VERSATILE COFFEE CARBON NANOPARTICLES AS Pb$^{2+}$, Cu$^{2+}$ ION DETECTORS AND COPPER CORROSION INHIBITORS

KALEMA CHRISTOPHER

GRADUATE SCHOOL
IPB UNIVERSITY
BOGOR
2019
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Bogor, August 2019

Kalema Christopher
NIM G451178271
SUMMARY

KALEMA CHRISTOPHER. Versatile Coffee Carbon Nanoparticles as Pb\(^{2+}\), Cu\(^{2+}\) ion Detectors and Copper Corrosion Inhibitors. Supervised by ZAINAL ALIM MAS’UD and NOVRIYANDI HANIF.

A simple and tandem hydrothermal and pyrolysis method was developed for the synthesis of blue fluorescence carbon nanoparticles from coffee green bean powder and urea as raw materials. The carbon nanoparticles were characterized by ultraviolet visible spectrophotometer, Fourier-transform infrared spectroscopy and ocean optics spectrophotometer. The carbon dots had a bright blue emission centered at 505 nm under UV light with the excitation wavelength at 360 nm.

The carbon dots also showed a quenching effect with lead (ii) ions and copper (ii) ions. Furthermore, a method for copper (ii) and lead (ii) ion detection in aqueous solution was developed with selectivity to some common ions and acceptable linearity of 0.961 and 0.951 respectively. The limit of detection for lead (ii) ions and copper (ii) ions was 1.358 µg/L and 0.447 mg/L respectively.

The carbon dots also demonstrated the ability to act as copper corrosion inhibitors in 1% sodium chloride solution showing an inhibition efficiency of 76.98% at a concentration of 1000 mg/L. It is worth noting that the synthesized fluorescent carbon dots are eco-friendly and inexpensive. They could find application in chemical sensing and copper corrosion inhibition in salt environments.

Keywords: Carbon nanoparticles, chemical sensing, corrosion inhibitor, pyrolysis, quenching.
RINGKASAN

KALEMA CHRISTOPHER. Nanopartikel Karbon dari Kopi sebagai Detektor \(\text{Pb}^{2+}\), \(\text{Cu}^{2+}\) dan Inhibitor Korosi Tembaga. Dibimbing oleh ZAINAL ALIM MAS’UD dan NOVRIYANDI HANIF.

Metode sederhana yang merupakan gabungan antara hidrotermal dengan pirolisis telah berhasil dikembangkan untuk menyintesis nanopartikel karbon berfluoresensi warna biru dari bubuk biji kopi hijau dan urea sebagai bahan baku. Nanopartikel karbon dikarakterisasi dengan spektrofotometer UV-Vis, spektroskopi inframerah dan spektrofotometer “ocean optics”. Karbon nanopartikel yang sudah disintesis memiliki emisi warna biru terang pada 505 nm di bawah sinar UV dengan panjang gelombang eksitasi pada 360 nm.

\(\text{Pb}^{2+}\) dan \(\text{Cu}^{2+}\) memberikan efek penurunan intensitas fluoresensi karbon dot yang dihasilkan. Penurunan fluoresensi tersebut selektif terhadap \(\text{Pb}^{2+}\) dan \(\text{Cu}^{2+}\) dibandingkan dengan beberapa ion lain dengan nilai linearitas masing-masing 0,961 dan 0,951. Limit deteksi untuk \(\text{Pb}^{2+}\) dan \(\text{Cu}^{2+}\) adalah masing-masing 1,358 \(\mu\text{g/L}\) dan 0,447 mg/L.

Karbon dot juga menunjukkan kemampuan sebagai inhibitor korosi tembaga dalam larutan NaCl 1% dengan nilai efisiensi penghambatan 76.98% pada konsentrasi 1000 mg/L. Karbon dot yang dihasilkan bersifat ramah lingkungan dan murah. Selain itu, karbon dot dapat juga diaplikasikan sebagai sensor kimia dan penghambatan korosi tembaga dalam lingkungan garam.

