Effect of pH on the photo-Fenton degradation of rhodamine B by Prussian blue/g-C₃N₄

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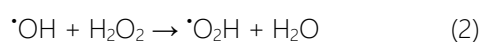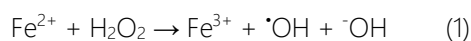
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ABSTRACT

The pH solution is one of the critical factors affecting the photo-Fenton degradation of dyes in wastewater. The photoactivity of Prussian blue/g-C₃N₄ was investigated using the photodegradation of RhB acidic, neutral, and essential medium. The results implicated that more than 98.5% removal of RhB was achieved at pH = 3.62 after irradiation for 60 minutes under visible light. The photocatalytic activity of Prussian blue/g-C₃N₄ showed the best performance in an acidic medium. This is due to the formation of hydroxyl radicals during the photocatalytic degradation of RhB. Thus, this study has shown the role and potential of the application of photocatalysts in the degradation of toxic organic compounds the wastewater.

Introduction

Today, freshwater resources are increasingly scarce, and environmental pollution is increasing, attracting the attention of researchers. This polluted environment because toxic organic substances are discharged mainly from the textile and dyeing industries, so specific treatment methods are required to reduce the waste content to the required level [1]. In the past few years, different wastewater treatment techniques have been used, such as adsorption [2], biodegradation [3], and advanced oxidation [4]... Advanced oxidation processes such as photocatalyzed Fenton reactions have been extensively studied due to their high degradability to organic pollutants [5]. Fenton reaction can generate more OH• radicals when iron ions react with hydrogen peroxide (H₂O₂). However, homogenous Fenton processes often operate a narrow pH range (pH < 4) and a large number of iron slurry precipitates [6], high cost of catalyst recovery. To overcome this shortcoming, heterogeneous Fenton photoreactivity has been studied extensively with low H₂O₂ in a wide pH range effectively [7-9].

The basic principle of a homogeneous Fenton reaction is the oxidation of Fe^{2+} ions to Fe^{3+} and the reduction of H_2O_2 to ^-OH ions and $^\bullet OH$ radicals. Accordingly, these radicals with strong oxidizing activity will degrade organic compounds into less toxic inorganic compounds.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + {}^-OH \qquad (1)$$

$${}^\bullet OH + H_2O_2 \rightarrow {}^\bullet O_2H + H_2O \qquad (2)$$

$${}^\bullet O_2H + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+ \qquad (3)$$

Graphite carbon nitride material (g-C₃N₄) is a two-dimensional (2D) material widely used in photocatalysis because of its narrow band gap (2.7 eV) and good chemical stability [10]. However, the catalytic efficiency of the material is still low due to the standard charge generation efficiency, the slow charge transfer rate, and the fast photogenerated electron-hole recombination ability. Therefore, many methods have

been applied to improve the photocatalytic efficiency of the materials [11].

Ferric hexacyanoferrate (Fe$_4$[Fe(CN$_6$)]$_3$), commonly known as Prussian Blue (PB), is one of the synthetic metal coordination compounds [12]. Beside the presence of both nitrogen coordination bond with Fe(III) high spin site and carbon coordination bond with low spin Fe(II) create unity of electrical, catalytic and magnetic properties [13]. These things make PB increasingly expanded and applied in many different fields. The influence of pH on the photocatalytic activity is one of the complex factors that needs to be evaluated because the reaction process involves the role of electrostatic interactions between the surface of the catalyst molecule, the substrate, and the charge origin of the catalysts [14]. During photocatalysis, dyes can be degraded by the attack of hydroxyl radicals, direct oxidation by positively charged hole sites on the valence band, and direct reduction by electrons in the conduction band [15]. The pH of the solution affects the exchange surface of the catalyst, the deionization of the dye molecules, and the formation of hydroxyl radicals [16]. Therefore, in this paper, the effect of pH on the photocatalytic degradation of rhodamine B (RhB) is studied.

Experimental

Materials and chemicals

All the chemicals for materials synthesis, including potassium ferrocyanide trihydrate (K$_4$Fe(CN)$_6$, ≥99%), hydrochloric acid (HCl, ∼37%), urea (CO(NH$_2$)$_2$, ≥99%), rhodamine B (RhB) were purchased from Sigma-Aldrich and used directly without further purification.

Synthesized g-C$_3$N$_4$ material

The pure g-C$_3$N$_4$ was prepared by solid-state decomposition and condensation from urea as a precursor. Typically, a well-ground urea powder was transferred to an alumina crucible covered by an aluminum foil and then treated at 550 °C in Ar gas for 1 hour with a temperature ramping of 10 °C·min^{-1}. The obtained solid product was re-ground and denoted as CN.

