Adsorption of Paraquat Dichloride by Graphitic Carbon Nitride Synthesized from Melamine Scraps

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Abstract. In this research, graphitic carbon nitride (g-C₃N₄) was synthesized from useless melamine scraps. Mixture of melamine powder and urea was directly burned in the muffle furnace at 550 °C. Later as-synthesized g-C₃N₄ was modified with hydrochloric acid. The g-C₃N₄ powder was characterized by several techniques including X-ray diffraction, scanning electron microscope, and specific surface area analyser. Adsorption of the herbicide paraquat from an aqueous solution to suspended particles of g-C₃N₄ was investigated, taking into consideration several parameters such as initial concentration of paraquat, initial pH, and dosage of g-C₃N₄. The results showed that with the same amount of g-C₃N₄, the increase in the paraquat concentration caused the reduction in the removal efficiency and the higher the amount of g-C₃N₄, the less residual paraquat remained in the bulk solution. G-C₃N₄ showed better adsorption behaviour in the basic condition. Finally, Langmuir and Freundlich adsorption isotherms were also evaluated. Paraquat adsorption by g-C₃N₄ was in accordance with Langmuir more than Freundlich adsorption isotherm.

1. Introduction
Nowadays, environmental problem is a big issue worldwide. Industrial wastes from many industries had to manage appropriately. Big amount of investment was utilized for solid waste disposal facilities. For melamine tableware industry in Nakhon Ratchasima province, Thailand, huge amount of melamine scraps occurred each day of production. Moreover, the disposal cost of this waste as hazardous waste was rather expensive. Therefore the aim of this research was to utilize these non-valuable solid wastes.

Paraquat dichloride (1,1′-dimethyl-4,4′-bipyridinium dichloride) commonly referred to “paraquat,” is one of the most widely used herbicides registered in Thailand. Paraquat is also often referred to Gramoxone (a common trade name). It is a widely utilized for the control of broadleaf weed in many agricultural and non-agricultural use sites. It is classified in non-selective herbicides. Recently, in the north of Thailand, farmers used paraquat 2-3 times/year in corn planting for animal food industry. Consequently, huge amount of paraquat remained in agricultural area. The reported half-life for paraquat in soil ranges from 16 months (aerobic laboratory conditions) to 13 years (field study) [1]. It affected to both animals and human. Paraquat exposures studies using frogs, birds and rodents at environmentally related concentrations, promote risks of declines in reproductive success due to

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embryotoxicity, delayed conception and malformations [2]. Accidental and intentional exposure of humans to paraquat still occurs even though its use is restricted. Brain damages and deaths can occurred in patients, who drank paraquat solution. Particularly, several studies suggest a link between paraquat use and Parkinson’s disease (PD) [3]-[6]. Paraquat is highly soluble in water up to 620 g/L at 25 °C hence straightforwardly contamination into surface water by runoff. Conventional water supply unit process is unable to remove paraquat. Therefore, specific unit, for example, adsorption tank is required. From literatures review, graphitic carbon nitride (g-C₃N₄) was feasible adsorption material [7]. It can be synthesize from melamine directly. Consequently, this research will focus on synthesizing graphitic carbon nitride from useless melamine scraps and testing for paraquat adsorption.

2. Materials and Methods

2.1. Synthesis of Graphitic Carbon Nitride

The reagents used in this research were analytical grade. Melamine scraps was obtained from melamine tableware industry in Nakhon Ratchasima province, Thailand. The obtained melamine was crushed and sieved. In this experiment, melamine powder with the size of 100 mesh (0.149 -0.177 mm) was used. G-C₃N₄ was prepared by directly heating melamine with urea additive in the muffle furnace. The melamine to urea ratio was 10:0.3 g. The heating up rate was 10 °C per minute and after temperature reached 550 °C this temperature was holed for 4 hours. After it was naturally cooled to room temperature, g-C₃N₄ was obtained. The as-synthesized sample had been modified with 37% HCl for 3 hours. Then the modified sample had been washed with DI water for several time until the pH of water was 7. Finally, the sample had been dried in the oven at 105 °C for 3 hours. The finished sample was ground into powder before being used in the experiment.

2.2. Characterization of Graphitic Carbon Nitride

Powder X-ray diffraction (XRD) patterns of the g-C₃N₄ samples were recorded with an X-ray diffractometer model XD 6000. The morphology of g-C₃N₄ sample was observed on a scanning electron microscope (SEM) at 5kV for 30000X and 50000X magnification. The specific surface areas of the g-C₃N₄ sample was measured by nitrogen sorption on an autosorb iQ surface area analyzer model AUTOSORB and calculated by the Brunauer–Emmett–Teller (BET) method.