Kata kunci: Inhibitor korosi, nanopartikel karbon, pirolisis, sensor kimia.
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VERSATILE COFFEE CARBON NANOPARTICLES AS Pb²⁺, Cu²⁺ ION DETECTORS AND COPPER CORROSION INHIBITORS

KALEMA CHRISTOPHER

A thesis
Submitted in fulfilment of the requirements for the
Master of Science
Degree in
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GRADUATE SCHOOL
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External Examiner for Thesis Final Examination: Dr Drs Komar Sutriah, MSi
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Date of graduation: 19 Aug 2019
PREFACE

In the name of Allah, the most merciful

First and foremost I would like to thank God, the most merciful that this scientific research has been completed successfully. The topic of my research since January 2019 was Versatile Coffee Carbon Nanoparticles as Pb\(^{2+}\), Cu\(^{2+}\) ion Detectors and Copper Corrosion Inhibitors.

I would like to send sincere thanks to Dr Drs Zainal Alim Mas’ud, DEA and Novriyanda Hanif, SSi, MSc, DSc for the continuous academic support during my masters study. Their motivation, patience, enthusiasm, knowledge and timely feedbacks during my masters study. I am also grateful to the Government of Indonesia through the Ministry of Research, Technology and Higher Education (RISTEKDIKTI) for their generous funding that made by master degree study possible. Special thanks go to the chemistry lecturers and non-teaching staff for training and encouraging me.

My thanks also extend to the all my classmates during my masters study for welcoming me in the chemistry department, helping me, guidance and friendship. Finally, I would like to thank my family, my parents, my siblings for the encouragement and being patient.

Bogor, August 2019

Kalema Christopher
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1 INTRODUCTION

Background

Fluorescent carbon dots (C-dots) are one of the quintessential classes of carbon-based nanomaterials less than 10 nm in size that have attracted attention due to their remarkable properties such low toxicity, biodegradation ability, high water solubility, good biocompatibility, and unique photoluminescence properties (Song et al., 2017; Jiang et al. 2015; Pan et al. 2015; Tao et al. 2011). These properties support their application in biomedicine, catalysis optoelectronic devices, corrosion inhibition and metal sensing (Roy et al. 2015; Yang et al. 2014). C-dots can be synthesized from both synthetic and natural precursors. However, natural precursors are favored due to their large abundance. These include; glucose (Yang et al. 2011), bread, jaggery and sugar caramel (Sk et al. 2012), banana (De et al. 2013), grass (Liu et al. 2012), orange juice (Sahu et al. 2012), pear juice (Liu et al. 2018), Nescafe original instant coffee (Jiang et al. 2014) etc. Synthetic methods of C-dots include arc discharge, ultrasonic/microwaves, laser ablation, electrochemical synthesis and hydrothermal treatments (Mishra et al. 2018.). The versatility of carbon dots is also another aspect that we investigated. In this research, the coffee carbon dots synthesized demonstrated the ability to act as corrosion inhibitors and Pb$^{2+}$ and Cu$^{2+}$ ion sensors as in appendix 1.

Numerous fluorescent systems such as fluorescence quenching, energy transfer and the sensitivity of fluorescent spectra to molecular environments support the application of carbon dots in bio and chemo sensing. Fluorescence detection offers a fast response and facile to carry out. However, fluorescence detection with a high selectivity and sensitivity still needs more research (Liu et al. 2018). C-dots are widely applied in metal detection also partly due to the affinity and the coordination of the varied metal ions with the aromatic residues that make up the carbon dots (Tan et al. 2014). Copper II ions (Cu$^{2+}$) are a vital trace element. Nonetheless, elevated concentrations beyond tolerable limits of Cu$^{2+}$ is toxic to human cells and could trigger many severe disorders and diseases like kidney failure, Wilson disease and infant liver damage (Mubarak et al. 2017). Thus, the study, development and fabrication of swift and efficient detection for Cu$^{2+}$ is highly imperative. Another noxious heavy metal that requires swift detection is lead (ii) ions (Pb$^{2+}$) because too much exposure to lead sparks lead poisoning, which affects multiple body systems most especially in children, and when lead accumulates in the brain liver kidney and bones the effects are lethal (Wani et al. 2015). Fluorescent carbon dots from different sources were efficaciously used in the detection of Cu$^{2+}$ due to their photoluminescence property (Cotrugo et al. 2015) and table sugar derived Carbon dot have also been reported as naked eye sensors for toxic Pb$^{2+}$ ions (Ansi et al. 2008).

