Research Article

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Removal of Congo red and malachite green from aqueous solution using heterogeneous Ag/ZnCo-ZIF catalyst in the presence of hydrogen peroxide

<https://doi.org/10.1515/gps-2020-0060>

received August 11, 2020; accepted September 27, 2020

Abstract: The bimetallic Zn/Co zeolitic imidazole frameworks (ZnCo-ZIFs) were successfully synthesized by a simple solvothermal method at room temperature. Silver elements were afterward doped onto the bimetallic frameworks to form Ag/ZnCo-ZIFs via a facile impregnation method in acetone solvent. The as-synthesized material was used as a heterogeneous catalyst for the removal reaction of Congo red (CR) and malachite green (MG) in the presence of hydrogen peroxide (H_2O_2). Effects of catalyst dosage, H_2O_2 concentration, initial concentration of the contaminants, reaction temperature, and reaction time were conducted in this work. The results showed that more than 94% and 98% removal of CR and MG were, respectively, achieved within 45 and 30 min. The presence of Ag also enhanced the removal efficiency of CR and MG. The main mechanism of removal reaction of the organic contaminants could be oxidation via hydroxyl radicals. Moreover, the catalytic activity of the material remained over 90% after four recycling cycles. Due to the efficient reactivity as well as high stability, Ag/ZnCo-ZIFs can be a potential heterogeneous catalyst to remove hazardous dyes from aqueous solution.

Keywords: Congo red, hydrogen peroxide, malachite green, zeolitic imidazole frameworks, ZnCo-ZIFs

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1 Introduction

Dyes currently are one of the most commonly used substances and play an important role in many different industries such as textiles, plastics, leather, paint, paper, cosmetics, and so on [1]. However, they are the major factor which causes water pollution and directly affects human health. Even with very low concentrations, dyes may cause allergenic, teratogenic, mutagenic, carcinogenic, and a series of disorders to human health such as dysfunction of the kidneys, reproductive system, liver, and central nervous system [2,3]. Moreover, these dyes normally possessing complex aromatic structures that provide optical, thermal, and physicochemical stability are nonbiodegradable compounds [4–7]. Congo red (CR) and malachite green (MG) are known as two dyes widely used in industrial applications [4]. CR is one of the most frequently used anion diazo dyes which can be metabolized to benzidine, a human carcinogen [8]. MG is typically a cationic triphenylmethane dye and acts as a liver tumor enhancing agent [9]. Besides, CR and MG also can cause many other dangers to the environment. Their chemical structures have many complex and durable aromatics which are shown in Figure 1. Therefore, several methods have been applied to treat the dyes from wastewater such as adsorption, ion exchange, Fenton oxidation, photocatalytic degradation, and advanced oxidation processes [8–14]. Although these methods are effective, they still have some disadvantages. Typically, for adsorption, some adsorbents can be costly [1] and easily lose their activity due to the adsorption of nondegradable contaminants onto active sites [15]. Meanwhile, Fenton oxidation requires low pH conditions and generates a huge iron sludge that can lead to heavy metal pollution as it cannot be removed after the treatment [16]. Hence, it is very important to find a simpler and more environmentally friendly method for removing the organic contaminants from aqueous solution.

Zeolitic imidazole frameworks (ZIFs) are a kind of porous crystalline material that is made of both inorganic and organic components, in which the transition metal

Figure 1: Chemical structures of (a) CR and (b) MR.

ions (e.g., Co^{2+} or Zn^{2+}) are linked together by imidazolate bridges (Im^-) [17,18]. With diverse properties such as large specific surface area and excellent thermal and chemical stability, ZIFs have been widely used in many application fields including adsorption, gas storage, separation, sensing, and catalysis [19–24]. In recent years, bimetallic ZnCo-ZIF materials with a combination of both Co and Zn ions in the structural framework have been paid much attention due to their outstanding characteristics compared to monometallic ZIFs (e.g., ZIF-8, ZIF-67) [25]. Hybrid ZIF materials are also attracting many scientists because of their potential applications. In particular, the combination of ZIFs and metal nanoparticles can create a new material that integrates the advantages of each individual component, such as synthesis of Pd/ZIF-8 material using a simple route with liquid impregnation and chemical reduction methods [26], synthesis of Pd@ZIF-67 for Cr reduction from high-valent ion(VI) to low-valent ion(III) with high catalytic activity and excellent cycle durability [27], and synthesis of Ag/ZIF-67 using a simple impregnation method applying for degradation reaction of methyl orange in the presence of hydrogen peroxide with excellent efficiency [28].

