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RESEARCH PAPER

Detection of Cu^{2+}, Degradation of Acid Brown and Removing Cd^{2+} from the Water by High Photoluminescence Carbon Dots Synthesized from Milk

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ABSTRACT

In this experimental work, nitrogen-doped carbon quantum dots were successfully synthesized with hydrothermal of the milk. The product was composed of a powder and a stable colloid. The structure of the product was examined by XRD, EDS and FT-IR analysis. Also the particle size of the product was investigated by SEM and TEM images and the results showed the product is mainly composed of the particles with less than 5 nm in diameter. The photoluminescence intensity of the product was obtained by PL analysis and it was found the product has high photoluminescence intensity that can be improved by surface modification with N-Methyl-2-pyrrolidone. Due to high photoluminescence intensity of the obtained quantum dots they were used as a sensor to detection of Cu^{2+} and it was observed they can detect this ion in the aqueous medium for 0-80 uM concentration range. Also it was found by surface modification of carbon dots with N-Methyl-2-pyrrolidone, the detection sensitivity is improved. The optical properties of the product were studied by UV-Vis spectroscopy. The results showed the product can absorb light in the visible range and by increasing the Cu^{2+} concentration the band gap is increased that is mainly due to decrease of electron trap centers. The photocatalytic activity of the product was examined by degradation of Acid brown and it was found the product can decompose the dye after 30 min of irradiation. Due to huge surface of the product, it was served to adsorb Cd^{2+} ions from aqueous medium. The results showed the synthesized quantum dots can adsorb the ions more than 69% from the water. It was concluded that due to high photocatalytic and surface adsorption activity of the product it can be used for water purification potentially to degrade of organic pollution and removing heavy metal ions from the water.

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INTRODUCTION

In recent years using nanostructure materials have been attract much attentions due to their unique properties [1, 2]. Until know different carbon nanostructures (0D, 1D, 2D and 3D) have been synthesized with various chemical, thermal, electrical and mechanical electrical properties [3-6]. Carbon quantum dots, are semiconductor nanocrystals in the range 1 to 10 nm. Due to the quantum confinement effect, the optical properties of the nanostructures are significantly depended on the particle size and can be used in bioimaging [7] and biosensing [8]. Due to high toxicity of the elemental quantum dots [9], it is necessary using of

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safe quantum dots like the carbon dots. Although a low-value Cu^{2+} is essential for many living organisms, but due to the presence of plenty of Cu^{2+} in the wastewater, it threat the human's health and the environment [10]. Since Conventional analysis methods, such as electrochemical and atomic absorption spectrometry ones [11] are widely used to determine of Cu^{2+}, but they are time-consuming and usually use toxic reagents to prepare the sample. Therefore, it is necessary to develop a fast, accurate, and low-cost method to determine Cu^{2+} in the low values. Carbon quantum dots can be synthesized from both top-down and bottom-up methods like the other nanomaterials. Chemical oxidation [12], and ultrasonic synthesis [13] of bulk carbon materials like the graphite and activated carbons can be classified in the top-down method. Also, these valuable materials can be also synthesized via bottom-up methods such as microwave [14] and hydrothermal method [15] of carbon molecular precursors like that sucrose, citric acid and so on. Carbon quantum dots along with semiconductors can be widely used as photocatalyst due to fast electron transportation and high absorption coefficient [16]. To removing the toxic reagents and reducing the synthesis cost, many works focused on the synthesis of carbon quantum dots on large scale with low cost and high yield from biomass and green materials [17, 18]. Due to the electronegativity difference between carbon and the other elements, doping the hetero atoms in the carbon quantum dots structure can influence on the electronic and optical properties of these carbon nanomaterials [19]. Due to the presence of a high number of surface carbons in the carbon dots, they can be functionalized with different groups like –OH, $-NH_2$ etc that is very suitable for increasing their solubility in both organic and inorganic solvents [20]. In this research work, very tiny and high photoluminescence carbon quantum dots were synthesized via simple hydrothermal of the milk. The synthesized quantum dots were used to detection of Cu^{2+}, degradation of acid brown and removing Cd^{2+} from the water and it was found that the quantum dots are capable to detect Cu^{2+} in the 0-80 uM concentration, degrade acid brown after 30 min and remove Cd^{2+} about 90% from the water.