Synthesis of materials PB/g-C$_3$N$_4$

To synthesize the composites of PB and CN, 0.1 g of as-prepared CN was well-dispersed to the 100 mL of 0.3 mol·L^{-1} K$_4$Fe(CN)$_6$ solution under continuous stirring for 12h. After that, the solid was collected using centrifugation and dried at 80 °C overnight. A composite synthesis reactor was constructed from two vials with different diameters of 1.4 and 3.2 cm, wherein the small vial was put entirely inside the other. The obtained solid was transferred to the large vial while the small vial concentrated hydrochloric acid (1 mL) was taken into the small vial. Subsequently, the reactor was sealed and aged at room temperature for 24 hours. After completing the reaction, the solid powder turned from yellow-white to light-blue. The sample was then rinsed thoroughly with deionized (DI) water and ethanol three times before drying at 80 °C. The obtained product was denoted as PB/CN. The pure PB was also prepared in the same procedure directly from K$_4$Fe(CN)$_6$ precursor and hydrochloric acid. The dark-blue solid was rinsed with ethanol, dried at 80 °C, and denoted as PB.

Effect of pH on the photocatalytic degradation of RhB

Each type of wastewater has a different pH value. Therefore, the effect of pH on the efficiency of the photocatalytic degradation of RhB pigments was conducted at different pH environments, respectively, at 1; 3; 5; 7; 9 with a PB/g-C$_3$N$_4$ catalyst mass of 50 mg in 100 mL of RhB solution. The pH index was adjusted using NaOH 0.1M and HCl 0.1 M agents.

Results and discussion

Effect of pH on the photocatalytic activity of the materials

The pH factor plays a very important role in the photocatalytic degradation of dyes. Figure 1 shows the effect of pH on the photocatalytic degradation of RhB on the PB/g-C$_3$N$_4$ catalyst.

The results in Figure 1 show that the decomposition efficiency of RhB increased gradually in the acidic region, reaching 68.9% to 98.6% after 60 minutes of illumination at pH of 1.98 and 3.62, respectively. When the pH gradually increased to the neutral region, the decomposition efficiency decreased insignificantly, to 96.4% and 93.9% with pH values at 5.01 and 6.91, respectively. The material has a marked decrease in activity when entering the basic medium, shown in the efficiency of only 59.3% at pH 9.03. Thus, it proves that the material can work in a fairly wide pH range and is most suitable in an acidic environment.
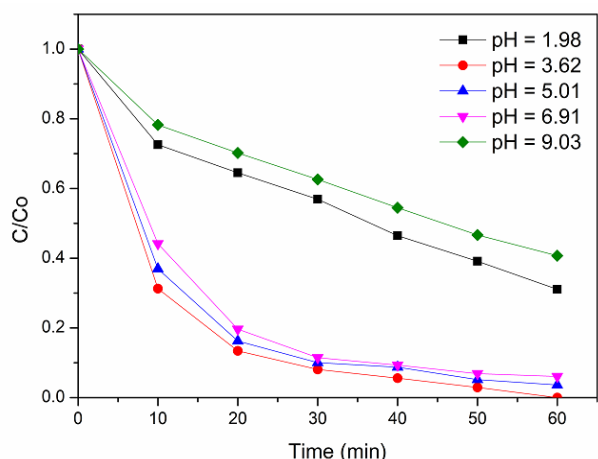
Figure 1: Effect of pH on the degradation of RhB dye (CRhB = 10 mg/L, m catalyst = 0.05 g)

Table 1: The photocatalytic efficiency of PB/g-C$_3$N$_4$ materials on the photocatalytic degradation of RhB

pH value	1.98	3.62	5.01	6.91	9.03
Efficiency (%)	68.9	98.6	96.4	93.9	59.3

To explain this phenomenon, the effect of pH on the surface charge of the material or the isoelectric point (pH$_{pzc}$) of the PB/g-C$_3$N$_4$ materials was determined (Figure 2).

