording the time of reaching the equilibrium state in only 15 min. The dye treatment efficiency is improved over the control condition (no inorganic anions) only when the CO₃²⁻ concentration is low. At the anion concentrations of 10 mM or more, the MB degradation by Co-CA is hindered since the treatment efficiency is reduced. This study successfully develops functional Co-CA owning remarkable MB removal efficiency, indicating their great potential in dye-polluted wastewater management.

1. Introduction

Industrial production activities increasingly generate massive wastewater containing toxic contaminants such as heavy metals or organic dyes, which are harmful to the environment and human health. Even at low concentrations, the dyes can have a severe effect on the ecosystem by interfering with the transmission of light into the water, thereby harming underwater organisms (Ghaedi et al., 2015). One of the latest technologies to deal with dye-contaminated water is Fenton as well as Fenton-like reactions to induce the decomposition of H₂O₂ for the generation of strong oxidative species hydroxyl radicals ($\cdot\text{OH}$). These radicals simultaneously decompose organic pollutants like methylene blue, methyl orange, or even commercial dyes (Wang et al., 2021). Besides advantages, this technology produces by-products after promoting dye degradation, thus challenging the practical application of homogenous Fenton reaction. Although adsorption is a low-cost and simple method to remove dyes in water, the contaminants are mostly retained on the surface of the adsorbents without any decomposition. Therefore, the development of functional adsorbents owning the adsorption centers to attract dyes while promoting Fenton-like reactions to decompose the adsorbed dyes will effectively enhance the dye removal efficiency. Recently, various adsorbents like zeolites (Bencheqroun et al., 2022), graphene aerogels (Wang et al., 2021), activated carbon (Omorogie et al., 2020), etc. have been modified with transition metals to produce functionalized catalysts for heterogeneous Fenton-like process.

Towards sustainable development, biomass is commonly studied and converted into advanced materials like aerogels with super-porous structures, extremely low density, large specific surface area, and high pore volume. Taking advantage of these features, if transition metals can be distributed uniformly into the aerogel framework, the metal-doped aerogels provide an abundance of tiny spaces for the occurrence of a heterogeneous Fenton-like process to degrade MB at the contact regions. Specifically, to treat cationic dyes such as methylene blue, crystal violet, rhodamine B, etc., carbon-based aerogels are applied due to their negatively charged property. The simple and time-saving method to produce carbon aerogels from agricultural waste is pyrolysis or carbonization of biomass-based aerogels in inert gas. Therefore, to synthesize metal-doped carbon aerogels, the biomass aerogels can be immersed in transition metal salts before drying and carbonization.

When developing technology to produce high-performance materials, the selection of raw materials is one of the key factors. Among different kinds of biomass, fruit waste is a potential natural source and should be utilized to fabricate valuable goods because more than 60% of its weight is inedible with the jackfruit core accounting for about 6% (Kalse and Swami, 2022). The jackfruit waste if not treated properly can cause serious environmental problems such as water pollution, unpleasant odors, asphyxiation, and even greenhouse gas emissions. Many efforts have been made to exploit jackfruit waste into beneficial products such as carbon aerogel electrodes for desalination (Tran et al., 2022), carbon nanostructure for energy storage (Rajabathar et al., 2020), eco-friendly activated carbon (Awitdrus et al., 2022), but to the best of our knowledge, there has been no study on synthesizing metal-doped carbon aerogels from jackfruit waste for cationic dye degradation via Fenton-like process.

For the first time, jackfruit waste-derived aerogels are successfully obtained from simple hydrothermal, followed by the cobalt salt impregnation and pyrolysis in the N₂ atmosphere to create novel Co-carbon aerogels (Co-CA). The porous features of the synthesized aerogels are comprehensively investigated. For applications in dye removal, the methylene blue (MB) degradation efficiency of the Co-CA is determined in the presence of H₂O₂ and different anions, e.g. chloride, sulfate, carbonate, and phosphate. In some cases, the addition of these anions may negatively or positively affect the dye removal efficiency.

2. Material and Methods

2.1 Materials

All chemicals such as cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), hydrogen peroxide (H₂O₂, 30 %), sodium chloride (NaCl), sodium carbonate (Na₂CO₃), sodium sulfate (Na₂SO₄), sodium phosphate (Na₃PO₄) were purchased from Xilong, China. Ethanol (C₂H₅OH) in analytical grade was bought in Vietnam. Biomass waste from jackfruit was collected from the market in Ho Chi Minh City. Deionized water (DI) was used for all experiments in this study.

