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# POTENTIALITY OF NANOSILICA-DOPED CARBON DOTS AS FLUORESCENCE DETECTOR FOR COPPER ($Cu^{2+}$) IONS IN SIMULATED WASTEWATER

## (Potensi Nanosilica-Didop Titik Carbon Sebagai Pengesan Pendaflour untuk Ion Kuprum ($Cu^{2+}$) dalam Simulasi Air Sisa)

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## Abstract

Industrialization has a major impact on the ecosystem and the natural water composition particularly in places close to cities and manufacturing areas. Copper ($Cu^{2+}$) ion is one of the heavy metals present in the industrial effluent and is considered to be a toxic heavy-metal contaminant accounting to its extreme persistence and bioaccumulation. Current techniques for determining $Cu^{2+}$ ions in water include atomic absorption spectrometry (AAS), X-ray fluorescence spectrometry (XRF) and electrochemical methods, which provide high precision but have high maintenance costs and complicated preparation. Thus, an inexpensive, nontoxic and rapid sensing system for copper detection is needed. Herein, a simple and effective route for designing a fluorescence detector for $Cu^{2+}$ ions tracing was developed through a microwave-assisted rapid synthesis of carbon dots and nanosilica from Taal volcanic as its dopant. The parameters affecting the performance of the Taal Volcanic Ash Nanosilica-doped Carbon Dots (TVA/$SiO_2$-Cdots), such as silica dosage, agitation speed and contact time were investigated and optimized. Under optimized conditions, the TVA/$SiO_2$-Cdots showed the detection of $Cu^{2+}$ ions in simulated wastewater. The optical properties of the synthesized TVA/$SiO_2$-Cdots were determined using Fourier transform infrared spectroscopy (FTIR) and UV-Visible spectrophotometer which explained the quenching of TVA/$SiO_2$-Cdots photoluminescence upon addition of $Cu^{2+}$ ions. It has functional groups of Amine, C=C and C-O bonds. The mathematical correlation between photoluminescence (PL) intensity ratio of $SiO_2$-Cdots and $Cu^{2+}$ ion concentration in simulated wastewater was found to be a Gaussian equation. The result showed that the model has no significant difference with the detected concentrations using ultraviolet spectrophotometric screening method.

**Keywords:** carbon dots, copper ions, mathematical modelling, nanosilica, photoluminescence intensity

## Abstrak

Pembangunan industri memberi impak besar terhadap ekosistem dan komposisi air semulajadi terutamanya di kawasan-kawasan berdekatan dengan bandar dan kawasan pembuatan. Ion kuprum ($Cu^{2+}$) adalah salah satu daripada logam berat yang terdapat dalam air sisa industri dan dianggap sebagai pencemar logam berat toksik kerana ketekalan dan bioakumulasi yang tinggi. Teknik semasa untuk menentukan ion $Cu^{2+}$ dalam air termasuk spektrometri serapan atom (AAS), spektrometri sinar-X pendaflour (XRF) dan kaedah elektrokimia, yang memberikan ketepatan yang tinggi tetapi memerlukan kos penyelenggaraan yang tinggi dan persediaan yang rumit. Oleh itu, sistem pengesanan untuk penentuan kuprum yang murah, tidak toksik dan cepat diperlukan. Di sini, satu laluan yang mudah dan berkesan untuk reka bentuk pengesan pendaflour untuk pengesan ion $Cu^{2+}$ telah dibangunkan melalui sintesis cepat bantuan gelombang mikro titik karbon dan nanosilika dari abu gunung berapi Taal sebagai bahan tambahannya. Parameter-parameter yang mempengaruhi prestasi abu gunung berapi Taal nanosilika-didop titik karbon (TVA/SiO2-Cdots), seperti dos silika, kelajuan pengadunan, dan masa sentuhan telah dikaji dan dioptimumkan. Di bawah keadaan yang dioptimumkan, TVA/$SiO_2$-Cdots menunjukkan pengesanan ion $Cu^{2+}$ dalam simulasi air sisa. Sifat optik TVA/$SiO_2$-Cdots yang disintesis ditentukan menggunakan spektroskopi inframerah transformasi Fourier (FTIR) dan spektrofotometer UV-Cahaya Nampak yang menjelaskan pemelindapan fotoluminesens TVA/$SiO_2$-Cdots dengan penambahan ion $Cu^{2+}$. Ia mempunyai kumpulan berfungsi amina, C=C, dan C-O. Korelasi matematik antara nisbah intensiti fotoluminesen (PL) $SiO_2$-Cdots dan kepekatan ion $Cu^{2+}$ dalam simulasi air sisa didapati sebagai persamaan Gauss. Keputusan menunjukkan bahawa model ini tidak mempunyai perbezaan yang signifikan dengan kepekatan yang dikesan menggunakan kaedah saringan spektrofotometri ultraungu.

**Kata kunci:** titik karbon, ion kuprum, pemodelan matematik, nanosilika, intensiti fotoluminesens

## Introduction

Heavy metal contamination is one of the prevailing issues detrimental to human health and environment. As a result of continuous industrialization, the heavy metals found in nature seep through municipal water supplies. Concentrations of copper, lead, cadmium, chromium, mercury and arsenic are the most concerning, mainly because of their relatively high concentrations in industrial wastewater. Copper exposure can have serious consequences for human health. At great amounts of exposure, copper attacks the internal organs and builds up in the brain to cause nausea, vomiting, coma, and even death. People who survive contact with high exposures of copper may be left with pruritic dermatitis, anemia, and muscular convulsions. Due to these complications, the regulation and detection of the amount of copper in municipal wastewaters is needed [1].