In this study, ZnCo-ZIFs combined with silver nanoparticles via the impregnation method in acetone solvent were applied as a heterogeneous catalyst for the removal of CR and MG from aqueous solutions in the presence of H_2O_2 .

2 Experimental

2.1 Materials

All reagents and starting materials were purchased from Sigma-Aldrich and Acros and used as received without further purification.

2.2 Synthesis of ZnCo-ZIFs

ZnCo-ZIFs were synthesized by the solvothermal method at room temperature in methanol solvent. The ratio of cobalt nitrate and zinc nitrate was fixed to 3:1 as previously reported [25]. The molar ratio of metal salts and 2-MIm was 1:8. Typically, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.873 g, 3 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.297 g, 1 mmol) were separately dissolved in methanol (10 mL). Another solution was prepared by dissolving 2-MIm (2-MIm = 2-methylimidazole; 2.6272 g, 32 mmol) in 30 mL of methanol. Subsequently, zinc nitrate was added to the cobalt nitrate under magnetic stirring for 15 min to form a homogeneous mixture. Then, the material was synthesized via slow dripping of metal salt mixture into the 2-MIm solution under magnetic stirring; a purple suspension was formed and maintained at room temperature for 24 h. Thereafter, the purple solid was collected by centrifugation (6,000 rpm, 15 min), washed with methanol (3×10 mL), and finally dried at 60°C in air to obtain the ZnCo-ZIF crystals.

2.3 Synthesis of Ag/ZnCo-ZIF catalysts

Ag/ZnCo-ZIF catalysts were prepared by the impregnation method in acetone solvent. The mass ratio of bimetallic frameworks (ZnCo-ZIFs) to silver nitrate (AgNO_3) was 4:1. Typically, 62.5 mg of AgNO_3 was dissolved in 30 mL of acetone, then 250 mg of ZnCo-ZIFs was added into the solution under magnetic stirring for 1 h at 56°C . Subsequently, 0.25 mL of formic acid (HCOOH) was slowly added into the mixture with magnetic stirring, resulting in the formation of the dark solid. The product was separated through centrifugation, washed with acetone several times, and dried at 60°C for 8 h to obtain the Ag/ZnCo-ZIFs.

2.4 Catalyst experiments

Two typical dyes, namely CR and MG, were chosen for testing the catalytic activity of Ag/ZnCo-ZIFs. In each experiment, different catalyst dosages of Ag/ZnCo-ZIF material and H_2O_2 concentrations were added into 10 mL of dye solution at various initial dye concentrations, reaction temperatures, and reaction times. The concentration of the residual dye solution was analyzed by a UV-Vis spectrophotometer at 497 nm for CR and 617 nm for MG.

The removal efficiency of CR and MG was defined as follows:

$$\text{Removal efficiency} = \left(1 - \frac{C_e}{C_0}\right) \times 100\%, \quad (1)$$

where C_0 is the initial concentration (mg L^{-1}) and C_e is the residual dye concentration (mg L^{-1}).

For testing the reusability of Ag/ZnCo-ZIFs in removal of CR and MG, the experiments were repeatedly conducted. The optimal catalyst dosages of Ag/ZnCo-ZIF material and H_2O_2 concentrations were added into 10 mL of dye solution under optimal conditions of initial dye concentration, reaction temperature, and reaction time. After the reaction time, the materials were taken out of the solution by filtering, then washed several times with acetone, while the concentration of the residual dye solution was analyzed by a UV-Vis spectrophotometer at 497 nm for CR and 617 nm for MG.

3 Results and discussion

The ZnCo-ZIFs and Ag/ZnCo-ZIFs were analyzed by several characterization techniques, including PXRD, SEM, EDX, FT-IR, and TGA (Figures A1–A5). The results showed the successful combination of Ag with ZnCo-ZIF bimetallic framework. The catalytic activity of Ag/ZnCo-ZIFs was demonstrated for CR and MG in the presence of hydrogen peroxide.