MATERIALS AND METHODS

All the used materials were of analytical grade and used as purchased. Fourier transform infrared (FT-IR) spectra were detected on Shimadzu Varian 4300 spectrophotometer in KBr pellets. X-ray diffraction (XRD) patterns were recorded by a Panalytical -X'pertpro, X-ray diffractometer using Ni-filtered Cu Ka radiation. Scanning electron microscopy (SEM) image was applied on TESCAN equipped with an energy dispersive X-ray spectroscopy. The EDX analysis with 20 kV accelerated voltage was applied. Transmission electron microscopy (TEM) image was achieved on a Zeiss transmission electron microscope with an accelerating voltage of 200 kV. UV-Vis spectra were recorded using a UV–Vis spectrophotometer (PerkinElmer). To synthesis of carbon quantum dots, 100 ml of milk without any modification was transferred to the autoclave and heated at 180 ^{o}C for two, four six and eight hours. After that, the product that was composed of both powder and stable colloid was separated by centrifuge. The powder was washed with distilled water and ethanol several times and then dried at 80 ^{o}C for 8 h and used for analysis and applications.

RESULTS AND DISCUSSION

Fig. 1a shows the XRD pattern of the synthesized product. It can be seen that the product has an amorphous structure and there are no peaks to confirm the crystallinity of the product. The peak located at 22^{o} is related to the carbon quantum dots. To further approve the synthesis of carbon quantum dots, beside the XRD pattern EDS analysis was served. As shown in Fig. 1b the EDS spectra shows the product has three carbon, oxygen and nitrogen elements. The carbon peak confirms the synthesis of carbon quantum dots. The oxygen peak is related to the carboxyl and hydroxyl groups on the quantum dots surface. Also the nitrogen peak in the EDS analysis can be related to the nitrogen doped in the carbon quantum dots. From XRD and EDS analysis, it can be concluded that the product is composed of nitrogen-doped carbon quantum dots. The other analysis was served to the investigation of the product structure was FT-IR analysis (Fig. 1c). The peak is located at 3409 cm^{-1}, is related to stretching vibration of OH group that can be attributed to the hydroxyl groups on the carbon quantum dots and also the water molecules adsorbed on the quantum dots. In fact due to the high surface of the carbon quantum dots, they can adsorb the water molecules existed in the medium and hence in their FT-IR spectra,

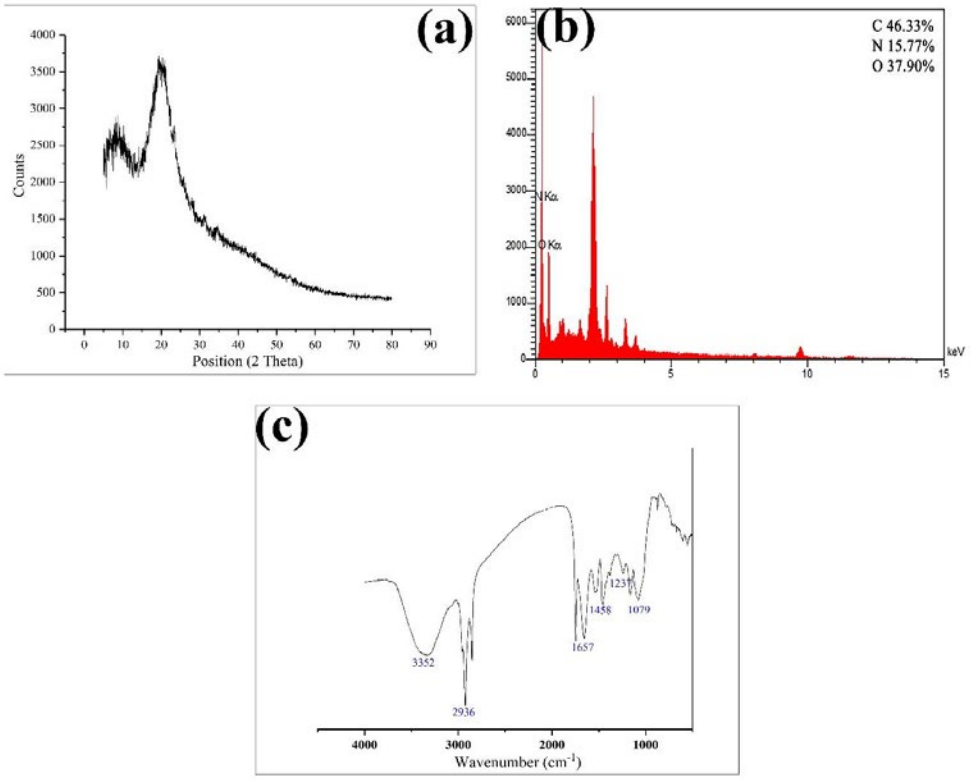

Fig. 1. a) XRD, b) EDS and c) FT-IR analysis of the product.