High performance liquid chromatography (HPLC) combined with electrochemical- or UV-Vis-detectors and atomic absorption spectroscopy (AAS) are the most used methods for the detection of heavy metal ions. Despite the high levels of sensitivity and precision achieved by these techniques, the majority of them need expensive, complicated equipment that must be operated by skilled personnel, making them challenging to employ in on-site measurements for portable detection [2]. This leads to the discovery of photometry, fluorescence analysis, electrochemical methods, phosphorescence analysis, and chemiluminescence. These methods are operationally simple, fast, and low cost. Therefore, the developments of simple, sensitive, and reliable spectral analytical methods are still greatly significant.

Due to their multiple intriguing features, carbon dots (CDs) have recently become a distinct class of fluorescent nanomaterials. They are thought to be superior to traditional fluorescent materials like semiconductor quantum dots and organic dyes due to their exceptional features like high aqueous solubility, low toxicity, great biocompatibility, functionalizability, and photostability [3]. Moreover, studies show that silica doping in carbon dots improves its efficiency and luminosity. These silicas are extracted either from wastes such as bricks, concrete, and other construction waste materials, or in nature including sand, gravel, clay, and volcanic ash. In bulk volcanic ash, the chemical composition is mainly determined by the magma from which it is generated. The mineral composition of volcanic ash consists of about 45–75 wt.% of silica [4].

Many studies prove how detrimental the emission of volcanic ash is for both human health and the surroundings. This ash is also a potential source of silica, which could be synthesized to nanosilica, and doped into metal detecting carbon dots. Previous studies proved that doping carbon dots had led to an improved quantum yield. Moreover, heteroatom dope escalates as a more effective and general strategy to construct the optic and electron transfer properties of CDs. Hence, in this study, the researchers assessed the potentiality of utilizing nanosilica from Taal volcanic ash as a doping agent to carbon dots for $Cu^{2+}$ ions tracing. The researchers also concentrated on the goal of developing a mathematical model that could be utilized to assess its applicability in determining copper ion pollutants with reasonable sensitivity and validity.

The nanosilica-doped dots were used for the detection of Copper ($Cu^{2+}$) ions in wastewater. Taal volcanic ash (TVA) underwent a series of processes to produce silica, and afterward was subjected for characterization. Taal volcanic ash silica-doped carbon dots (TVA/$SiO_2$-Cdots) served as a fluorescence detector that is limited to $Cu^{2+}$ ions tracing only. In this study, its reactivity with other metals was no longer investigated. The effects of silica dosage, agitation and contact time in the PL intensity ratio of TVA/$SiO_2$-Cdots with Copper ($Cu^{2+}$) ions in simulated wastewater were determined in this study. Included also is the characterization of physicochemical properties of both carbon dots and TVA/$SiO_2$-Cdots. Moreover, the determination of the effects of PL intensity ratio of TVA/$SiO_2$-Cdots in simulated wastewater with an increasing amount of $Cu^{2+}$ ions was conducted. The simulated wastewater was prepared for a practical application of $Cu^{2+}$ tracing.

## Materials and Methods

### Production of nanosilica

Volcanic ash samples collected were subject to sieving to separate it according to particle size. A 40g sample of volcanic ash was prepared. This undergoes acid leaching particularly, 3M HCl solution to remove impurities. The sample was allowed to be soaked in the acid for three hours. Then washed until neutral (with pH ranging from 6.5 to 7.5) and dried in an oven at 100 °C for 6 hours. After drying, the sample went through reflux with 4M NaOH solution at 1:8 (w/v ratio) for four hours at 90-100 °C. The sample was left undisturbed overnight. Then, filtered using silica crucible and washed with warm water. After that, the HCl was added via burette. Note that there is a continuous addition of HCl until there is the formation of white gel, which is the Silica, and until the solution is acidic. Then, subjected it to further washing to be neutralized (with pH ranging from 6.5 to 7.5) and then dried in the oven for 6 hours at 120 °C.

To turn this silica into nanosilica, the dried sample was refluxed at 90-100 °C with 200 mL of 6M HCl solution for 5 hours. After 5 hours of reflux, HCl was decanted and added 160 mL 4M NaOH solution. This solution was subjected to constant stirring for about 4 hours before the addition of $H_2SO_4$. Note that there is a continuous addition of sulfuric acid until the formation of white precipitates and until the solution is acidic. The precipitates that will be formed is filtered and washed until neutral (with pH ranging from 6.5 to 7.5) and then, dried in the oven for 30 hours at 70 °C. The mass of the completely dried solid was recorded, which is the Nanosilica and the sample was prepared for the next stage of the study.

### Preparation of carbon dots

The carbon dots were prepared by microwave-assisted rapid production. Under agitation, 0.57g of L-cysteine was dissolved in 10 mL of deionized water, and 1.5g of citric acid was then added. The resulting solution was heated in a microwave for 4 minutes after being subjected to ultrasonication for 10 minutes. After the reaction, the product was allowed to cool naturally to room temperature before being dissolved with agitation in 10 mL of deionized water to produce a brown solution. In order to eliminate the contaminant, it was centrifuged for 10 minutes at 4000 rpm before being filtered. The obtained solution was extracted by ethyl acetate and then kept in a refrigerator under 4 °C for later use [5].