2.2 Fabrication of the biomass aerogel (BA)

CA was synthesized by hydrothermal methods. Firstly, the core of jackfruit waste was separated, washed with DI water three times, and cut into small pieces (about 1 x 1 x 1 cm³), then placed into a Teflon-lined stainless autoclave. After the drying oven reached 180 °C, the autoclave was placed in it and kept at this temperature for 10 h. When the time was over, the hydrogel was soaked in a solution mixture of ethanol and DI water (volume ratio is 1:1) for two days. The solution was renewed every 5 h. Finally, the hydrogel was pre-frozen at -10 °C overnight before being freeze-dried at -50 °C for 48 h to obtain biomass aerogel (BA).

2.3 Modification biomass aerogel

1,000 mg BA was soaked in 60 mL ethanol solution of Co(NO₃)₂·6H₂O (35 mmol). The mixture was placed in a water bath and the temperature was held at 50 °C in 12 h. The obtained Co-loaded biomass aerogel (Co-BA) was dried at 60 °C for 12 h and after pyrolysis at 350 °C with a heating rate of 4 °C /min and maintained for 2 h under the protection of nitrogen, the Co-carbon aerogel (Co-CA) catalysts were obtained.

2.4 Characterization

The surface morphology and compositional distribution of the specimen were observed by Scanning Electron Spectroscopy with Energy-dispersive X-ray Spectroscopy (SEM/EDX, JSM-IT200, Jeol, Japan). Samples were coated with a thin layer of Pt before analysis to enhance the imaging signal. The chemical structure of the fabricated samples was characterized by Fourier Transform Infrared (FT-IR) spectroscopy within a wavenumber of 4,000-400 cm⁻¹. The crystallographic structure of the materials was analyzed with the aid of X-ray Diffraction (XRD, D2 Phaser, Bruker, Germany) with the application of Cu-K α radiation source ($\lambda = 0.1542$ nm). The scan step and the rate of the scan step are respectively 0.02° and 0.6 °/min in the range of 5-80° (2 θ). Characteristic parameters such as specific surface area, average pore diameter, and total pore volume of the prepared aerogels are analyzed by nitrogen physisorption measurement with PMI BET Sorptometer BET-201A. In

particular, the specific surface area of the aerogels is determined by using the Brunauer-Emmett-Teller (BET) equation, while their average pore diameter and total pore volume are calculated on the Barrett-Joyner-Halenda (BJH) model.

2.5 Degradation of MB by heterogeneous Fenton-like

In the experiment, 600 mg of Co-BA was dispersed in 200 mL of solution containing MB (50 mg/L) under mechanical stirring (100 rpm). The amount of H₂O₂ (30 %) added for all experiments was 20 mL and the anion concentration (Cl⁻, SO₄²⁻, CO₃²⁻, PO₄³⁻) was varied from 1 to 100 mM. The MB concentrations at desired time intervals were measured using a UV – Vis spectrophotometer at wavelength 640 nm. The MB removal efficiency (%) was calculated using the following equation:

$$H = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C₀ is the inlet concentration (mg/L) and C_t is the concentration (mg/L) of MB at any time t.

3. Results and discussion

3.1 The physicochemical properties of the material

Figure 1a displays the porous structure of Co-BA after the hydrothermal and freeze-drying process. The network of Co-BA contains numerous voids among the lignocellulosic matrix of jackfruit waste. At higher magnification, it can be seen that cobalt particles are randomly distributed on the surface of the aerogel (Figure 1b). In contrast, the lignocellulosic fiber bundles of Co-BA disappear and transform into crystalline arrays because of the hemicellulose and cellulose decomposition (Figure 1c). However, the distribution of cobalt particles is observed on the surface of Co-CA (Figure 1d), indicating that the carbonization still retains the metal particles in the aerogel network. Figure 1e obtained from EDX analysis shows that the cobalt particles are distributed uniformly at all points on the aerogel surface without any bunching regions.