The experiment was carried out by titration method to measure the pH of NaCl 0.1M electrolyte solution. Specifically, with a solution volume of 100 mL of NaCl 0.1M, the solutions were initially adjusted to pH values of 1.08; 3.02; 5.03; 7.09; 9.05, and 11.02. The adsorption process of the material was carried out for 24 hours. The solution was filtered to remove solids and measured again for pH$_f$. The graph pH$_i$ = pH$_i$ – pH$_f$ intersects the horizontal axis at the exact value of pH$_{pzc}$.
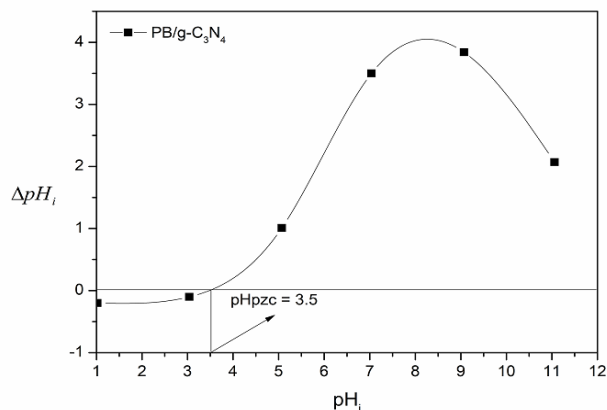

Figure 2: The dependence of ΔpH$_i$ on pH$_i$ to determine the zero-pH$_{pzc}$ charge point of the sample PB/g-C$_3$N$_4$

From the results in Figure 2, the isoelectric point value of the material is determined to be pH$_{pzc}$ = 3.5. This means that when pH < pH$_{pzc}$, the functional groups are protonated thereby increasing the positive charge on the photocatalyst surface. Conversely, when pH > pH$_{pzc}$, the photocatalyst surface is negatively charged. Therefore, at pH=3.62 (closest to the pHpzc of the material), the photocatalytic adsorption efficiency of the material is best as observed.

Another factor that can also be used to explain the effect of pH on RhB degradation efficiency is the structural nature of the pigment. The RhB pigment molecule exists in two states, namely the cationic form and the ionic dipole form shown in Figure 3 [17].
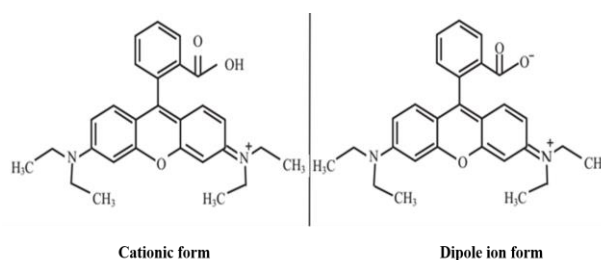
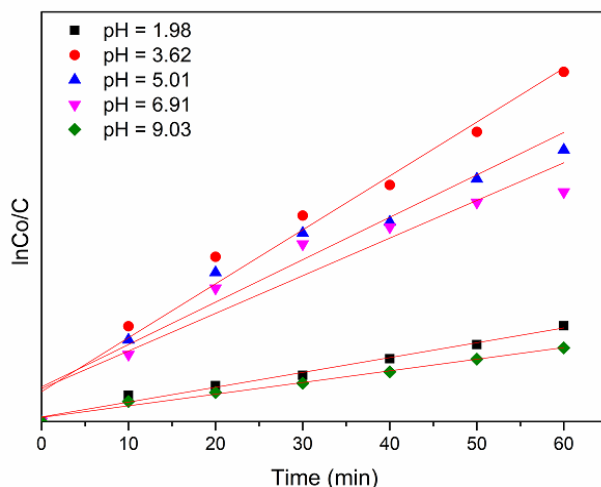

Figure 3: Two forms of RhB in an aqueous solution

Figure 4: Time dependence of lnCo/C value according to Langmuir-Hinshelwood kinetic model

Since the acid dissociation constant pKa of the carboxyl group in the RhB molecule has a value of about 3.7 [18]. Thus, in the region of pH < 3.7, RhB exists in cationic form and pH > 3.7, RhB exists in dipole ion form. Therefore, at the value of pH = 1.98 (pH < pH$_{pzc}$), the surface of the material carries a positive charge and RhB itself is in the cation form, so there is an electrostatic repulsion between RhB and the surface of the material, causing the adsorption of cationic organic molecules on the photocatalyst surface decreased, leading to the degradation efficiency of RhB pigments

of the materials down to only 68.9%. Through the pH = 3.62 region, at this time, the surface of the material is negatively charged (pH > pH_{pzc}) due to the deprotonation of the carboxyl group, while RhB still exists in the cation form, it increases the adsorption capacity of cationic organic substances on the surface of the material, making the photocatalytic efficiency increase to 98.6%. After passing pH = 3.62 and moving towards a neutral environment, RhB exists as a dipole ion, so it easily leads to the agglomeration of RhB molecules to form a dime, reducing the adsorption of RhB on the surface of the catalyst. However, an increase in pH means an increase in hydroxyl radicals [19] so this process is still quite efficient. In the basic environment, the photocatalytic efficiency decreased significantly, only 59.3% at pH = 9.03. This is because the higher the pH, the more hydroxyl groups in the environment, causing competition between the hydroxyl groups and organic compounds [20]. Besides, in this environment, the surface of the material is negatively charged, so there is an electrostatic repulsion between the negative charges on the surface of the adsorbent, and the carboxylate group reduces the adsorption capacity of RhB on the material, reducing the photocatalytic efficiency of the material.