Most corrosion inhibitors applied regularly are organic compounds containing some electronegative atoms Nitrogen (N), Sulphur (S), Phosphorus (P), Oxygen (O) and multiple bonds, which have free electron pairs to form a bond with the metal surface (Sigurcik et al. 2015; Abd El Haleem et al. 2013; Doner et al. 2013). Today, the inhibition efficiency of many organic compounds has been
reported. These include; imidazoles, triazoles, ionic liquids and Schiff bases (Cui et al. 2017). However, due to concerns on environmental safety and human health, the application of some of those organic inhibitors is limited due to their toxicity (Qiang et al. 2017). Robusta coffee beans contain more caffeine (hence more nitrogen content) compared to Arabica coffee (Dias et al. 2015; BPS, 2019). This implies that robusta offers a better choice of coffee for the synthesis of carbon dots that can be applied as metal corrosion inhibitors.

In this study, a simple synthesis of carbon dots using coffee and urea by tandem hydrothermal and pyrolysis method was established. The absorption, functional group characterizations and fluorescence property of the prepared carbon dots were investigated. The fluorescence of C-dots could be directly quenched by Cu\(^{2+}\) and Pb\(^{2+}\) linearly in the concentration range from 0.1-50.0 mg/L and 5.0 -50 µg/L respectively. The C-dots could inhibit the corrosion of copper by 76.98 % at 1000 mg/L in 1% NaCl solution.

**Statement of the Problem**

Numerous fluorescent systems such as fluorescence quenching, energy transfer and the sensitivity of fluorescent spectra to molecular environments support the application of carbon dots in bio and chemo sensing. Fluorescence detection offers a fast response and facile to carry out. However, fluorescence detection with a high selectivity and sensitivity still needs more research. In this research carbon nanoparticles were synthesized and applied in the detection of Pb\(^{2+}\) and Cu\(^{2+}\). Corrosion refers to the electrochemical degradation of metals as a result of reactions with the environment. It leads to the loss of materials when they lose their physical, chemical and electrical properties subsequently leading to loss of or low performance. A vast number of methods have been applied to inhibit corrosion such as using corrosion inhibitors. This is because they are relatively effective and inexpensive. However, most of the inorganic and organic corrosion inhibitors are relatively toxic and require complex synthetic methods. Therefore, there is a need to search for eco-friendly and highly efficient ones. This study will involve the tandem hydrothermal and pyrolysis synthesis of fluorescent carbon dots from coffee as an inhibitor for copper corrosion in 1% sodium chloride solution. This is because its powder contains nitrogen based groups that are vital in the forming of adsorption interactions with the metal surface.

**Objectives of the research**

This research was aimed at the synthesis of carbon dots from coffee; detect Pb\(^{2+}\) and Cu\(^{2+}\) ions in aqueous solution using the synthesized carbon dots and testing their corrosion inhibition efficiency dots on copper coupon in 1 % NaCl at room temperature.

**Benefits of the research**

This research Expands knowledge on the synthesis of C-dots from natural precursors and can lead to fabrication of electrochemical sensors.
2 METHOD

Materials

Robusta Coffee (*Coffea canephora*) was obtained from the local farmers group (Koperasi Kopi Bogor), Ethanol (96%), acetone (99.5%), copper, coupon (99.9%), H\textsubscript{2}SO\textsubscript{4} (98%), KBr (99%) CuSO\textsubscript{4}, NaCl, KCl, FeCl\textsubscript{2}, Pb(NO\textsubscript{3})\textsubscript{2}, urea. All the reagents were purchased from commercial sources and used without any further purification.

Tools

These include; Barnstead Furnace 47900, 365 nm UV lamp, 1700 UV-Vis Spectrophotometer Shimadzu, Ocean Optics Spectrophotometer USB 4000, FTIR Spectrometer and a DY 2300 potentiostat.