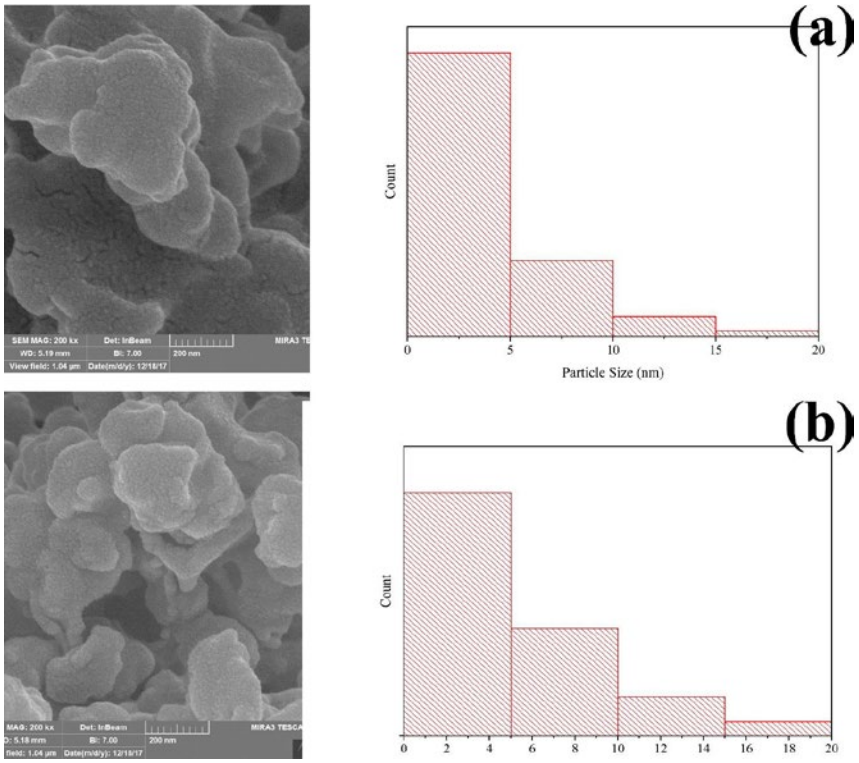

Fig. 2. SEM image (left) and particle size histogram (right) of the product synthesized at 180 °C for a) 2h and b) 4h.

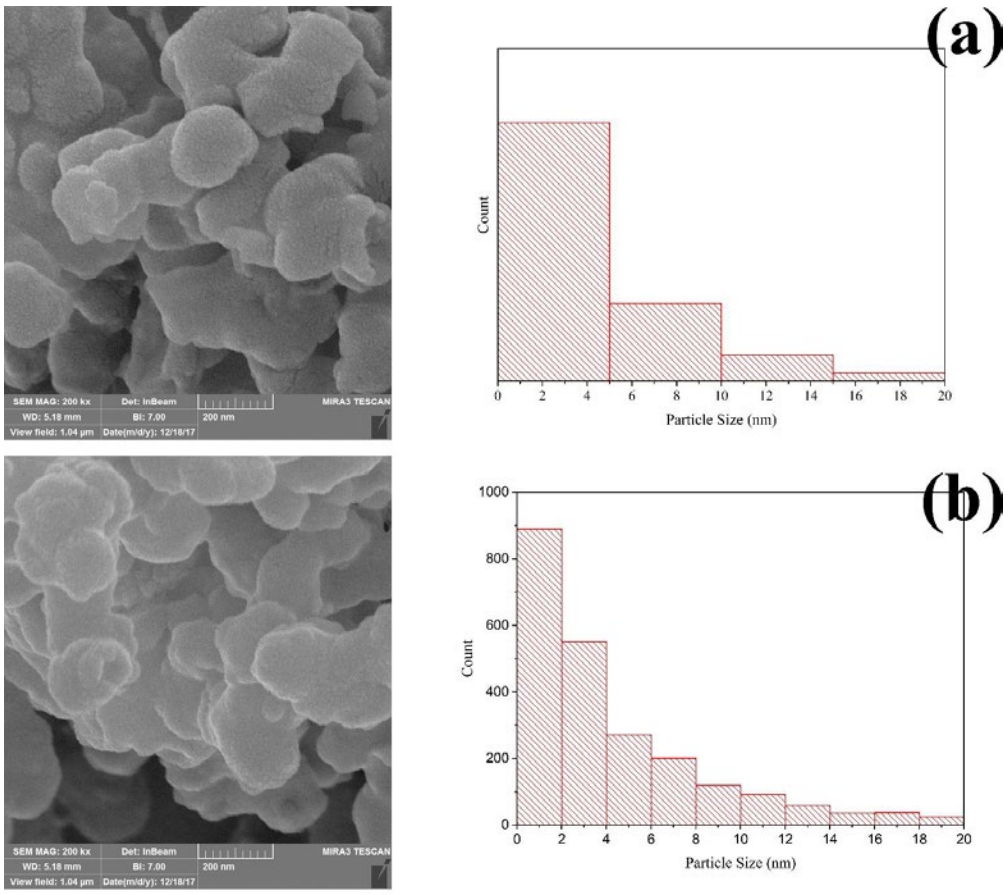

Fig. 3. SEM image (left) and particle size histogram (right) of the product synthesized at 180 °C for a) 6h and b) 8h.