### Preparation of nanosilica-doped carbon dots

An amount 5 mL of carbon dots was mixed with various concentrations of silica (0.1, 0.3 and 0.5 g). It was then added to 25 mL of ethanol separately, and was stirred for 30 minutes at room temperature. After that, the reaction mixture was centrifuged at 3000-5000 rpm for 15-45 mins and the supernatant was discarded. The remaining pellets of silica-doped carbon dots were collected and washed three times with ethanol, and finally resuspended in ethanol with a concentration of 10 mg/mL.

### Photoluminescence intensity metering of best TVA/$SiO_2$-Cdots

The prepared TVA/$SiO_2$-Cdots with varying parameters were mixed with copper-containing and non-copper-containing simulated wastewater. The simulated wastewater in this study was made using a standard preparation by Official Methods of Analysis of AOAC International. Simulated wastewater was prepared by dissolving 1.9645 g $CuSO_4 \cdot 5H_2O$ in $H_2O$ and diluting it to 500 mL (1 mL = 1 mg Cu). After mixing thoroughly, the fluorescence spectra were recorded after 10 minutes at room temperature. Photos of the carbon dots were taken using an iPhone 11 Pro to collect light frequency, and the photographs were converted to luminous intensity using Image J Batch Software [6]. The fluorescence intensity ratio is measured at the excitation wavelength ($\lambda_{ex}$) of 365 nm using UV light [7].

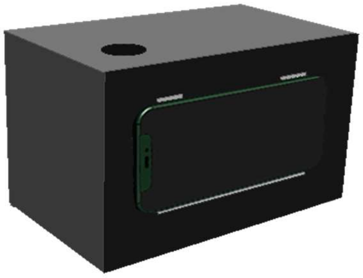

Figure 1. Luminous intensity metering set up

The difference in the photoluminescence ratio of TVA/$SiO_2$-Cdots in simulated wastewater and copper-containing-simulated water was used to determine the reactivity of TVA/$SiO_2$-Cdots with Copper ions. Thus, the parameters having the highest photoluminescence intensity difference were considered to be the best parameters.

### Preparation of simulated wastewater at increasing $Cu^{2+}$ ions concentration

For $Cu^{2+}$ detection, copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) was utilized as the source for $Cu^{2+}$ ions. 20 mL of prepared TVA/$SiO_2$-Cdots was dissolved in 100 mL of simulated wastewater. 5 mL TVA/$SiO_2$-Cdots aqueous solution was added to a beaker and the $CuSO_4 \cdot 5H_2O$ solution was subsequently added along with increasing concentrations. The concentrations of $Cu^{2+}$ ions are 0,1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ppm. Magnetic stirrer rotating at 3000 rpm facilitates uniform concentration at 20 °C.

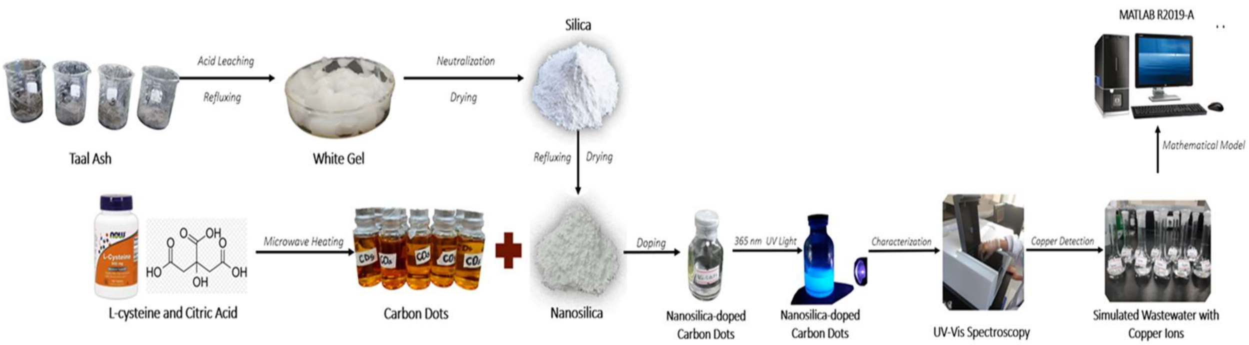

Figure 2. Schematic Roadmap of Research Methodology

### Characterization of nanosilica-doped carbon dots: Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FT-IR) spectrum was conducted to recognize the surface functional groups and conjugations existing on the TVA/$SiO_2$-Cdots' surface. Specific functional group of the molecule is read by its band association which gives the identification of the functional groups that constitute the material.

### Dynamic light scattering (DLS)

To determine the particle size and particle size distribution of the sample, DLS was used. It determines the particle size distribution by measuring the random changes in the intensity of light scattered from a suspension or solution.

### Formulation of mathematical model

In order to formulate a mathematical model that will describe the relationship between the photoluminescence intensity ratio of $SiO_2$-Cdots and $Cu^{2+}$ ion concentration in simulated wastewater, Matlab R2011-A was used in calculating the desired parameters for the mathematical model. After analysis of different models, the Gaussian method of modeling was selected as the best fit to represent the effects of increasing heavy metal concentration in simulated wastewater to photoluminescence intensity of TVA/$SiO_2$-Cdots. This method was selected over the other five methods namely exponential of 2nd power, Fourier of 2nd power, linear model of 3rd power and rational. For all generated equations, P(C) is the photoluminescence intensity (RLU) as a function of heavy metal concentration, C in parts per million.