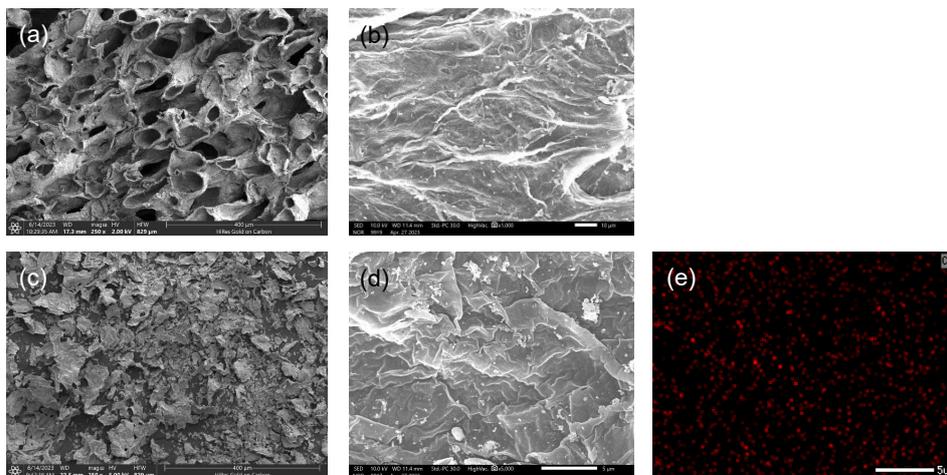


Figure 1: SEM images of (a,b) Co-BA, and (c,d) Co-CA. Co distribution map on the surface of Co-CA (e).

The spectra of BA, Co-BA, and Co-CA are shown in Figure 2a. As can be shown, the peaks in the range of 3000-3500 cm⁻¹ are witnessed in both FTIR spectra of BA and Co-BA, indicating the presence of hydroxyl groups in the biomass aerogels (Tran et al., 2022). It is noted that the peaks at 2,920 which are attributed to the -CH₂ stretching bonds are only present in the spectra of BA. After carbonization, the network of carbon aerogels is substantially formed by C-C linkages among the carbon chains, thus the signals of -OH and C-H bonds become weaker. The peaks at 1,626 cm⁻¹ can be attributed to moisture (-OH stretching) and -COO groups in both BA and Co-BA. In addition, FTIR spectra of BA and Co-BA exhibit peaks at 1,030 cm⁻¹ assigned to C-O bonds. However, these bonds (-OH, -COO, C-O) are eliminated after the carbonization of BA according to the absence of the peaks. It should be noted that the peak at 1,705 cm⁻¹ in the spectra of BA disappears, demonstrating that the strong interactions between -COO groups of BA with the Co particles, ensuring their stabilization and good dispersion in the aerogel matrix (Idrissi et al., 2020). Moreover, there are two distinct peaks at 1,560 and 1,382 cm⁻¹ only observed in the spectra of Co-CA, demonstrating the presence of polyaromatic C=C linkages and C-N bonds of aryl amines, respectively. The C=C stretching vibrations indicate the hydrophobic nature of Co-CA

while the signal of C-N bonds is due to the original chemical structure of the jackfruit core containing nitrogenous compounds like amino acids (Nagalakshmi et al., 2019).

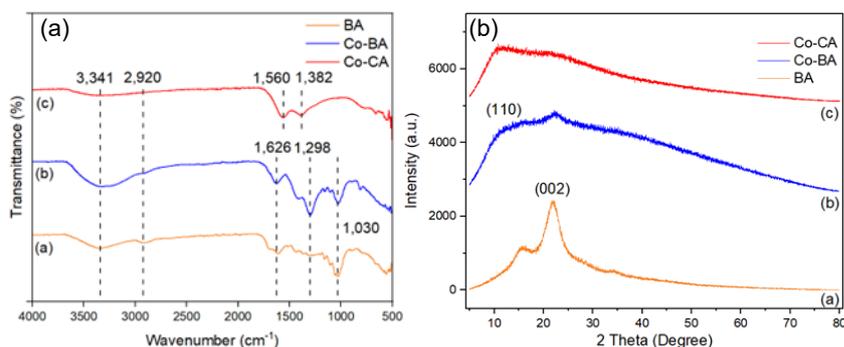


Figure 2: (a) FTIR and (b) XRD spectra of BA, Co-BA, and Co-CA.