there is always a peak located at 3400 cm^{-1}. The peak located at 2920 cm^{-1} can be attributed to the stretching vibration of C-H group. Also, the peaks placed at 1656 cm^{-1}, 1385 cm^{-1} and 1057 cm^{-1} are related to the vibrational absorption of the C=O, C-O (carboxy group) and C-O (alkoxy group). Also the peak located at 1449 cm^{-1} shows N-H group bending vibration that can be attributed to the nitrogen doped in the quantum dots structure. The product size was obtained by SEM image. The result is shown in Fig. 2 and 3. It can be seen that the product synthesized at 180 °C for 2h is composed of very tiny particles that due to their high surface energy, they aggregated together and bulky structures were achieved (Fig. 2a). The effect of hydrothermal time on the product size was investigated by SEM images. Due to high aggregation particles, it is difficult to compare the particle size with SEM images only. So the particle size histograms of the different products were prepared and we compared the particle size with these histograms. As it can be seen in Fig. 2b by increasing the time, the numbers of particle with larger than 5 nm was increased that can be attributed to higher energy prepared during four hours in the hydrothermal medium. In fact by increasing the time to four hours, the reaction medium prepare more energy and hence the particles are aggregated together and create the larger particles. By changing the reaction time to six hours, the particle size didn't change significantly (Fig. 3a). In fact due to low surface energy of the particles, they don't aggregated together and hence the particle size don't change significantly. By increasing the hydrothermal time to eight hours, the particle size is decreased (Fig. 3b). In fact due to very high energy prepared by the hydrothermal medium after eight hours, the particles were separated from each other and hence the particle size were decreased. The