### Validation of generated model using ultraviolet spectrophotometric screening method

To validate the degree of acceptability of the generated models, various concentrations of $Cu^{2+}$ in simulated wastewater were prepared prior to ultraviolet spectrophotometric screening. A Shimadzu UV/VIS spectrophotometer, UV-2700 was used for measuring the absorbance and recording the spectra. Wavelength range for copper examination using UV-Vis spectrophotometry is 185-500 nm [8]. The results were used to plot a calibration graph which was used to determine the concentration of $Cu^{2+}$ in produced water.

A 20 mL of prepared TVA/$SiO_2$-Cdots was dissolved in 100 mL of simulated wastewater. 5 mL TVA/$SiO_2$-Cdots aqueous solution was added to a 10 mL volumetric flask and the 5 mL of $CuSO_4 \cdot 5H_2O$ solution was subsequently added along with concentrations of 1 ppm to 10 ppm. The solutions were left to stand for 30 minutes and then analyzed using the UV-Vis spectrometer at a wavelength of 206 nm and the absorbance was taken.

### Statistical treatment

For the determination of the effect of given parameters to the photoluminescence intensity of synthesized TVA/$SiO_2$-Cdots, Minitab and analysis of variance was used. The Taguchi orthogonal array design was utilized to determine the effect of TVA/$SiO_2$-Cdots with copper ions ($Cu^{2+}$) in photoluminescence (PL) intensity in terms of three factors including silica dosage, agitation rate, and contact time.

For the simulated wastewater with $Cu^{2+}$, empirical models and data curves relating the photoluminescence intensity and the increasing concentration $Cu^{2+}$ ions were constructed using MATLAB R2011-A. One-way ANOVA was used to determine the effect PL Intensity of TVA/$SiO_2$-Cdots upon increasing $Cu^{2+}$ Ion concentration in simulated wastewater. Two paired t-tests were employed to determine the degree of comparability between the concentrations obtained from the generated model from that of detected concentration using ultraviolet spectrophotometric screening method.

## Results and Discussion

### Parameters that affect the PL intensity of TVA/$SiO_2$-Cdots with copper ($Cu^{2+}$) ions in simulated wastewater

Using Image J batch software, the PL intensity of the synthesized carbon dots was recorded at 17.692. This intensity is low and suggests that doping carbon dots with other material is a must in order to increase its PL intensity. In this study, the effect of varying parameters including silica dosage, agitation rate and contact time to the photoluminescence (PL) intensity of TVA/$SiO_2$-Cdots copper ions ($Cu^{2+}$) in simulated wastewater was evaluated using the $3^3$ Taguchi design which has 3 levels and 3 factors. The difference in the PL intensity of TVA/$SiO_2$-Cdots in simulated wastewater and copper-containing water determined the reactivity of TVA/$SiO_2$-Cdots with copper ions.

Table 1. PL Intensities of TVA/$SiO_2$-Cdots with and without copper

| **Silica Dosage** | **Agitation Rate** | **Contact Time** | **PL Intensity (Without $Cu^{2+}$)** | **PL Intensity (With $Cu^{2+}$)** |
|---|---|---|---|---|
| **0.1** | 3000 | 15 | 41.509 | 49.276 |
| **0.1** | 4000 | 30 | 43.059 | 51.139 |
| **0.1** | 5000 | 45 | 45.198 | 52.808 |
| **0.3** | 3000 | 30 | 44.110 | 52.79 |
| **0.3** | 4000 | 45 | 46.694 | 55.445 |
| **0.3** | 5000 | 15 | 43.956 | 53.159 |
| **0.5** | 3000 | 45 | 51.529 | 64.677 |
| **0.5** | 4000 | 15 | 45.268 | 55.092 |
| **0.5** | 5000 | 30 | 45.682 | 55.498 |

Based on the experimental results, the highest PL intensity recorded from both with and without copper ions were under the operational conditions 0.5 g, 3000 rpm and 45 minutes.

Table 2. Response table for signal to noise ratios

| | **Level** | **Silica Dosage (g)** | **Agitation Rate (rpm)** | **Contact Time (min)** |
|---|---|---|---|---|
| **Without Copper** | 1 | 32.72 | 33.16 | 32.78 |
| | 2 | 33.05 | 33.06 | 32.92 |
| | 3 | 33.52 | 33.05 | 33.58 |
| | Delta | 0.80 | 0.11 | 0.80 |
| | Rank | 1 | 3 | 2 |
| **With Copper** | 1 | 34.16 | 34.84 | 34.39 |
| | 2 | 34.61 | 34.62 | 34.50 |
| | 3 | 35.31 | 34.62 | 35.18 |
| | Delta | 1.15 | 0.22 | 0.79 |
| | Rank | 1 | 3 | 2 |

According to the values of S/N ratios for with and without copper ions, level 3 is considered best for silica dosage, level 1 for agitation rate and level 3 for contact time. These findings relate to the optimized value for each parameter such as 0.5 grams silica dosage, 3000 rpm agitation rate and 45 minutes contact time. From the table, it was shown that the most significant factor in PL intensity for with and without copper ions is the silica dosage which has the highest S/N ratio followed by the contact time and lastly is the agitation rate.

The results obtained are likewise comparable to those observed in the S/N ratios. According to the data, level 3 had the highest value in silica dosage, level 1 is best for agitation rate, and level 3 for contact time both for with and without copper ions. These results are also related to the optimal value for each parameter, such as 0.5 grams silica dosage, 3000 rpm agitation rate and 45 minutes contact time. According to the table, the silica dosage is the most important parameter in PL intensity followed by the contact time and lastly is the agitation rate with respect to means.

