Photocatalytic degradation of methyl orange using Carbon Quantum Dots (CQDs) derived from watermelon rinds

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Photocatalytic degradation of methyl orange using Carbon Quantum Dots (CQDs) derived from watermelon rinds

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Abstract. In this study, a facile synthesis of carbon quantum dots (CQDs) was successfully conducted by hydrothermal treatment at mild temperature (120 ˚C) using watermelon rinds as carbon precursor. The synthesized CQDs was aimed to harvest the visible light from artificial source for photocatalytic degradation of methyl orange (MO) dye. The prepared CQDs were characterized by TEM to check the physical properties. The produced CQDs demonstrated a band of spherical dots which display a complete dispersion of particles in water. The spherical morphology of the CQDs was clearly seen with narrow size distribution, averagely around 1-5 nm in diameter. The CQDs exhibited an excellent photocatalytic performance with 68.9% of MO degradation rate within 120 min reaction owing to the large surface area for adsorption and reaction process to take place.

1. Introduction

Carbon quantum dots (CQDs) is a carbonaceous nanoparticles that emerged with a prominent properties for example brilliant photostability, excitation wavelength dependent fluorescence, low toxicity, effective infrared-responded up conversion photoluminescence (UCPL) and tunable fluorescence emission [1,2]. They were firstly discovered by accident when purifying carbon nanotubes fabricated by arc- discharge methods [3,4]. CQDs are typically discrete, quasi- spherical and mostly less than 10 nm in size [5]. They predominantly composed of amorphous carbon together with nanocrystalline regions of sp^2/ sp^3-hybridized carbon atom and have various surface functional groups. Unlike many other carbon nanomaterials like carbon nanotubes, graphene oxide and graphene quantum dots, CQDs are easily and inexpensively synthesized using a cheap and sustainable source of biomass such as watermelon rinds, hair and even cow manure [6]. Meanwhile, in perspective on green science approach, hydrothermal treatment is considered as green synthetic approach because its simplicity, direct and productive among other methods. Alternatively, hydrothermal synthesis of CQDs using various natural carbon sources has provided great advantages due to the plentiful accessibility of carbon precursor, bio- degradable and low toxicity of the product for biological application [7,8].

Since discovery, CQDs exhibit a series of fascinating qualities which settle them as potential substitutes of conventional semiconductor quantum dots for photocatalytic applications. Mainly, they possess a strong photoluminescence (PL) which can be tuned and controlled by the nanoparticles' size. Surface passivation with the formation of thin insulating capping layer which can help to further improve the fluorescence intensity of the CQDs. Moreover, since CQDs are carbon based materials,

they may as well possess oxygen groups, their surfaces can be easily functionalized with the organic molecules which can introducing various heteroatoms and tailoring their wavelength emission and consequently their applicability [9]. At the same time, CQDs can also provide additional surface area for adsorption and reaction process to occur owing to its smaller size. As a nanomaterial, CQDs hold a larger surface area to volume ratio, and thus provide more surface area which thereby increasing the adsorption capacity [5]. Most CQDs show chemical inertness, high stability and resistivity to photo bleaching. Besides, CQDs own two extra and very essential characteristics; low cytotoxicity and excellent biocompatibility that render them superior compared to conventional semiconducting quantum dots and endow them with the potential of biological use [4, 9,10].

Herein, in this context we present a simple hydrothermal treatment to synthesis CQDs which believed possess a vital role in improving photocatalytic activity using watermelon rinds as carbon precursor. Watermelon rind is chosen since they contain protein, carotenoids, cellulose, citrulline, pectin and flavonoids with abundant of various functional groups such as carboxyl, hydroxyl and amine that can easily attract cationic ions renders them a potential candidates in water and wastewater treatment. In addition, because of antioxidant activity of citrulline it produce hydroxyl radicals strong oxidizing agent which is suitable for degradation process [11]. Moreover, many researchers speculate that flavonoids in the WMR are potential scavenger of hydroxyl that can be used for photocatalytic activity [12–14]. In this paper also, we discussed further on one of the beneficial roles of CQDs materials in enhancing photocatalysis process. We systematically investigated the physical properties of CQDs prepared by hydrothermal treatment using scanning electron transmission electron microscope (TEM to further proving its ability in photocatalytic degradation of methyl orange (MO).