3.1 Catalyst activity of Ag/ZnCo-ZIFs to CR and MG

The Ag/ZnCo-ZIFs' dosage is an important parameter because it has a catalytic role in producing 'OH radical — a reducing agent for the removal reaction of CR and MG. To study the role of Ag/ZnCo-ZIFs in the removal of both contaminants, a series of experiments were conducted with different catalyst dosages from 0 to 200 mg L^{-1} . The results are shown in Table 1. It can be seen that removal yield increased with increasing Ag/ZnCo-ZIFs' dosage. This trend can be observed in MG removal compared to CR removal. In fact, without catalyst, both CR and MG were removed from aqueous solution at low yields, 7.1% and 39.7%, respectively. When catalyst dosage increased to 50 mg L^{-1} , the removal yield significantly increased to 88.6% for CR and 91.8% for MG. The removal yield continuously increased and then slightly decreased as the catalyst dosage increased from 50 to 200 mg L^{-1} . The highest yield could be achieved at 92.0%

Table 1: Effects of catalyst dose on the removal efficiency of CR and MG

Catalyst dosage (mg L^{-1})	Removal efficiency (%)	
	CR ^a	MG ^b
0	7.1	37.4
50	88.6	91.8
100	90.6	99.1
150	92.0	96.8
200	91.4	96.5

^a pH 7.1, $[\text{H}_2\text{O}_2] = 0.025 \text{ mol L}^{-1}$, initial $[\text{CR}] = 30 \text{ mg L}^{-1}$, temperature = 30°C, time = 30 min. ^b pH 6.0, $[\text{H}_2\text{O}_2] = 0.05 \text{ mol L}^{-1}$, initial $[\text{MG}] = 30 \text{ mg L}^{-1}$, temperature = 30°C, time = 30 min.

for CR and 99.1% for MG as the catalyst dosage was, respectively, 150 and 100 mg L^{-1} . If further the dosage is increased, the removal efficiency faintly decreased. The reason would be aggregation of particles, which led to decrease in surface area of the catalyst. The above observation showed the essential role of catalyst in the removal process of CR and MG. The reason could be that the active Ag sites accelerated the decomposition of H_2O_2 to lead to an increase in the number of 'OH radicals. This radical can be attributed to crack down the structure of both contaminants. To maintain high removal efficiency and facilitate the reusable performance, in the following experiments Ag/ZnCo-ZIFs' dosage was chosen to be 150 mg L^{-1} for CR and 100 mg L^{-1} for MG.

Another important parameter that could not be ignored in this study is the concentration of hydrogen peroxide because it is directly related to the number of hydroxyl radicals generated during the treatment process. To study the effect of H_2O_2 concentration on the CR and MG removal efficiency, the variation of H_2O_2 concentration was conducted from 0 to 0.2 mol L^{-1} , and the results are shown in Figure 2. In the absence of H_2O_2 , the removal efficiencies of both CR and MG were achieved at high levels, 91.7 and 78.1%, respectively. This may be caused by the inherent adsorption properties of ZnCo-ZIFs, which are famous for their high surface area. However, the main purpose of this study is to decompose organic dyes into less toxic molecules, thus adsorption is an undesirable result. Therefore, H_2O_2 was added before the adsorption process took place. As can be seen from Figure 2, in general, the higher the H_2O_2 concentration added, the higher the removal efficiency achieved. In fact, when the concentration of H_2O_2 varied from 0.025 to 0.10 mol L^{-1} , the removal efficiency increased from 92.0 to 96.8% for CR and from 93.4 to 96.5% for MG. However, when the H_2O_2 concentration was greater than 0.1 mol L^{-1} , the removal of CR slightly reduced to 91.9% at 0.15 mol L^{-1} and

Figure 2: Effect of H₂O₂ concentration on the removal efficiency. CR: pH 7.1, catalyst dosage = 150 mg L⁻¹, initial [CR] = 30 mg L⁻¹, temperature = 30°C, time = 30 min. MG: pH 6.0, catalyst dosage = 100 mg L⁻¹, initial [MG] = 30 mg L⁻¹, temperature = 30°C, time = 30 min.

Figure 3: Effect of initial concentration on the removal efficiency. CR: pH 7.1, catalyst dosage = 150 mg L⁻¹, [H₂O₂] = 0.05 mol L⁻¹, temperature = 30°C, time = 30 min. MG: pH 6.0, catalyst dosage = 100 mg L⁻¹, [H₂O₂] = 0.05 mol L⁻¹, temperature = 30°C, time = 30 min.

dropped down to 72.3% at 0.20 mol H₂O₂ L⁻¹. In the meantime, the removal of MG was maintained unchanged as the concentration of H₂O₂ increased to 0.15 mol L⁻¹ and slightly decreased by 1.3% as H₂O₂ concentration continuously increased to 0.20 mol L⁻¹. This falling tendency may be attributed to the nonselective of hydroxyl radicals as Eq. 2 and 3:

This radical can attack H₂O₂ or even themselves instead of organic dyes. Hence, the addition of a higher concentration of H₂O₂ did not improve the removal efficiency. Therefore, the optimum H₂O₂ concentration was found to be 0.05 mol L⁻¹ for further experiments of both CR and MG.