Table 3. Response table for means

| | Level | Silica Dosage (g) | Agitation Rate (rpm) | Contact Time (min) |
|---|---|---|---|---|
| **Without Copper** | 1 | 43.26 | 45.72 | 43.58 |
| | 2 | 44.92 | 45.01 | 44.28 |
| | 3 | 47.49 | 44.95 | 47.81 |
| | Delta | 4.24 | 0.77 | 4.23 |
| | Rank | 1 | 3 | 2 |
| **With Copper** | 1 | 51.07 | 55.58 | 52.51 |
| | 2 | 53.79 | 53.89 | 53.14 |
| | 3 | 58.42 | 53.82 | 57.64 |
| | Delta | 7.35 | 1.76 | 5.14 |
| | Rank | 1 | 3 | 2 |

Analysis of Variance (ANOVA) is used to determine and evaluate the overall effect of the different parameters on the experiment response, which is the PL intensity of the TVA/$SiO_2$-Cdots. The *p*-values of silica dosage, agitation rate and contact time without copper ions are both 0.011, 0.048, and 0.011, respectively. With copper ions, the *p*-values of silica dosage and contact time are 0.011 and 0.042, respectively while the agitation rate is 0.393. The values of the parameters are all less than the significance level of 0.05, therefore it indicates that there is a significant effect between the response (PL intensity) and factors (silica dosage, agitation rate and contact time).

The *F*-value is the test statistic that also determines the association of the response variable to the factors. The large *F*-value of silica dosage from with and without Copper ions compared to other parameters implies that it is statistically significant. The value of sum of squares (SS) is crucial as it influences the effectiveness of the response. The greater the SS value, the more effective it is. The SS values of each parameter are 26.9367 for silica dosage, 0.8909 for agitation rate and 26.8309 for contact time without copper ions and 80.990, 4.660, and 39.593 respectively for copper ions. The percentage contribution of silica dosage, agitation rate, and contact time are 42.44%, 1.41% and 42.28%, respectively without copper ions. On the other hand, the percent contribution for the TVA/$SiO_2$ with copper ions are 53.29% for silica dosage, 3.07 for agitation rate and 26.04% for contact time. The silica dosage for both the TVA/$SiO_2$ with and without copper ions has the highest SS value and % contribution which indicates that the silica dosage heavily impacted the absorption process. On the other hand, the agitation rate had the lowest % contribution. As can be observed, the results of ANOVA analysis for PL intensity of TVA/$SiO_2$-Cdots is similar to those of the results from S/N ratios.

In addition, using *t*-test, the *p*-value of TVA/$SiO_2$-Cdots with and without the addition of copper ions is 6.86E-0.5, it is found out that there is a significant difference in PL intensity ratio of TVA/$SiO_2$-Cdots upon the addition of $Cu^{2+}$ ions in simulated wastewater.

### Characterization of the best TVA/$SiO_2$-Cdots particle size and particle size distribution

The synthesized Cdots presented an average particle size diameter of 6.37 nm. After doping with nanosilica particles, the average diameter of the obtained TVA/$SiO_2$-Cdots increased to about 17.46 nm, suggesting the successful doping of nanosilica on the surface of carbon dots.

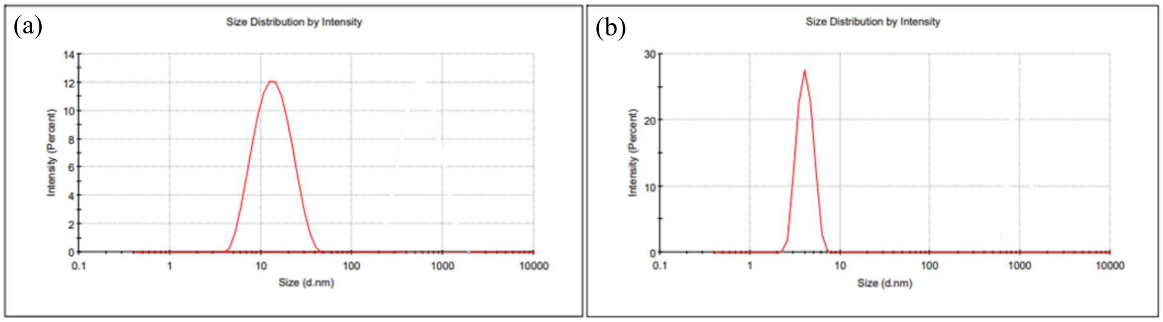

Figure 3. Particle size distribution of (a) Cdots and (b) TVA/$SiO_2$-Cdots

Table 4. Particle Size Distribution of Cdots and TVA/$SiO_2$ – Cdots

| **Sample** | **Z – Average (d.nm)** | **Peak** | **Size** | **Intensity** | **St. Dev. (d.nm)** |
|---|---|---|---|---|---|
| **Cdots** | 6.37 nm | Peak 1 | 7.63 | 100.0 | 2.797 |
| **TVA/$SiO_2$ – Cdots** | 17.46 nm | Peak 1 | 14.92 | 100.0 | 19.62 |

Particle size distribution is determined through dynamic light scattering (DLS) by measuring the random changes in the intensity of light scattered from a suspension or solution. The synthesized Cdots presented an average particle size diameter of 6.37 nm. A stable nanometric solution must have a size diameter of 1 to 100 nm. This confirms that the Cdots are nanometric. Particle size distribution of Cdots were shown in Figure 3 and Table 4. After doping with nanosilica particles, the average diameter of the obtained TVA/$SiO_2$-Cdots increased to about 17.46 nm, suggesting the successful doping of nanosilica on the surface of carbon dots.