Table 2: Data obtained when investigating the Langmuir-Hinshelwood kinetic model

pH	1.98	3.62	5.01	6.91	9.03
k (min^{-1})	0.018	0.065	0.051	0.045	0.014
R^2	0.98	0.97	0.93	0.90	0.98

The results in Table 2 show that the rate of RhB decomposition on PB/g-C_3N_4 catalyst (pH = 3.62) is 3.6 times faster than that of pH values in an acidic medium (pH = 1.98) as well as in a basic environment (pH = 1.98 or pH = 9.03).

Evaluation of the reusability of PB/g-C₃N₄ materials

The reusability of PB/g-C_3N_4 materials was investigated after 5 reactions. The results shown in Figure 5 show that, after 5 times of reactions, the material still shows high catalytic activity with RhB decomposition efficiency of 89.5%. This indicates that the synthesized PB/g-C_3N_4 material has good photocatalytic activity and is stable in the treatment of RhB difficult-to-decompose pigments in the aqueous environment under the irradiation effect of the visible light region.

The X-ray diffraction pattern of PB/g-C_3N_4 material is shown in Figure 6, structure and phase composition do

not change after 5 times of use. This proves that the reusability of PB/g-C_3N_4 material is quite high and stable.
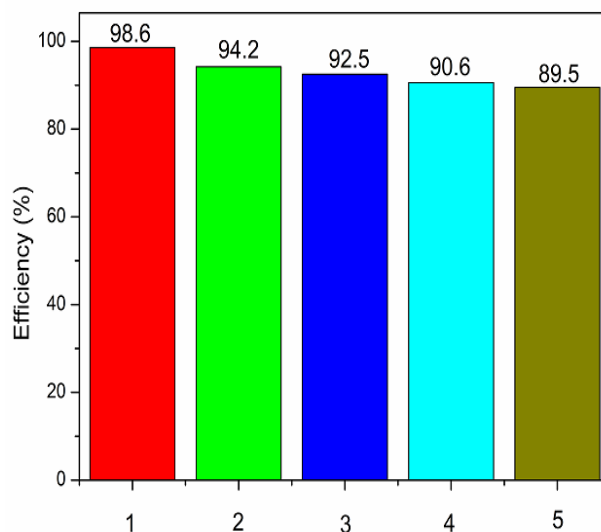

Figure 5: Activity stability of PB/g-C_3N_4 materials for photocatalysis of RhB decomposition under visible light radiation
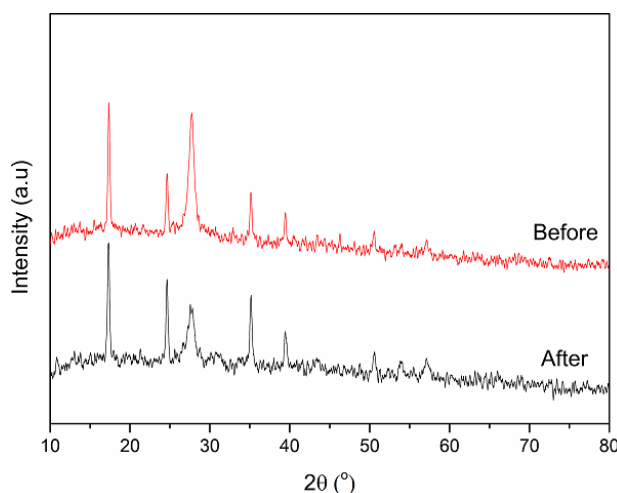

Figure 6: XRD pattern of PB/g-C_3N_4 material after 5 reuses

Conclusion

In this work, the effect of pH and stability in RhB degradation over PB/g-C_3N_4 catalyst in photo-Fenton reaction was investigated. As the result, the catalytic performance of PB/g-C_3N_4 exhibits as high efficiency in weak acid to neutral pH and significantly decrease in strong acid and basic media. The stability of catalyst after 5 times of reaction is demonstrated by the endurable efficiency without observable variation in crystal structure. These results indicate the potential of PB/ g-C_3N_4 catalyst in practical application.

Acknowledgments

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