2. Experimental

2.1. Reagents and materials

Watermelon rinds were collected from Universiti Malaysia Pahang (UMP) Cafeteria and used as source of carbon. Ethanol (C_2H_6O, 95%), dichloromethane (CH_2Cl_2, 99.8%) and acetone [$(CH_3)_2CO$, 99%] were purchased from Sigma Aldrich Chemical Co. All chemicals were analytical grade and used without further purification. Distilled water was used for sample preparation.

2.2. Preparation of CQDs.

CQDs was prepared using the mixture of watermelon rinds juice and ethanol via hydrothermal treatment. Watermelon rinds were collected from KK3 kiosk at Cafeteria. The watermelon rinds then washed thoroughly with distilled water and drained to remove excess water. The watermelon rinds were cut into smaller pieces and grinded into fine paste using a blender and filter using 0.1 mm sieve. 40 ml of watermelon rinds juice was mixed with 30 ml ethanol under vigorous stirring for 5 min. Then, the mixture was poured into Teflon-lined-stainless-steel autoclave and heated at constant temperature of 120°C for 150 min in oven. The resulted dark brown solution is washed with dichloromethane (CH_2Cl_2) and centrifuged at 3000 rpm for separation of less fluorescence deposit. Excess acetone ($(CH_3)_2CO$) is added to upper parts of solution and centrifuged at 6000 rpm to obtain highly fluorescent CQDs of size ranging from 1.5 – 4.5 nm [5].

2.3. Characterization

The morphologies and the structure of the CQDs was examined by Transmission Electron Microscope (TEM, TECNAI G2 20 LaB6) with an accelerating voltage of 390 kV. The sample was dispersed in water to identify the size range and shape that might involve in the adsorption process.

2.4. Measurement of photocatalytic activity

The photocatalytic activity was conducted using a self-made reactor equipped with a Halogen lamp (500 W) with <420 nm UV cut- off filter to stimulate the irradiation and light intensity in visible range. The photocatalytic activity of CQDs were conducted by evaluating the removal rate of methyl

orange (MO), 464 nm. 0.1g of CQDs was prepared and dissolved in MO solution (5 mg/L). This mixture was kept under magnetic stirring for I hour in dark to ensure the establishment of adsorption equilibrium before light irradiation. After 1 hour, 3.5 ml of the solution was taken out to evaluate the concentration. After that, 500 W halogen lamp was switch on and positioned above 11 cm from the surface of reaction of solution. The reaction was performed for 120 min and the solutions were collected for every 20 min. The absorbance for both solutions was determined by measuring the absorbance using a UV-1800 Spectrophotometer in the range between 200 nm to 1100 nm. The degradation rate of dyes can be calculated by using the following equation:

$$Degradation\ rate,\ \% = \frac{C_o - C}{C_o} \times 100\% \quad (1)$$

Where,

C_o = Initial concentration of pollutant
C = Final concentration of pollutant

3. Result and Discussion

3.1 Characterization

TEM was carried out to identify the structure and morphology of CQDs. Figure 1 shows the morphology of CQDs as obtained from TEM images by the hydrothermal treatment at 120˚C and their size distribution. As depicted in the picture, a band of spherical dots can be observed from the image which also revealed that the particles were completely dispersed in water. The spherical morphology was clearly visible to be seen with narrow size distribution, averagely around 1-5 nm range [5,7,10,15,16]. High photocatalytic activity generally depends on the crystallite size as small size produce larger surface area and proved that smaller size of CQDs is an essential key in improving photocatalytic degradation. Moreover, the adsorption capacity of CQDs emanated from flexible sp^2-bonded carbon structure and the large surface area contains abundance of oxygenated functional group [5]. This oxygenated groups can be useful in energy- transfer for photocatalytic process [10] and its adsorption depends on the capability of them to interact with the adsorbate. At the same time, the presence of carbonyl and hydroxyl functional groups on the CQDs surface can promotes the adsorption of several of molecules and metal ions. Increasing the adsorption of target reactants on the photocatalysts surface can increase their chance in reacting with photogenerated reactive species, thus enhancing the photocatalytic activity [5].