**Functional group and its conjugation**

The distinct absorption peaks that defined the optical properties of Cdots were 3319.79, 1732.54, 1625.16, 1398.57, 1243.27 and 1013.58 $cm^{-1}$. The functional groups determined were N-H group, C=O group, C=C bond having an olefinic conjugated diene [9], C-H group, C-O group respectively. Typical conjugations with other double bond structures such as the C=C, C=O or aromatic rings will reduce the intensity frequency with strong or intense absorption bands [2].

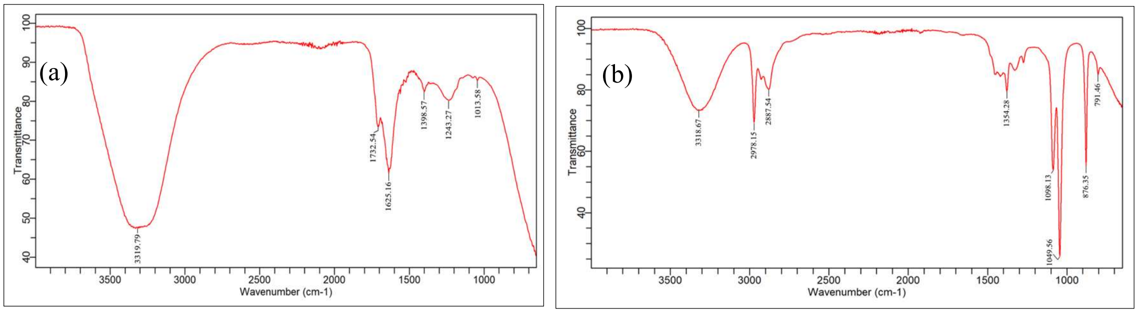

Figure 4. FTIR spectra of Cdots (a); TVA/$SiO_2$Cdots (b)

As for synthesized TVA/$SiO_2$-Cdots, the distinct peaks that determined their optical properties were observed at 3318.67, 2978.15, 1354.28, 1098.13, 1049.56, 876.35 and 791.46 $cm^{-1}$. The functional groups determined were N-H group, O-H group, sulfoxide group, C-O bond, strong Si-O-C bond, and strong C-Cl bond, respectively. The participation of the carbon dots in the synthesis of TVA/$SiO_2$-Cdots is determined because all the bands were shifted. The broad bands at 2978.15-2887.54 and 3318.67 $cm^{-1}$ in the synthesized TVA/$SiO_2$-Cdots which are assigned to the O-H and N-H functional groups accounts to the solubility and stability of the synthesized TVA/$SiO_2$-Cdots [9]. The presence of the said functional also plays a major factor in the color tuning of the synthesized TVA/$SiO_2$-Cdots. The blue shift in the emission wavelength of the TVA/$SiO_2$-CDots can be attributed to an amine state, which can emit shorter wavelengths under UV excitation [2]. The presence of functional groups such as hydroxyl group containing medium emission, and sulfoxide and C-Cl bond which both contain strong emission proves the higher strength of emission of TVA/$SiO_2$-Cdots compared to the synthesized carbon dots. In addition, the greater number of chemical bonds present in the TVA/$SiO_2$-Cdots indicates its high reactivity to heavy metals [10].

### Determination of PL Intensity TVA/$SiO_2$-Cdots upon increasing $Cu^{2+}$ ion concentration in simulated wastewater

The detection of $Cu^{2+}$ ions using TVA/$SiO_2$-Cdots was conducted at different concentrations between a range of 0 to 10 ppm. The results revealed that there was a drastic reduction in the PL intensity at 365 nm as the $Cu^{2+}$ concentration increased, demonstrating excellent sensing of the metal ion in the system. The PL intensity is significantly reduced and the emission wavelength of the fluorescent material along with a quencher do not change. As the concentration of $Cu^{2+}$ increases from 0 ppm to 10 ppm, the PL intensity of TVA/$SiO_2$-Cdots decreases from 245.9760 to 58.7867. Thus, the PL intensity of synthesized TVA/$SiO_2$-Cdots is $Cu^{2+}$ metal-ion-concentration-dependent.

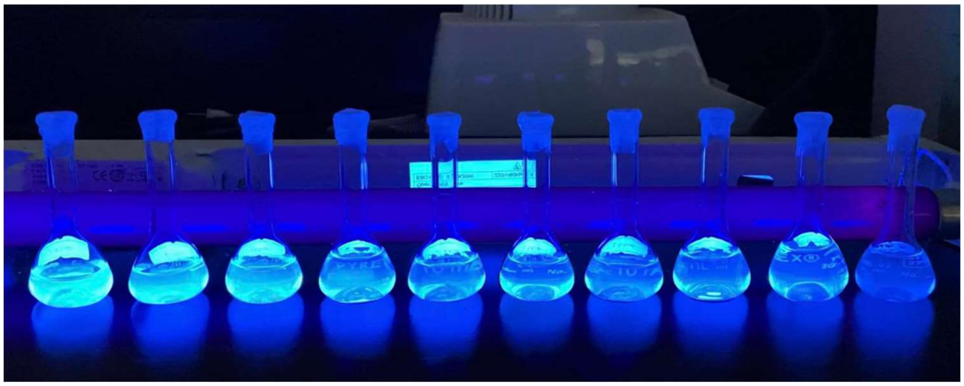

Figure 5. PL intensity of TVA/$SiO_2$-Cdots with the increasing $Cu^{2+}$ ion concentration in simulated wastewater