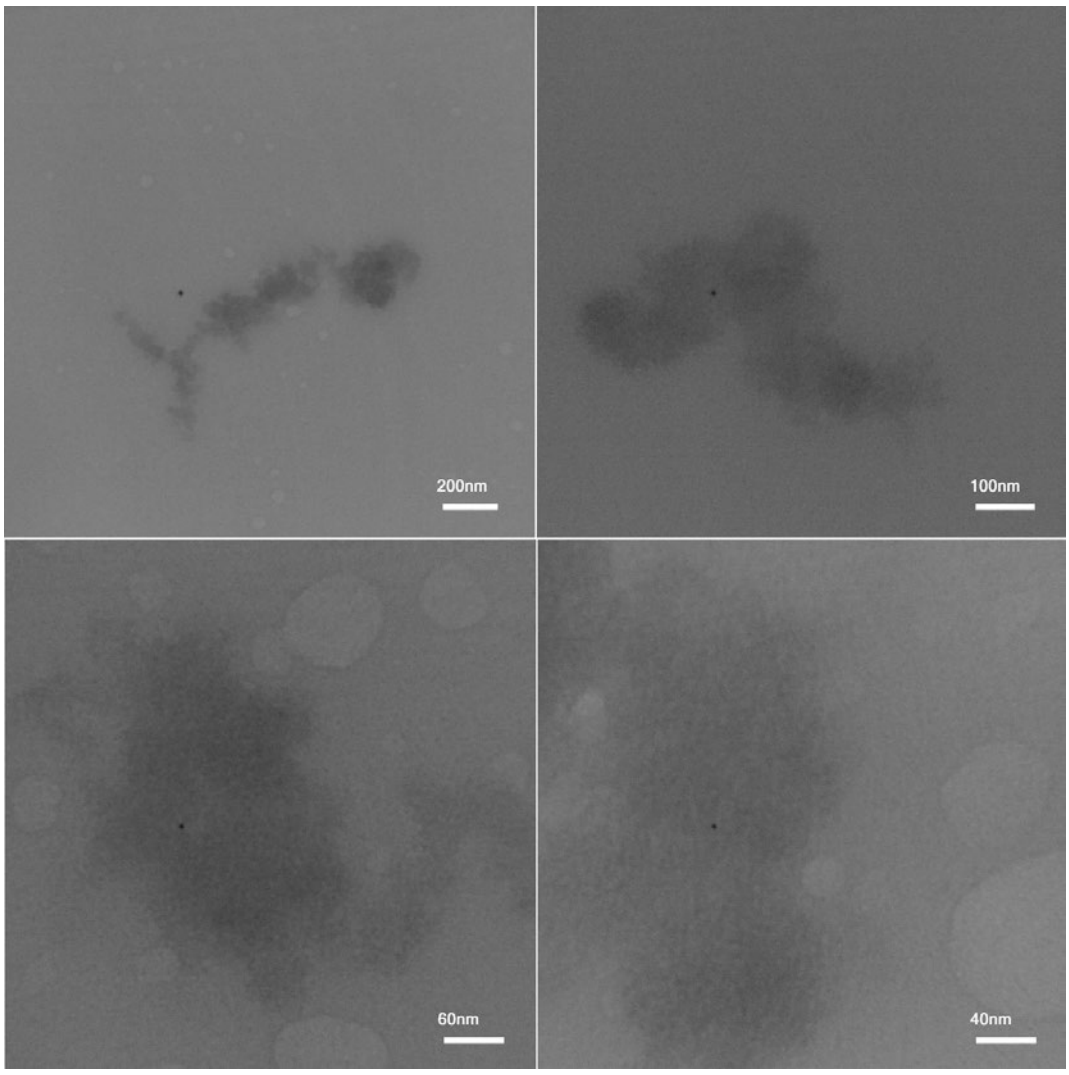

Fig. 4. TEM images of the product.

product size and morphology were studied more by TEM images (Fig. 4) and it was found the product is composed of very tiny particles aggregated together. The photoluminescence intensity of the product was studied by PL analysis (Fig. 5). It can be seen that the synthesized quantum dots have high photoluminescence intensity that is very useful for using in the optoelectronic devices. The PL intensity was increased by quantum dots surfaces modification with N-Methyl-2-pyrrolidone. In fact the main reason for the decrease of PL intensity of such quantum dots is the defects that existed in their structures that led to trap electrons and hence decrease the PL intensity. By surface modification of the quantum dots, the defects centers were significantly decreased and therefore the PL intensity is increased. Due to the high PL intensity of the synthesized carbon quantum dots, we used them to the detection of Cu^{2+} ions. The results showed Cu^{2+} can quench PL intensity of carbon dots due to the bonding between of N functional groups of CQD and Cu^{2+} (Fig. 6a). Also, it was found by surface modification of carbon quantum dots with N-Methyl-2-pyrrolidone, the detection was improved that is mainly due to the increase of N functional groups on the CQDs and also high photoluminescence intensity of the modified CQDs. As shown in Fig. 6b the quenching of PL intensity of the modified CQDs with Cu^{2+} was followed from better linear relationship respect to

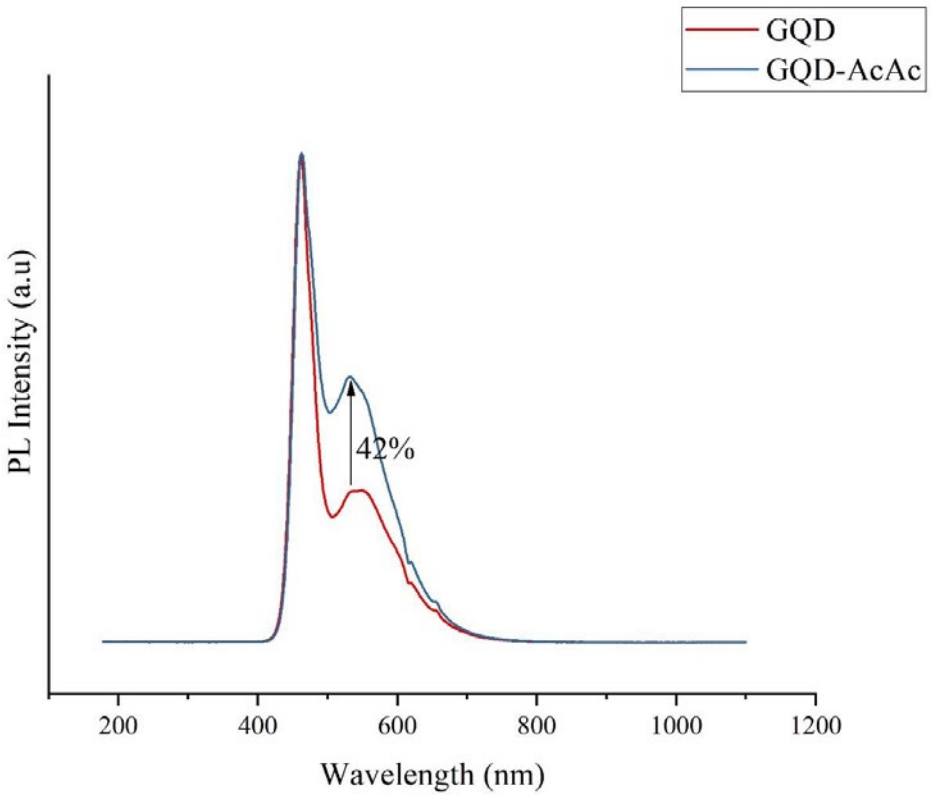

Fig. 5. PL analysis of bare N-CQDs and N-CQDs modified with N-Methyl-2-pyrrolidone.