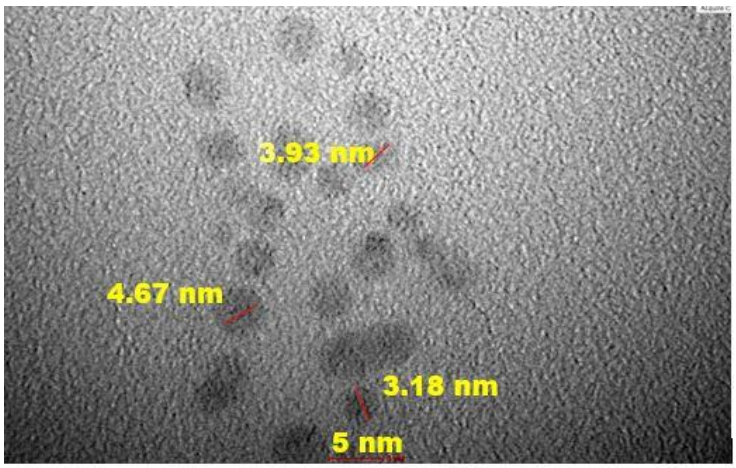

Figure 1. TEM morphology and size distribution of CQDs

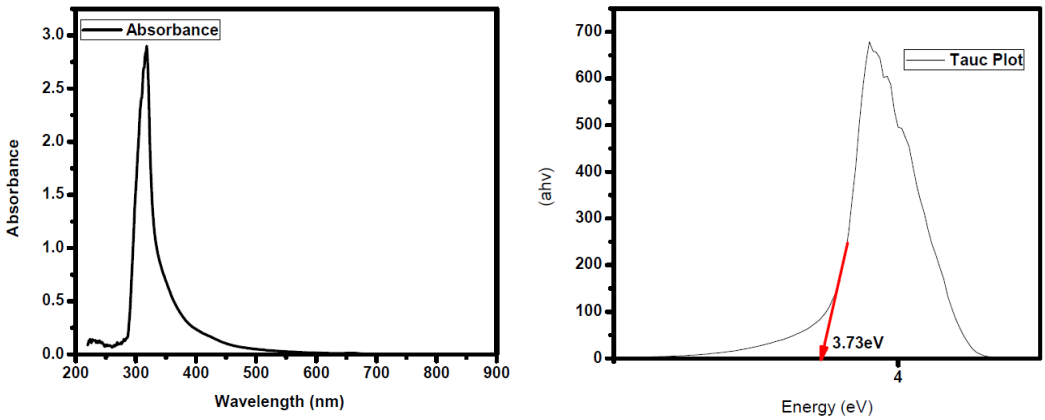

Figure 2. (a) UV-Vis spectrum of CQDs (b) Band gap energy of CQDs

The remarkable optical properties of CQDs are viewed as one of the essential factor that will influence the uses of CQDs. The UV-Vis absorption spectrum of CQDs solution in the range of 200 nm to 900 nm was exhibited in the Figure 2a, which display only one intense absorption peak in the UV region at about 318 nm, which correlated to n-π* transitions of C=O bonds in CQDs with a tail elongate to the visible range. These results are in agreement with the previously reported studies [7]. At the same time, since one of the beneficial roles of CQDs is extending the optical absorption range of photocatalyst, this optical characteristic lead to bandgap narrowing of the semiconductor when incorporate with CQDs owing to the chemical bonding that will be formed between the semiconductor and CQDs which in result can extend the light absorption range in enhancing photocatalytic degradation. Figure 2b shows the band gap energy of CQDs. The result show that the bandgap energy increasing with the decreasing of particles size. It is observed that when particles size is less than 6 nm, a substantial increase in E_g occur. This result is in agreement with other study [17]. Additionally, according to the quantum confinement theory which proposes that the holes in the valence band and the electrons in the conduction band are bound or confined by the potential barriers of the surface or potential well of a quantum box. Therefore, on account to the confinement of the electrons- holes, the energy bandgap increases between the valence and the conduction band with decreasing the particle size [17].