2.3. Adsorption Experiment

Paraquat adsorption experiment was conducted in batch type reactor. The experiment was divided into three parts. First experiment, paraquat at pH 7 was prepared in different initial concentration: 2, 6, and 8 mg/L and g-C₃N₄ of 2 g was used in each concentration. Second experiment, g-C₃N₄ with different amount of 0.4, 1, and 2 g was used in 8 mg/L paraquat at pH 7. Third experiment, 8 mg/L paraquat was prepared in different initial pH of 3, 7, and 10 and g-C₃N₄ of 2 g was used in each pH. All adsorption experiments were done in the dark. The adsorption experiments were conducted in a 1 L reactor containing 1 L paraquat solution with magnetic agitation. For each run of experiment, sample solution was taken off by a syringe at 5, 10, 15, 20, 25, 30, 45, 60, 90, 120, 180, 240, 300, and 360 minutes. Five mL turbid sample solution was filtered with 0.2 micron nylon filter. Then 1% alkaline sodium dithionite solution of 1 mL was added to the clear solution. Shortly afterwards, the light blue color solution was obtained. Their respective concentrations were spectrophotometrically monitored at analytical wavelengths of 398 nm using a UV-VIS spectrophotometer.

3. Results and Discussion

3.1. Characterization of Graphitic Carbon Nitride

The XRD patterns for g-C₃N₄ sample was shown in Figure 1. The strongest XRD peak at 27.62°, was indexed for graphitic materials as (0 0 2) diffraction plane (JCPDS 87-1526) which is consistent with the reported g-C₃N₄ [8]. Figure 2 showed the SEM images of acid modified g-C₃N₄ particles at a magnification of 30,000x and 50,000x. The size of these nanoparticles was approximately 80 - 250 nm. G- C₃N₄ sample presented a BET specific surface area of 42.06 m²/g (multi point mode measurement)
which was slightly less than other reports of 393.8 m$^2$/g for urea as precursor or 303.9 m$^2$/g for melamine as precursor [9]. However, its specific surface area was higher than natural clay (13.8 m$^2$/g) [10].

![XRD patterns of g-C$_3$N$_4$.](image)

**Figure 1.** XRD patterns of g-$\text{C}_3\text{N}_4$.

![SEM images of g-C$_3$N$_4$ with a) 30000X and b) 50000X.](image)

**Figure 2.** SEM images of g-$\text{C}_3\text{N}_4$ with a) 30000X and b) 50000X.

3.2. *Paraquat Adsorption*

From Figure 3 and Figure 4, the higher the amount of g-$\text{C}_3\text{N}_4$, the less residual paraquat remained in the bulk solution. This denoted the adsorption capacity of the g-$\text{C}_3\text{N}_4$ for a given concentration of paraquat. Considering the same initial quantity of paraquat, the increase in the adsorbent dosage caused an improvement in the removal efficiency leading to a greater amount of adsorbed paraquat, as expected.
Figure 3. Variation in paraquat concentration overtime for g-C$_3$N$_4$ (2 g/L) suspensions exposed to a different concentration of paraquat solution pH 7 at room temperature.

Figure 4. Variation in paraquat concentration overtime for different dosages of g-C$_3$N$_4$ (0, 0.4, 1, and 2 g/L) suspensions exposed to 8mg/L paraquat concentration solution pH 7 at room temperature.

From Figure 5, the effect of pH on adsorption capacity was evaluated using three different pH values (3, 7, and 10). The pH of solution was an important variable in the adsorption processes. The results showed that the adsorption behavior in basic condition was slightly higher than natural condition and obviously higher than acidic condition. Some researchers reported that the optimal pH range for the removal of paraquat was within 6–8, by also taking into consideration the realistic working pH conditions [11].
Figure 5. Variation in paraquat concentration overtime for different pH of 8mg/L paraquat solution with dosages of g-C₃N₄ 2 g/L at room temperature.

3.3. Paraquat Adsorption Isotherms
Two adsorption isotherms were investigated, Langmuir and Freundlich isotherms. Both models (Langmuir and Freundlich) fit the experimental data quite well as in Figure 6. The correlation coefficient values (R²) of these two isotherms were 0.9873 and 0.9623, respectively. The Langmuir isotherm presented slightly higher correlation coefficient values (R²) which indicated that paraquat adsorption by g-C₃N₄ was in accordance with Langmuir adsorption isotherm. The Langmuir adsorption constant of 0.115 L/mg was calculated. This trend was in accordance with Hao’s experiment [12] which studied the adsorption behavior of paraquat from aqueous solution using star fish particles.
Figure 6. Adsorption isotherm of 8mg/L paraquat by different dosages of g-C_3N_4 (0.4, 1, and 2 g/L) at pH 7 a) Langmuir adsorption plot and b) Freundlich adsorption plot.

4. Conclusion
In summary, we have successfully fabricated the g-C_3N_4 material by directly heating the mixture of melamine and urea. The BET specific surface area of 42.06 m^2/g was achieved. Our results clearly indicated that the g-C_3N_4 has impartial performance in the paraquat adsorption. The higher the amount of g-C_3N_4 is, the higher adsorption capacity will be. It showed better adsorption behaviour in the basic condition. However, other important parameters such as particle size of adsorbent, contact time, stirring speed, and temperature should be examined in the future. Paraquat adsorption by g-C_3N_4 show good agreement to Langmuir more than Freundlich adsorption isotherm.

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