the bare carbon dots. The optical properties of the product were investigated by UV-Vis spectroscopy. The results showed the product can absorb light in the visible range and hence it can be used for photocatalytic applications (Fig. 7). The band gap of the carbon quantum dots was obtained by Tauc equation. As it can be seen, by increasing the Cu^{2+} concentration the band gap is increased. In fact, when Cu^{2+} concentration has increased the defects and trap states are decreased and hence the excited electron doesn't trap in these defect centers and therefore the band gap is increased. The photocatalytic activity of the synthesized carbon dots was investigated by the degradation of Acid brown under ultraviolet radiation. Firstly, 0.022 g of the dye was dissolved into 250 ml of water and then 0.1 g of the quantum dots was poured in the solution and stirred for two hours. After that, the prepared suspension was exposed to the ultraviolet radiation. The results showed after 30 min irradiation, dye molecules were completely degraded in the presence of carbon dots (Fig. 8). It can be said when the carbon dots were exposed under ultraviolet irradiation, electron-hole pairs were created which leads to producing reactive oxide species in the presence of the water. These species attack to the dye molecules and decompose them from a radical mechanism. Due to very small particles of the product and also their huge surface, the adsorption of Cd^{2+} ions from aqueous solution was studied. For this purpose, a solution contain Cd^{2+} ions with certain concentration were prepared and after that 0.01 g of the quantum dots were poured into the solution. The solution was then stirred for 24 h and two solution (before and after of adding carbon dots) were analyzed with atomic absorption spectroscopy (AAS) to determine the heavy metal ions concentration. The results showed the product adsorb 69 % of heavy metal ions from the water that is mainly due to the very high activate surface of the carbon dots (Fig. 9).

CONCLUSION

In this experimental work, very tiny nitrogen-doped carbon quantum dots were synthesized