Table 6. PL Intensities of TVA/$SiO_2$-Cdots with the increasing $Cu^{2+}$ ion concentration in simulated wastewater

| **$CuSO_4 \cdot 5H_2O$ Concentration (ppm)** | **Photoluminescence Intensity (Simulated Wastewater)** |
|---|---|
| **0** | 245.9760 |
| **1** | 162.4328 |
| **2** | 134.9339 |
| **3** | 128.6127 |
| **4** | 125.5015 |
| **5** | 119.3487 |
| **6** | 108.4712 |
| **7** | 98.4624 |
| **8** | 86.7122 |
| **9** | 72.5457 |
| **10** | 58.7867 |

The fluorescence-quenching mechanism of normal CDs can be attributed to several factors such as inner filter effects, non-radiative recombination pathways, electron transfer and ion-binding interaction [11]. The fluorescence-quenching mechanism of TVA/$SiO_2$-Cdots was assessed using the UV–visible spectroscopy. The broad absorption band of TVA/$SiO_2$-Cdots around 185 and 400 nm showed definite reduction upon increasing $Cu^{2+}$ metal ion concentrations, therefore indicating the formation of complexations between the functional groups of TVA/$SiO_2$-Cdots and $Cu^{2+}$ ions.

On the basis of this observation, the researchers propose that the formation of complexation between TVA/$SiO_2$-Cdots and $Cu^{2+}$ results in electron transfer between $Cu^{2+}$ ions and TVA/$SiO_2$-Cdots (nonradiative energy), which plays a major role in quenching the PL intensity of TVA/$SiO_2$-Cdots. The figure below shows the fluorescence-quenching mechanism of TVA/$SiO_2$-Cdots by $Cu^{2+}$ metal ions. 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 $Cu^{2+}$.

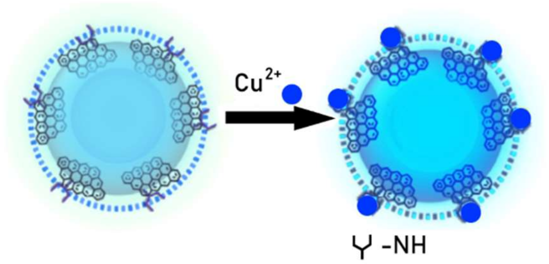

Figure 6. Quenching mechanism of carbon dots

A one-way ANOVA was performed to compare the effect of increasing $Cu^{2+}$ ion concentration in simulated wastewater and TVA/$SiO_2$-Cdots PL intensity. Since the data obtained had a p-value of 2.34E-07, which is less than 0.05, it meant that increasing $Cu^{2+}$ ion concentration in simulated wastewater has a high effect on the PL intensity of TVA/$SiO_2$-Cdots. The obtained F-stat value (58.41) is greater than the *F*-critical value (4.35) which is equivalent to a *p*-value less than alpha. Both of these mean that the PL intensity of TVA/$SiO_2$-Cdots was significantly affected by an increase in $Cu^{2+}$ ion concentration in simulated wastewater.

Table 7. Statistical result for the effect in PL intensity of TVA/$SiO_2$-Cdots upon increasing $Cu^{2+}$ ion concentration in simulated wastewater

| **Medium** | **Mean Square** | **Sum of Squares** | ***F*-Stat** | ***p* - value** | ***F*-critical** |
|---|---|---|---|---|---|
| **Simulated Wastewater** | 1288.45 | 25769.08 | 58.41 | 2.34E-07 | 4.35 |

### Mathematical model on the effect of $Cu^{2+}$ ion concentrations on the PL intensity of TVA/$SiO_2$-Cdots in simulated wastewater

After analysis of different models, the Gaussian method of modeling was selected as the best fit to represent the effects of increasing heavy metal concentration in simulated wastewater to photoluminescence intensity of TVA/$SiO_2$-Cdots. This method was selected over the other five methods namely exponential of 2nd power, Fourier of 2nd power, linear model of 3rd, power and rational.

Table 8. Generated model curves describing the effect of $Cu^{2+}$ ion concentrations to PL intensity of TVA/$SiO_2$-Cdots in simulated wastewater

| Types of Models Fit | Method | Equations Generated | SSE | $R^2$ | Adjusted $R^2$ | RMSE |
|---|---|---|---|---|---|---|
| Exponential (2nd Power) | Non-linear Squares | $P(C)= 73.73e^{-3.105C} + 172.3e^{-0.08933C}$ | 489.32 | 0.9811 | 0.9730 | 8.361 |
| Fourier (2nd Power) | Non-linear Squares | $P(C)= 1.791\times10^{14} - 2.387\times10^{14}\cos(0.0002733*C) - 3.831\times10^{11}\sin(0.0002733*C) + 5.969\times10^{13}\cos(5.466\times10^{-4}*C) + 1.915\times10^{11}\sin(5.466\times10^{-4}*C)$ | 127.86 | 0.9951 | 0.9901 | 5.0569 |
| **Gaussian (2 terms)** | **Non-linear Squares** | **$P(C)= 501.7e^{(\frac{-2.658-C}{2.308})^2} + 127.5e^{(\frac{2.839-C}{2.099})^2}$** | **12.908** | **0.9995** | **0.9990** | **1.1067** |
| Linear Model (Poly 3) | Linear Squares | $P(C)= -0.5801C^3 + 9.983C^2 - 59.85C + 230.9$ | 1268.2 | 0.9676 | 0.9230 | 13.46 |
| Power | Non-linear Squares | $P(C)= -7.128C^{1.1239} + 160$ | 1007.4 | 0.9798 | 0.9771 | 7.9349 |
| Rational | Linear Squares | $P(C)= \frac{-56.35C^3 - 7.285C^2 + 277C + 28}{C^2 + 2.889C + 2.382}$ | 22.598 | 0.9991 | 0.9983 | 2.126 |