3.2 Photocatalytic activity

To assess the photocatalytic activity under the irradiation of visible light, MO was used as target pollutant. As seen in Table 1 and Figure 3, the intensity of dye decreased when the irradiation time increased due to the degradation process of MO. The degradation process nearly achieved at 120 min, with degradation rate of 68.9% which is an improvised result compared to previous study from Prasannan and Imae [10]. This result implied that CQDs can play a vital role in photocatalytic application. Owing to the smaller size of CQDs leads to a higher surface area, this condition is favourable for light absorbing thus spared more surface coordination sites in the photocatalytic activity. At the initial state of the adsorption process, the reaction was fast with respect to the contact time and gradually become slower as equilibrium state was achieved. In the initial stage of adsorption process, the availability of the MO molecules uptake is higher due to the more vacant active surface sites of the catalysts. As time lapsed, the active sites were limited where the reaction will gradually slowing down. The result can be proved through Figure 3 where the amount of MO degrade between 100 min to 120 min does not have much difference [18–20].

Table 1. Percentage of MO degradation after 120 min photocatalytic activity was conducted

Irradiation Time (min)	Percentage of degradation (%)
Dark	0%
0	10.006
20	24.765
40	42.230
60	48.660
80	60.310
100	68.360
120	68.941

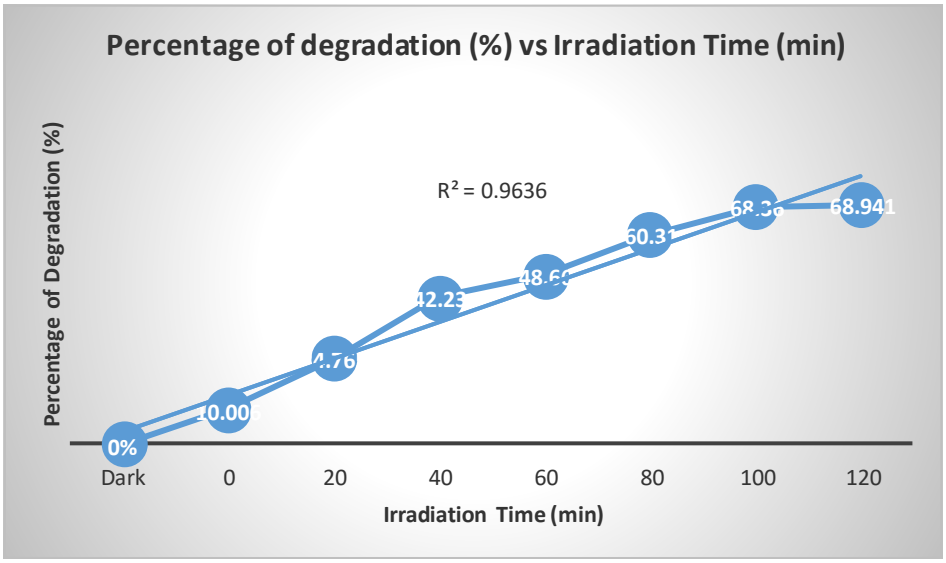

Figure 3. Percentage degradation of MO versus irradiation time

4. Conclusion

In summary, CQDs was successfully prepared under the facile hydrothermal method with cost effective strategy which is plausible for large scale synthesis. Reusability of readily available fruit wastes as precursor make the product cost effective whilst overcome the toxicity concerns using green approach. The characterization analysis that has been carried out suggested the successful preparation of the CQDs with nm dimensions that are useful in photocatalytic application in terms of providing additional surface area due to small particle size. Finally, the prepared CQDs are very worth attention due to its value in green synthesis that can enhance photocatalytic activity.

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