Procedures

Synthesis of Carbon dots from *coffea canephora*

The carbon dots were prepared by tandem hydrothermal treatment and pyrolysis of green coffee powder and urea. In a typical synthesis, 3.0 g coffee and 1.2 g urea were dissolved in 20 mL of deionized water. (Shi *et al.* 2019). The sticky cloudy solution was poured into 30 mL crucible as a reactor vessel. The reactor vessel was then wrapped in Aluminum foil, placed in a furnace and heated at 220 °C for 5 hours. After cooling down to room temperature, the black residue was dissolved in water and carbon dots were obtained by removing larger particles through centrifugation at 5000 rpm for 15 minutes. The supernatant was then evaporated at 80 °C to obtain the highly fluorescent blue carbon dots.

Characterization

The absorption spectra of the 100 mg/L carbon dots in aqueous solution were recorded with a Shimadzu UV-Vis Spectrophotometer. The absorbance measurements were carried out at a wavelength of 200-700 nm with a 0.5 nm wavelength interval to obtain the absorption spectrum. The FTIR spectrum of the C-dots was recorded on a Nicolet FTIR spectrometer (Impact-410, Madison, USA) using a KBr pellet. A total of 20 mg of C-dot was mixed with 0.2 g KBr and finally all the fluorescence intensity measurements were carried out on an ocean optics spectrophotometer USB 40000 at a wavelength of 400-700 nm.

Fluorescence intensity measurement of Cu\textsuperscript{2+} ions

Various concentrations of Cu\textsuperscript{2+} solutions namely; 0.1, 0.5, 1.0, 5.0, 10.0 and 50.0 mg/L were added separately to a cuvette containing 1.5 mL of carbon dots solution. The mixture was homogenized. The fluorescence emission spectra of carbon dots were recorded from 376 to 700 nm and the fluorescence intensity was monitored at 505 nm. at the excitation wavelength of 360 nm. The procedure was repeated with different concentrations of Pb\textsuperscript{2+} namely; 5, 10, 15, 20, 50 µg/L. To assess the selectivity of carbon dots quenching toward Cu\textsuperscript{2+} ion and Pb\textsuperscript{2+},
interference assays were performed under identical conditions using five 20 mg/L metal ions potassium ions (K⁺), sodium ions (Na⁺), iron II ions (Fe²⁺), copper II ions and lead II ions.

Preparation of electrode and solutions
The copper coupons were abraded, degreased with acetone, washed ultrasonically with deionized water. The corrosion medium was prepared with and without various concentrations (blank, 200, 400, 600, 800 and 1000 mg/L) of carbon dots. The 1 % NaCl was prepared by dissolving 1 g of sodium chloride crystals in 100 ml of deionized water. The experiments were carried out at room temperature and freshly prepared solutions were used for each set of experiments.

Weight loss measurements
The weight loss procedures were carried out according to the ASTM standard G31-72. Samples with a dimension of 1.0 cm × 1.0 cm × 0.02 cm were immersed in 1 % sodium chloride solution in a 20 mL vessel with and without various concentrations of the carbon dots for 14 days. The samples were then removed and washed with deionized water, dried and weighed at various time intervals. The average value of the weight loss obtained was used for corrosion rate and inhibition efficiency calculations.

Electrochemical measurements
The studies were conducted in 1% NaCl test solution using three electrodes setup in one compartment cell. A platinum sheet was used as the counter electrode and Ag/AgCl as the reference. The working electrode was copper (99.99% purity) cylindrical rod embedded in a resin with one bottom surface (3.34 cm²) exposed to the solution. The DY 2300 Potentiostat/Galvanostat was utilized. The detection was carried out at room temperature using the linear sweep voltammetry technique with a potential range of −2.0 V to 0.5 V, a scan rate of 0.01 V/s, and a sensitivity of 0.001.