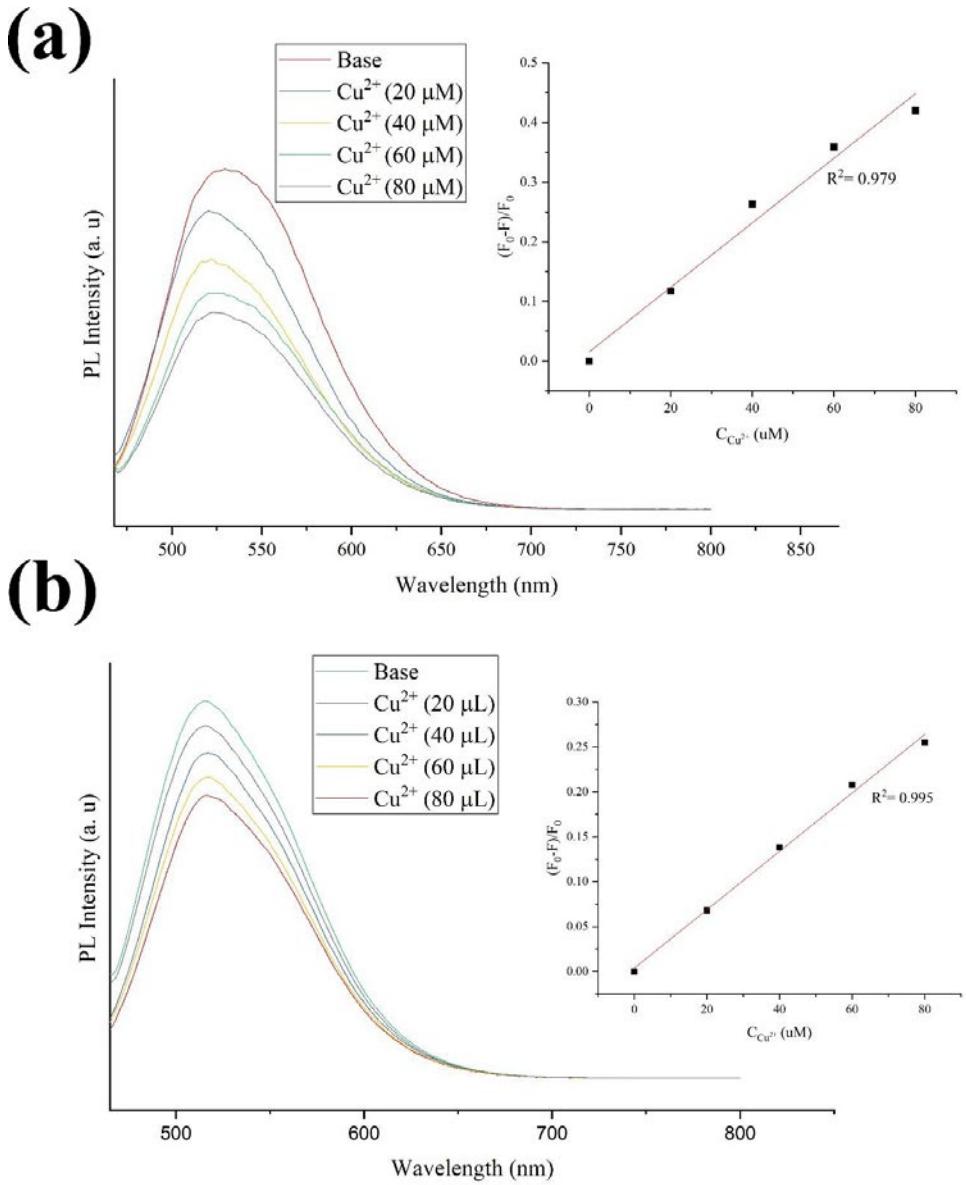

Fig. 6. Detection of Cu^{2+} with a) bare N-CQDs and b) N-CQDs modified with N-Methyl-2-pyrrolidone.

by a simple hydrothermal of milk. Different analysis such as XRD, FT-IR, EDS, SEM, and TEM showed the product has completely composed of very tiny nitrogen-doped carbon quantum dots. PL analysis showed the product has high photoluminescence intensity that was improved by surface modification of the quantum dots with N-Methyl-2-pyrrolidone that is mainly due to decreasing the trap states by surface modification. Due to high PL intensity of the product, we used them tothe detection of Cu^{2+} in the aqueous medium. The results showed the carbon dots can detect Cu^{2+} with 0-80 uM concentration that was improved by surface modification of the product with N-Methyl-2-pyrrolidone. The photocatalytic activity of the product was investigated by degradation of Acid brown. The results showed after 30 min the dye was completely decomposed in presence of carbon dots that is mainly due to high photocatalytic activity of the product. The surface adsorption of the product was studied by adsorption of Cd^{2+} heavy ions in the aqueous medium. It was found the product can adsorb the heavy metal ions up to 69 % from the water. It can

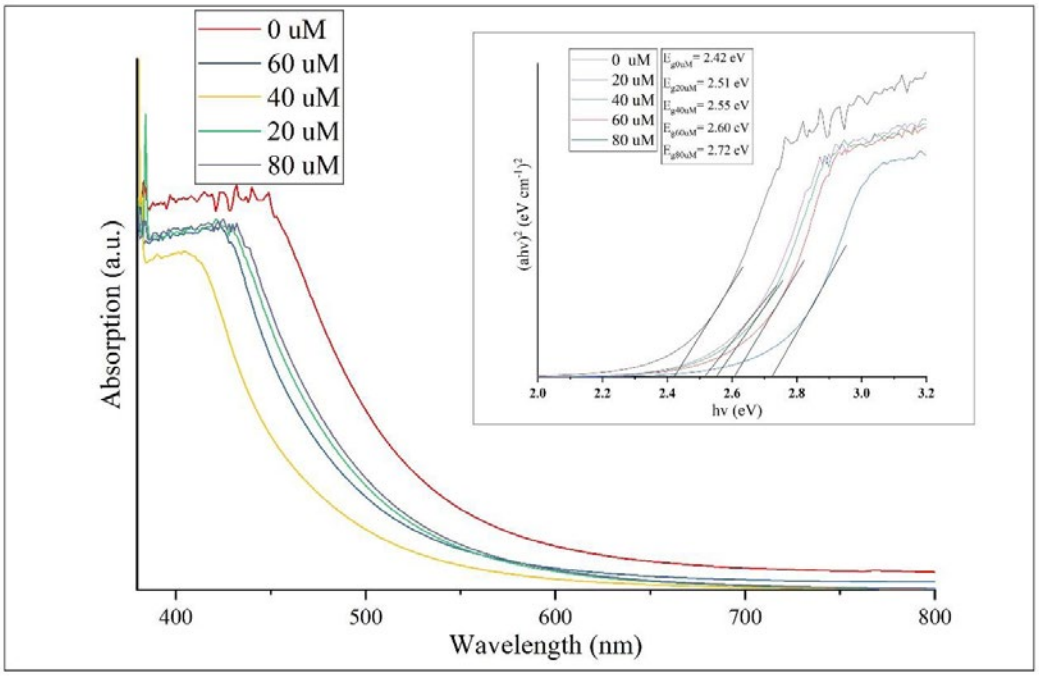

Fig. 7. UV-Vis spectroscopy of N-CQDs with Cu^{2+} with 0-80 uM concentration.