In selecting the best mathematical model from the generated equation shown above, the equation's fitness must be measured in terms of SSE, adjusted, and root mean squared error. Similarly, the model with the lowest SSE and RMSE is the best fit because these assess the errors from the data points. The model that is closest to one in terms of $R^2$ is the most suitable [12]. Based on the generated models, the Gaussian equation has the lowest SSE and RMSE and it also has the closest value of 1 in terms of the $R^2$ and adjusted $R^2$ values.

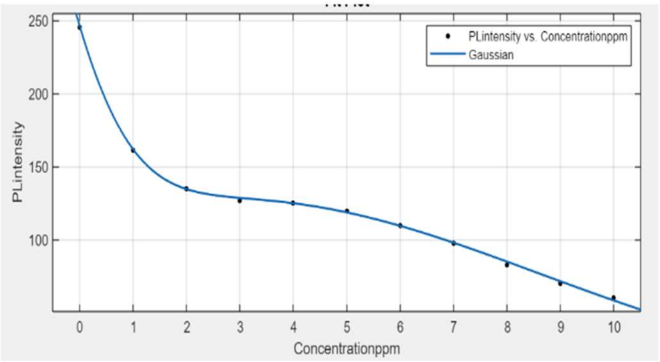

Figure 7. Curve fit of Gaussian method for $Cu^{2+}$

This model is best described by the equation for $Cu^{2+}$:

$$P(C) = 501.7\, e^{-(\frac{C+2.658}{2.308})^2} + 127.5\, e^{(\frac{2.839-C}{2.099})^2} \qquad (1)$$

where P(C) is the PL intensity in RLU as the function of heavy metal concentration, C in ppm.

### Comparison of the $Cu^{2+}$ ion concentration calculated from the generated model with the detected concentrations using ultraviolet spectrophotometric screening method

In the table above, the amount of calculated concentration from the selected model is shown. The photoluminescence intensity of TVA/$SiO_2$-Cdots decreases along with increasing formulated concentration of $Cu^{2+}$ ions. The calculated concentration using the model provides values that are approximately the same as the detected concentration using the ultraviolet spectrophotometric screening method, with a maximum deviation (by virtue of difference) of 0.2587 and minimum deviation of 0.0013. Furthermore, the model fits more effectively at low to moderate concentrations.

Table 8. Concentration of $Cu^{2+}$ ion based on calculated and detected values

| Formulated $CuSO_4{\cdot}5H_2O$ Concentration (ppm) | Photoluminescence Intensity | Calculated Concentration using the Model (ppm) | Detected Concentration |
|---|---|---|---|
| **1** | 162.4328 | 0.9869 | 0.9974 |
| **2** | 134.9339 | 1.9787 | 1.9653 |
| **3** | 128.6127 | 3.0212 | 2.9876 |
| **4** | 125.5015 | 3.8967 | 4.0259 |
| **5** | 119.3487 | 4.9221 | 4.9208 |
| **6** | 108.4712 | 6.0951 | 5.8364 |
| **7** | 98.4624 | 6.9563 | 7.0113 |
| **8** | 86.7122 | 7.8677 | 7.9274 |
| **9** | 72.5457 | 8.9208 | 9.0692 |
| **10** | 58.7867 | 9.9652 | 9.9865 |

Table 9. Statistical result for the comparison of calculated and detected concentration of $Cu^{2+}$ ion in simulated wastewater

| Mean Difference | Standard Deviation | Standard Error Mean | *t* -Value | *p* - value | *t*-Critical Value |
|---|---|---|---|---|---|
| **0.01171** | - | - | -0.331 | 7.48E-01 | 2.262 |

*Note. p – value depicts a value greater than α = 0.05 has no significant effect*

The p-value calculated is greater than 0.05 which denotes the acceptance of the null hypothesis. Thus, there is no significant difference between $Cu^{2+}$ concentrations calculated from the generated mathematical model with that detected from the UV-Vis screening method.

## Conclusion

The following conclusions were based on the mathematical analysis of the data using the appropriate computer software and the in-depth interpretation of the results and findings. Varying parameters such as silica dosage, agitation rate, and contact time play significant roles in copper detection. There is the presence of amine N-H, carbonyl C=O, C=C, C-H, and C-O groups in the Cdots, whereas the presence of N-H, O-H, and sulfoxide groups as well as C-O, strong C=C, and strong C-Cl bonds in TVA/$SiO_2$-Cdots, which are responsible for their color emission, stability, and reactivity. Moreover, the results of dynamic light scattering measurements indicated that upon silica doping, the average diameter of CDs in ethanol had increased, indicating a success in the doping process. The photoluminescence intensity at 365 nm decreased significantly along with the increasing $Cu^{2+}$ ion concentration in the range of 0 to 10 ppm in simulated wastewater, which indicated that the photoluminescence intensity of TVA/$SiO_2$-Cdots was quenched by $Cu^{2+}$ ions. The generated mathematical model in equation 1, can be used to determine $Cu^{2+}$ concentrations at specific ranges having no significant difference with the ultraviolet spectrophotometric screening method.

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