3 RESULTS AND DISCUSSIONS

Carbon dots obtained from coffee by tandem hydrothermal and pyrolysis synthesis method
The carbon dots were prepared by carbonization of urea and green bean coffee powder. Direct hydrothermal treatment followed by pyrolysis in a furnace at 220 °C for 5 hours produced a black-coloured fine powder with a high solubility in water. The aqueous solution of C-dot exhibited a light brown colour under daylight and emits intense blue light under 365 nm UV light exposure (Figure 1). Hence the aqueous solution qualitatively depicts the presence of fluorescent carbon nanoparticles.
The UV-Vis absorption spectrum of the aqueous solution of carbon dots showed a strong absorption peak at around 280 nm. The peak at 280 nm (Figure 2) is attributed to n-π* transition of the C=O bonds and that indicate the presence of carboxyl group on the carbon dots surfaces. The photoluminescence spectra of synthesized carbon dots showed a maximum emission at 505 nm at different carbon dot concentrations. The origin of this strong emission is probably due to the presence of several functional groups on the surface that act as emissive traps for the electronic transition (De et al. 2013).

FTIR spectrum of the carbon dots

FTIR analysis was carried out to elucidate the functional groups and surface functionalization of C-dots. The carbon dots exhibited the presence of many hydrophilic groups at the frequencies of 3237 cm\(^{-1}\), 1711 cm\(^{-1}\) and 1381 cm\(^{-1}\) correspond to the presence of –OH or –NH\(_2\), C=O, and C-N respectively. The presence of these functional groups ensured that the synthesized C-dots have excellent water solubility (Qin et al. 2011) (Figure 3).
**Figure 3** The FTIR spectra of the carbon dots

**Cu²⁺ and Pb²⁺ ion sensing using carbon dots**

The emission spectra of a fixed amount of carbon dots (100 mg/L) in response to the concentrations of copper and lead were plotted. They showed concentration dependent trend and since this was a quenching process, a standard Stern-Volmer relationship was adopted to model the intensities recorded at various wavelength of the maximum emissions.

\[ \frac{F_0}{F} = K_{SV} [C] + 1 \]

Where both \( F_0 \) and \( F \) denote the fluorescence intensities of carbon dots before and after adding the metal ions. \( K_{SV} \) denotes the Stern-Volmer quenching constant. From the equation, a linear relationship between the fluorescence intensities before and after addition of metal ions was obtained.

**Figure 4** (a) The fluorescence spectra of the carbon dots at various Cu²⁺ concentrations monitored at 505 nm. (b) the linearity of the expression from Stern-Volmer equation.
Figure 5 (a) The fluorescence spectra of the carbon dots at various Pb\textsuperscript{2+} concentrations, monitored at 505 nm. (b) the linearity of the expression from Stern-Volmer equation

The limits of detections of the synthesized carbon dots were calculated from

\[ \frac{3\sigma}{s} \]

where \( \sigma \) denotes the standard deviation of the carbon dots corrected blank signals (n=3) and \( s \) denotes the slope of the linear curve from the Stern-Volmer equation. The \( R^2 \) of the linear curve of copper (ii) ions was 0.951 and that of lead (ii) ions was 0.961 (appendix 5 and 6). The Non-specificity of the carbon dots towards lead (ii) ions and copper (ii) ions can be contributed to the effect of pyrolysis which degrades the surface of carbon dots leaving it bare to the environment hence can come into contact with the metal ions around (Tan et al. 2014). However, different metal ions induce different degree of disturbances on the material fluorescence process depending on their electronic configuration and the interaction affinities. Hence surface modification of carbon dots can be done to improve their specificity. The limit of detection of Cu\textsuperscript{2+} was 0.447 mg/L and that of Pb\textsuperscript{2+} was 1.358 µg/L.

Selectivity of the carbon dots

The Pb\textsuperscript{2+} and Cu\textsuperscript{2+} ions could quench the fluorescence intensity of the carbon dots but not any other ions. The addition of K\textsuperscript{+} and Na\textsuperscript{+} and Fe\textsuperscript{2+} did not change the fluorescence intensity of carbon dots. However, only 20.0 mg/L of Cu\textsuperscript{2+} and Pb\textsuperscript{2+} effectively quench the fluorescence intensity of carbon dots however the lead II ions quench the fluorescence intensity of the carbon dots further (Figure 6). The reason for the above results can be because K\textsuperscript{+}, Na\textsuperscript{+} are diamagnetic and lack the ability of paramagnetic quenching mechanism with the carbon dots. While iron (ii) Fe\textsuperscript{2+} when bonded to some ligands can form a diamagnetic compound because of the creation of a low spin situation.
Results from weight loss measurements