Figure 2b illustrates the XRD spectra of fabricated aerogels in the 2θ range of $5\text{--}80^\circ$. As can be seen, the peak at 22° witnessed in the spectra of BA and Co-BA corresponds to the (002) plane structure. However, the wider peak at 22° in XRD spectra of Co-CA indicates the amorphous structure in the carbonaceous aerogels (Lee et al., 2020). After being modified with the addition of cobalt particles, both XRD spectra of Co-BA and Co-CA prominently change with no detection of cobalt diffraction peak. Geng et al. (2021) observed the same results and explained it by the high dispersion and low loading of the metals.

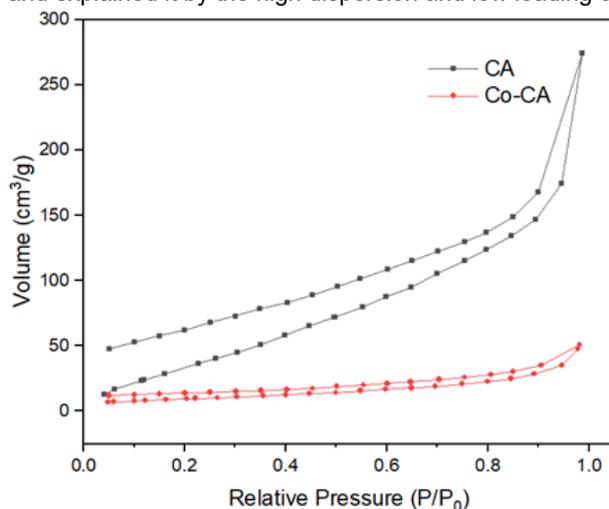


Figure 3: N_2 adsorption and desorption isotherms of carbonized biomass aerogel (CA) and Co-CA.

As seen in Figure 3, the N_2 adsorption-desorption curves of both CA and Co-CA with a hysteresis loop indicate a type IV isotherm (Zhang et al., 2012), meaning that the structure of the aerogels contains mesopores with a diameter in the range of 2-50 nm. Besides, at the low relative pressure, the two adsorption and desorption curves expand further away from each other, which may imply that the structure of Co-CA has a part of macropores as reported in the analysis of Shruthi et al. (2015) on N-doped amorphous carbon aerogels. The average pore diameter in the two aerogels is analyzed in the range of 9.2 – 10.5 nm (Table 1). The addition of cobalt particles in the aerogel matrix significantly reduce the specific surface area of the carbon aerogels from 160.4 to 34.2 m^2/g due to the metal particles blocking the voids in the aerogel porous matrix.

Table 1: Details of the structure of Co-CA and CA

	CA	Co-CA
Specific surface area (m^2/g)	160.4	34.2
Total pore volume (cm^3/g)	0.44	0.07
Average pore diameter (nm)	10.5	9.2

3.2 Effect of anion concentrations on methylene blue degradation

One of the methods to treat methylene blue (MB)-contaminated wastewater is to perform a Fenton-like reaction in the $\text{Co}^{2+}/\text{H}_2\text{O}_2$ system. To promote the reaction, anions such as chloride (Cl^-), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), and phosphate (PO_4^{3-}) are commonly added to the system for effectively generating hydroxyl radicals ($\cdot\text{OH}$) and enhancing the MB degradation efficiency. In this study, the influence of these anions has been studied in the concentration range of 1 - 100 mM.

Figures 4a and 4b show that the effects of Cl^- and SO_4^{2-} anions on the MB removal efficiency are insignificant. Without the presence of Cl^- and SO_4^{2-} , the equilibrium MB removal efficiency by Co-CA is around 88.48%. The addition of the two anions in the MB solution slightly reduces the dye removal efficiency of Co-CA by 4.82% owing to their interactions with the free radicals $\cdot\text{OH}$, producing the active species with lower oxidation abilities (Shi et al., 2022).