The organic concentration of wastewater is not fixed and so the effect of initial CR concentration is conducted. The results are depicted in Figure 3 with an initial concentration in a range of 10–50 mg L⁻¹. As can be seen from Figure 3, while removal of MG was maintained unchanged at about 98% in the range of 10–30 mg MG L⁻¹ and slightly reduced to 94.6 and 93.5% at 40 mg MG L⁻¹ and 50 mg MG L⁻¹, respectively, removal of CR presented a slight decrease from 96.9% to 94.9% as the initial concentration of CR varied from 10 to 30 mg L⁻¹ and dropped down to 81.1% at 40 mg CR L⁻¹ and 54.5% at 50 mg CR L⁻¹. The reason could be that at high concentrations, the dye molecules covered the silver sites of the catalyst, and this cover reduced catalytic activity of the material. Thus, the process of generating hydroxyl radicals was hindered.

Although tendencies of CR and MG concentration change are all falling, they are different, which are slightly reduced for MG but sharply reduced for CR. In other words, MG is easy to be removed by hydroxyl radicals, while CR is tough. The reason could be that the structure of CR is a longer chain of benzyl groups compared to the structure of MG, which are presented in Figure 1. Finally, an initial concentration of 30 mg L⁻¹ was chosen to conduct the next experiments.

Temperature is an enforce factor for oxidation reaction; hence, its effects on the removal efficiency were investigated and shown in Table 2. As can be seen from Table 2, the reaction temperature did not show a strong influence on the removal efficiency, except for the temperature of 20°C. In point of fact, removal efficiency of CR increased by 15.3% when reaction temperature increased from 20°C to 30°C. Meanwhile, removal efficiency of MG increased by 43.65% when reaction temperature increased at the same level. From 30°C to 60°C, removal efficiency of both CR and MG fluctuated around 92% for CR and 98% for MG. In other words, reaction temperature showed an insignificant influence on the removal efficiency. This is because high temperature accelerated the reaction rate between hydrogen peroxide and Ag; this thus increased the generation rate of hydroxyl radicals and generated more competition in reaction. Therefore, the removal efficiency increased as the number of hydroxyl radicals increased; however, it became insignificant as hydroxyl radicals were overwhelming due to their self-interaction. For simplicity, convenience, and efficiency, the temperature of 30°C was selected as the optimal temperature for further studies.

Table 2: Effects of temperature on the removal efficiency of CR and MG

Temperature (°C)	Removal efficiency (%)	
	CR ^a	MG ^b
20	78.6	54.4
30	93.9	98.0
40	92.5	97.6
50	92.9	99.0
60	92.5	98.9

^a pH 7.1, $[H_2O_2] = 0.05 \text{ mol L}^{-1}$, initial $[CR] = 30 \text{ mg L}^{-1}$, catalyst dosage = 150 mg L^{-1} , time = 30 min. ^b pH 6.0, $[H_2O_2] = 0.05 \text{ mol L}^{-1}$, initial $[MG] = 30 \text{ mg L}^{-1}$, catalyst dosage = 100 mg L^{-1} , time = 30 min.

Kinetics of a reaction is key information; hence, reaction time is investigated as follows. To determine the effect of reaction time on removal efficiency, the experiments were conducted at reaction time in the range of 5–60 min for CR and 5–50 min for MG while maintaining pH, catalyst dosage, H_2O_2 concentration, initial CR concentration, and temperature at 7.1, 150, 0.05, 30 mg L^{-1} , and 30°C , respectively. The effect of reaction time on CR and MG removal efficiency by Ag/ZnCo-ZIF catalyst is shown in Figure 4. As can be seen in Figure 4, the time increased and the efficiency increased. For CR, the efficiency achieved 66.4% in the first 5 min and increased to 90.7, 93.2, and 95.2% after 15, 30, and 45 min, respectively. When the reaction time continued to increase to 60 min, the removal efficiency maintained around 95%, which could be the equilibrium point of the reaction.