Using equations (1) and (2), the inhibition efficiency of the different concentrations of carbon dots was calculated and the corrosion rate of the copper piece.

\[
\nu_{corr} = \frac{K \times W}{A \times T \times D} \quad (1)
\]

\[
\eta_w (\%) = \frac{\nu_{corr} - \nu_{corr}^0}{\nu_{corr}^0} \times 100 \quad (2)
\]

Where \( K = 8.76 \times 10^4 \), \( W \) is the copper weight loss in grams, \( A \) is the total surface area of copper (cm\(^2\)), \( T \) is the immersion time (hours), \( D \) is the density of the test specimen \( \nu_{corr}^0 \) and \( \nu_{corr} \) are the blank corrosion rates and with inhibitor, respectively.

The corrosion rate of copper decreased with the increasing inhibitor concentration from 0 to 100 mg/L implying that the coffee carbon dots have a corrosion inhibition activity. Therefore in aqueous solution, the \( \pi \) electrons and the lone electron pair oxygen and nitrogen atoms donate to the unoccupied d orbital of copper to form strong coordinate bond thereby facilitating the adsorption of the inhibitor molecules to metal surfaces (Anindita et al. 2018, Qin et al. 2011). The highest inhibition efficiency was 84.94% at the carbon dot concentration of 1000 mg/L in 1% sodium chloride solution (appendix 2 and 3).
**Potentiodynamic polarization measurements**

The current–potential curves for copper in sodium chloride solutions were obtained in the absence and presence of various concentrations of the coffee carbon dots at room temperature. The obtained data was converted into a Tafel curve in order to obtain the equation of lines on cathode and anode (Table 1). The equation of the two equations of the line produced a value of corrosion current. Corrosion currents were the basis for calculating the efficiency of inhibition. The coffee carbon dots inhibitor is of a mixed type. This is because of its ability to form a film compound that reduces both anodic and cathodic reactions hence protecting the metal.

![Figure 8 The Tafel polarization curves of copper in 1% NaCl at different carbon dot concentrations.](image)

<table>
<thead>
<tr>
<th>Sample (mg/L)</th>
<th>Tafel Equation</th>
<th>Cathode Slope</th>
<th>Anode Slope</th>
<th>E (mV)</th>
<th>Y</th>
<th>I (mA)</th>
<th>θ</th>
<th>Corr. Rate (mm/yr)</th>
<th>IE</th>
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<tbody>
<tr>
<td>Blank</td>
<td>Y = -0.0047x – 5.7879 Y = 0.0045x + 2.8683</td>
<td>-940.9</td>
<td>-1.3657</td>
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<td>1</td>
<td>0.1492</td>
<td>0</td>
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<tr>
<td>400</td>
<td>Y = -0.0035x – 3.0199 Y = 0.0072x + 1.6899</td>
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<td>-1.4792</td>
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<td>0.233</td>
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<td>500</td>
<td>Y = -0.0038x – 3.7403 Y = 0.0093x + 3.5545</td>
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<td>-1.6241</td>
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<tr>
<td>600</td>
<td>Y = -0.0052x – 5.5516 Y = 0.0068x – 3.2926</td>
<td>-737</td>
<td>-1.7192</td>
<td>0.019</td>
<td>0.5581</td>
<td>0.06592</td>
<td>55.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>Y = -0.006x – 6.5246 Y = 0.0063x + 2.8067</td>
<td>-758.6</td>
<td>-1.973</td>
<td>0.0106</td>
<td>0.627</td>
<td>0.03677</td>
<td>75.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>Y = -0.0059x – 5.9374 Y = 0.0069x + 2.5963</td>
<td>-666.7</td>
<td>-2.004</td>
<td>0.0099</td>
<td>0.77</td>
<td>0.03435</td>
<td>76.98</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From the Table 1, it was observed that the maximum inhibition efficiency was 76.98% at the inhibitor concentration of 1000 mg/L (appendix). However the increase in inhibitor concentration led to increase in the inhibition efficiency due to the increasing number of molecules inhibitor molecules adsorbed on the metal surfaces. Also the surface coverage (θ) increased with the increasing inhibitor concentration since the protection of the metal increases (Anindita et al. 2018).
4 CONCLUSIONS AND RECOMMENDATIONS