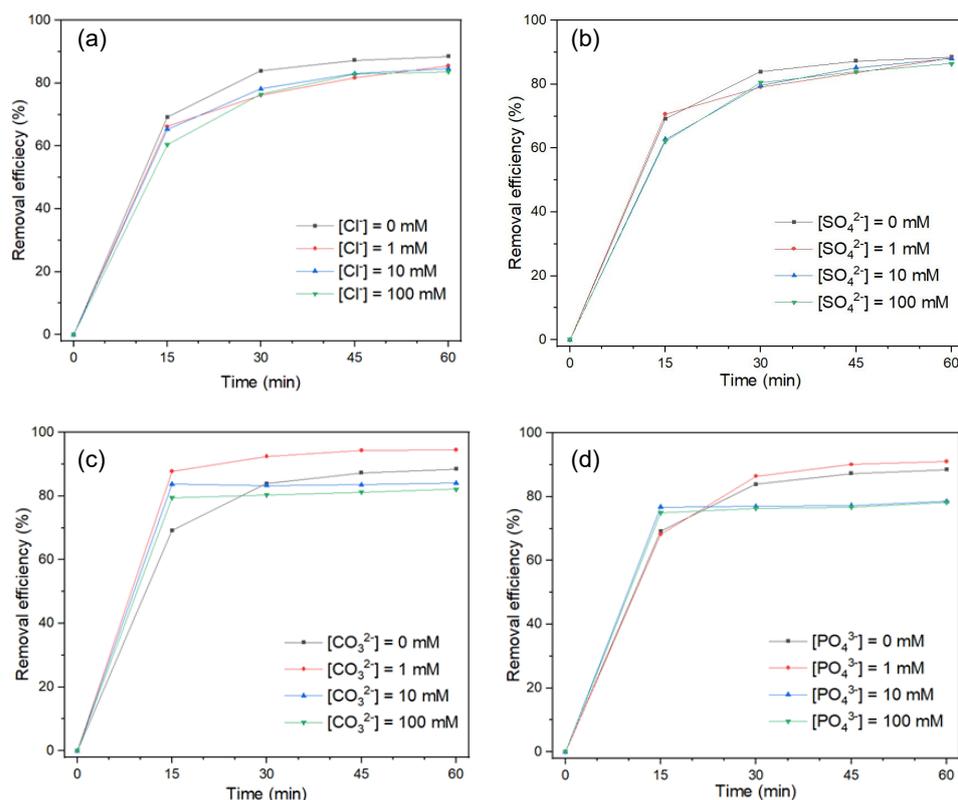


Figure 4: Effect of (a) chloride, (b) sulfate, (c) carbonate, (d) phosphate on degradation methylene blue

Unlike chloride and sulfate anions, the low concentration of carbonate CO_3^{2-} and phosphate PO_4^{3-} at 1 mM enhances the MB degradation efficiency by over 90%. Remarkably, the equilibrium state of MB degradation is reached only after 15 min at the CO_3^{2-} concentration of 1 mM, which is much faster than the experiments without the addition of carbonate ions or at higher CO_3^{2-} concentrations. The mechanism of MB degradation by Co-CA/ $\text{H}_2\text{O}_2/\text{CO}_3^{2-}$ may involve several steps including the initial complex formation of Co^{2+} and CO_3^{2-} , the MB coordination to the complex, production of free radicals ($\cdot\text{OH}$) by the reaction of H_2O_2 with the complex of Co/ CO_3^{2-} /MB, followed by the effective MB degradation by $\cdot\text{OH}$ radicals (Li et al., 2012).

Overall, the higher the anion concentration the lower the MB degradation efficiency of the Co-CA. The higher concentration of anions leads to better free radicals scavenging potency, thus inhibiting MB degradation by the activity of radicals (Xu et al., 2011). Based on the shorter time to reach the equilibrium state (15 min) and the higher MB removal efficiency, the concentration of CO_3^{2-} at 1 mM is chosen as a suitable condition to treat MB-contaminated water by Co-CA.

4. Conclusions

For the first time, cobalt-doped carbon aerogels (Co-CA) from jackfruit waste have been successfully synthesized by impregnation, followed by pyrolysis. The as-fabricated carbon aerogels exhibit a large surface

area of 160 m²/g with a uniform distribution of cobalt particles in the aerogel matrix. Remarkably, the Co-CA expresses the excellent MB degradation efficiency of over 90% in only 15 min with the addition of CO₃²⁻ at the very low concentration of 1 mM. It is also concluded that the higher anion concentrations (>10 mM) play a negative effect on the MB removal efficiency in aqueous solution. Considering all of these findings, the Co-doped carbon aerogels show great potential in the treatment of dye-contaminated water via a heterogeneous Fenton-like process.

Acknowledgment

We acknowledge Ho Chi Minh City University of Technology (HCMUT), VNU-HCM for supporting this study.

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