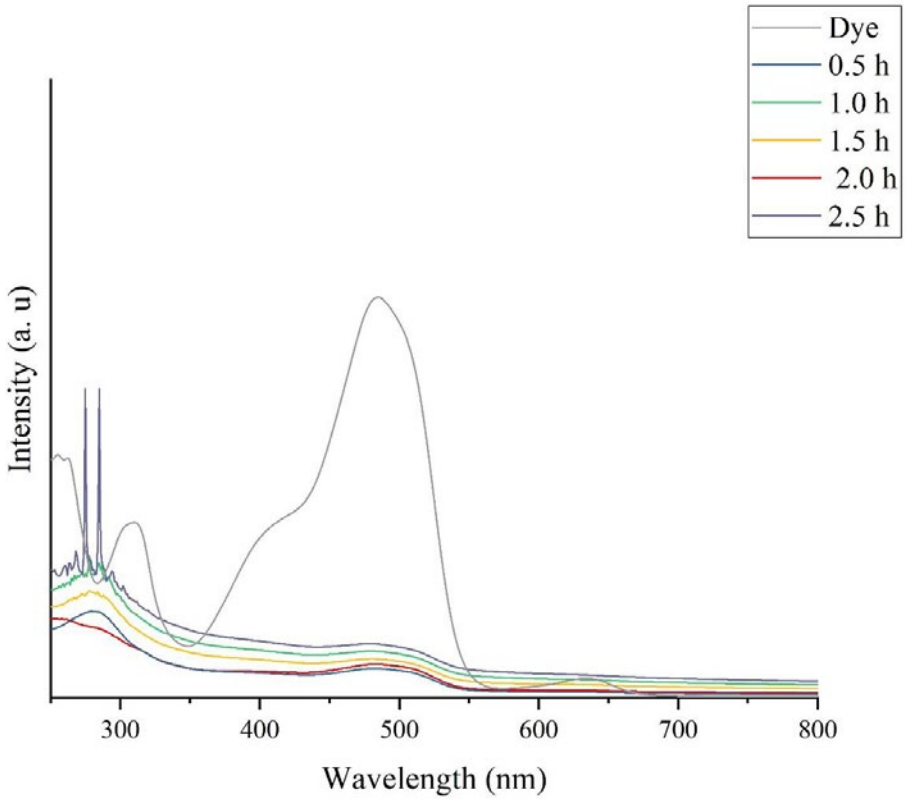

Fig. 8. Photocatalytic activity of N-CQDs.

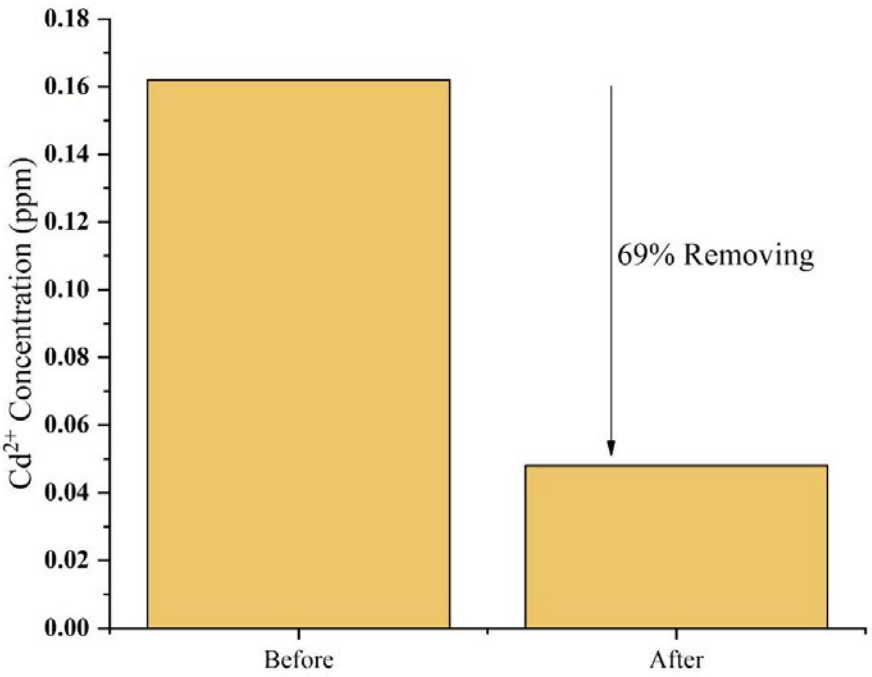

Fig. 9. Surface adsorption activity of N-CQDs.

be concluded that due to high photocatalytic and surface adsorption of the product, it can be used for water purification, potentially to degradation of organic pollution and removing heavy metal ions from the water.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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