Figure 4: Effect of reaction time on the removal efficiency. CR: pH 7.1, catalyst dosage = 150 mg L^{-1} , $[H_2O_2] = 0.05 \text{ mol L}^{-1}$, initial $[CR] = 30 \text{ mg L}^{-1}$, temperature = 30°C . MG: pH 6.0, catalyst dosage = 100 mg L^{-1} , $[H_2O_2] = 0.05 \text{ mol L}^{-1}$, initial $[MG] = 30 \text{ mg L}^{-1}$, temperature = 30°C .

Similarly, the removal efficiency of MG reached 92.6% after 10 min of reaction and slightly increased to 98.6% and 99.6% at 20 and 30 min, respectively. This value is then kept unchanged at about 99% until 60 min. Generally, removal of both CR and MG went fast and reached more than 90% after 20 min and was maintained unchanged around 95% for CR and 99% for MG after 45 min. Therefore, 45 min could be considered as the optimum reaction time.

In summary, the major agent to remove CR and MG was hydroxyl radicals which are generated by reaction of Ag/ZnCo-ZIFs and hydrogen peroxide (H_2O_2). The reaction is summarized as follows [29]:

The Ag particles here were considered as the result of reduction of $AgNO_3$ by reducing agent $HCOOH$ within ZnCo-ZIF substrate and solvent acetone. At boiling temperature of the solvent, the entropy of solution increases, and hence, the silver particles easily stick to the ZnCo-ZIF framework. The formation of Ag/ZnCo-ZIFs could be observed by the color transformation, from transparent to dark brown, which could be explained by the fact that the ZnCo-ZIFs carried Ag particles in them.

In Eq. 4, silver particles acted similar to iron in the Fenton process [30]. The hydroxyl radical is a very strong oxidizing radical which can attack and mineralize dye molecules [31]. The CR and MG removal pathways by hydrogen peroxide have been reported previously, as summarized in Figure 5.

3.2 Comparison of catalytic capacity of Ag/ZnCo-ZIFs with other catalysts

The catalytic activity of Ag/ZnCo-ZIFs was compared with some homogeneous and heterogeneous catalysts for both CR and MG removal processes. Homogeneous catalysts

included 2-MIm, cobalt nitrate salt, zinc nitrate salt, and silver nitrate, which were the initial agents to synthesis Ag/ZnCo-ZIFs (Figure 6). Some heterogeneous catalysts, such as activated carbon, ZIF-8, ZIF-67, and ZnCo-ZIFs, were also used to compare with Ag/ZnCo-ZIFs under the same conditions for each dye (Figure 7). For CR, catalyst dosage, H_2O_2 concentration, initial CR concentration, reaction temperature, reaction time, and pH were 150, 0.05, 30 mg L^{-1} , 30°C, 45 min, and 7.1, respectively. The optimal conditions of MG including H_2O_2 concentration, catalyst dosage, initial MG concentration, reaction time, reaction temperature, and pH were 0.05, 150, 30 mg L^{-1} , 45 min, 30°C, and 6.0, respectively.

As shown in Figure 6, the CR and MG removal efficiency of homogeneous catalysts were low. For CR, the efficiency of using 2-MIm, cobalt salt, zinc salt, and silver salt achieved, respectively, 8, 16, 17, and 12% after 45 min reaction. Obviously, they were much lower than the efficiency of Ag/ZnCo-ZIFs (94%). For MG, the performances of four homogeneous catalysts were approximately 37%, while Ag/ZnCo-ZIFs achieved an efficiency of more than 98%. The effect achieved when using these homogeneous catalysts can be due to the reaction conditions; under stirring speed, the salt ions can dissociate and act on dye molecules. In addition, H_2O_2 is unstable, so they can decompose into hydroxyl radicals under magnetic stirring and visible light condition according to the following equation [34]:

Figure 6: Comparison of CR and MG removal efficiency among homogeneous catalysts and Ag/ZnCo-ZIFs.

In Figure 7, the catalytic activity of Ag/ZnCo-ZIFs was compared to that of heterogeneous materials. The results showed that the CR and MG removal efficiency of using activated carbon were lowest with 14 and 30%, respectively. The efficiency of using ZIF-8, ZIF-67, and ZnCo-ZIFs achieved is relatively high. However, the catalytic efficiency of Ag/ZnCo-ZIFs was still highest in both removal processes. The ability to remove dyes of activated carbon may be due to its interaction with H_2O_2 to produce $\text{HO}^\cdot$; this process is similar to the Fenton process [35,36]:

Figure 5: Summary of the removal pathway of (a) CR and (b) MG [32,33].

Figure 7: Comparison of CR and MG removal efficiency among heterogeneous catalysts and Ag/ZnCo-ZIFs. CR: pH 7.1, catalyst dosage = 150 mg L⁻¹, [H₂O₂] = 0.05 mol L⁻¹, initial [CR] = 30 mg L⁻¹, temperature = 30°C, time = 45 min. MG: pH 6.0, catalyst dosage = 100 mg L⁻¹, [H₂O₂] = 0.05 mol L⁻¹, initial [MG] = 30 mg L⁻¹, temperature = 30°C, time = 30 min.

Metal centers, ZIF-8 and ZIF-67, are Zn²⁺ and Co²⁺, respectively. In particular, metal centers of ZnCo-ZIFs are a combination of both Zn²⁺ and Co²⁺. Previous studies have suggested that these ions are capable of activating H₂O₂, producing [•]OH by the following reaction [37]:

The hydroxyl radicals can attack the dye molecules and crack their structure. However, these metal centers of ZIFs are also the network node in the structural framework. Therefore, despite the high removal efficiency, the structure of the material may be changed after that.

3.3 Reusability of Ag/ZnCo-ZIF catalyst

Reusability is an important factor for heterogeneous catalysis. The experiments on repeating the usage of the catalyst were carried out. After removal of CR and MG, the catalysts used in the experiment were washed with acetone. The experiments were conducted four times under the optimal conditions of each dye. The results are shown in Figure 8. It was found that after four times of recycling reactions, the CR and MG removals retain a high efficiency. That is to say, the CR removal efficiency to some extent decreased from 94 to 91% and similarly for MG with a slight decrease from 98 to 93%. Hence, Ag/ZnCo-ZIFs maintained the high removal efficiency of more than 90 for both CR and MG after reusing four times.

Figure 8: The CR and MG removal efficiency after four times of reusing Ag/ZnCo-ZIFs. CR: pH 7.1, catalyst dosage = 150 mg L⁻¹, [H₂O₂] = 0.05 mol L⁻¹, initial [CR] = 30 mg L⁻¹, temperature = 30°C, time = 45 min. MG: pH 6.0, catalyst dosage = 100 mg L⁻¹, [H₂O₂] = 0.05 mol L⁻¹, initial [MG] = 30 mg L⁻¹, temperature = 30°C, time = 30 min.

4 Conclusions

In summary, Ag/ZnCo-ZIFs was successfully synthesized and used as a heterogeneous catalyst to remove CR and MG in the presence of H₂O₂. A good catalyst reactivity of Ag/ZnCo-ZIFs in the removal of CR was obtained with more than 94% at a catalyst dosage of 150 mg L⁻¹, an H₂O₂ concentration of 0.05 mol L⁻¹, an initial CR concentration of 30 mg L⁻¹, a reaction temperature of 30°C, a reaction time of 45 min, and pH 7.1. Such high reactivity of the catalyst also presented with 98% removal of MG at a catalyst dosage of 100 mg L⁻¹, an H₂O₂ concentration of 0.05 mol L⁻¹, an initial MG concentration of 30 mg L⁻¹, a reaction temperature of 30°C, a reaction time of 45 min, and pH 6.0. In addition, the as-synthesized solid catalyst maintained its high performance at least up to four times without significant degradation in catalytic activity. Finally, the Ag/ZnCo-ZIFs have high potential for effective removal of both anionic and cationic dyes from aqueous solution.

Acknowledgments: This study was funded in part by the Can Tho University Improvement Project VN14-P6, supported by a Japanese ODA loan.

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Appendix

Figure A1: Powder XRD of (a) Ag/ZnCo-ZIFs and (b) ZnCo-ZIFs.

Figure A2: SEM images of Ag/ZnCo-ZIFs at different magnification ratios: (a) 5,000×, (b) 10,000×, (c) 30,000×, and (d) ZnCo-ZIFs.

Figure A3: EDX spectra of (a) ZnCo-ZIFs and (b) Ag/ZnCo-ZIFs.

Figure A4: FT-IR spectra of 2-MIm, ZnCo-ZIFs, and Ag/ZnCo-ZIFs.

Figure A5: TGA analysis of ZnCo-ZIFs and Ag/ZnCo-ZIFs.