Conclusion

A tandem hydrothermal and pyrolysis method for highly fluorescent carbon dots using urea and coffee green bean powder as carbon source was studied. The synthesized carbon dots exhibited a bright blue colour under UV light. The carbon dots also exhibited a high fluorescence emission at 505 nm after characterization with fluorescence spectra and absorption at 280 nm in UV-vis spectra. The carbon dots also exhibited quenching effect with Cu$^{2+}$ ion and Pb$^{2+}$ ion and a method for Cu$^{2+}$ ion detection and Pb$^{2+}$ in water can be developed with required selectivity. Furthermore, the coffee carbon dots could inhibit copper corrosion for as high as 76.98% in 1% sodium chloride solution. Therefore coffee is an eco-friendly raw material for the preparation of carbon nanoparticles and the synthesized fluorescent carbon dots could be useful in fabricating sensors for metal detection and copper corrosion inhibitors in salt environments.

Recommendations

More techniques are required to improve this research for example X-ray photoelectron spectroscopy for measuring the elemental composition, electrochemical impedance spectroscopy for corrosion studies, and transmission electron microscope for size and morphology of the carbon dots. Further research is still needed on the versatility of coffee carbon dots.

REFERENCES


APPENDICES

Appendix 1 Flow chart of the research

1. Grind the dried coffee beans into powder.
2. Add urea and 20 ml of water and heat in the furnace at 220 °C for 5 hours.
3. Add water and centrifuge at 5000 rpm for 15 minutes.
4. A black product was obtained.
5. Grind the dried coffee beans into powder.
6. A black product was obtained.
7. Spectrophotometric studies – UV-Vis, Fluorescence, FTIR.
8. Coffee carbon dot powder
9. Characterization
10. Coffee carbon dot powder
11. Pb²⁺ and Cu²⁺ sensing
12. Weight loss and potentiodynamic polarization measurements
13. Corrosion inhibition tests

Characterization

Add water and centrifuge at 5000 rpm for 15 minutes.
### Appendix 2 Corrosion inhibition data using the weight loss method

<table>
<thead>
<tr>
<th>Concentration of carbon dots (mg/L)</th>
<th>Test</th>
<th>Weight of copper (g)</th>
<th>Before immersion (W&lt;sub&gt;b&lt;/sub&gt;)</th>
<th>After immersion (W&lt;sub&gt;a&lt;/sub&gt;)</th>
<th>W&lt;sub&gt;b&lt;/sub&gt; - W&lt;sub&gt;a&lt;/sub&gt;</th>
<th>Average</th>
<th>Corr. rate (mm/y)</th>
<th>Average corr. rate (mm/y)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1</td>
<td>0.2989</td>
<td>0.2947</td>
<td>0.0042</td>
<td>0.00465</td>
<td>0.0046</td>
<td>0.305</td>
<td>0.3659</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.3126</td>
<td>0.3075</td>
<td>0.0051</td>
<td>0.00405</td>
<td>0.0040</td>
<td>0.4013</td>
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<td></td>
</tr>
<tr>
<td>200</td>
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<td>0.2961</td>
<td>0.2926</td>
<td>0.0035</td>
<td>0.00405</td>
<td>0.0040</td>
<td>0.2754</td>
<td>0.3187</td>
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<tr>
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<td>0.3078</td>
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<td>0.0046</td>
<td>0.00405</td>
<td>0.0040</td>
<td>0.36196</td>
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<td>0.0022</td>
<td>0.00245</td>
<td>0.0024</td>
<td>0.1731</td>
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<td>0.00245</td>
<td>0.0024</td>
<td>0.21245</td>
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<td>600</td>
<td>1</td>
<td>0.3098</td>
<td>0.3083</td>
<td>0.0015</td>
<td>0.00165</td>
<td>0.0016</td>
<td>0.11803</td>
<td>0.1298</td>
<td>64.52</td>
</tr>
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<td></td>
<td>2</td>
<td>0.3151</td>
<td>0.3133</td>
<td>0.0018</td>
<td>0.00165</td>
<td>0.0016</td>
<td>0.1416</td>
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<td></td>
</tr>
<tr>
<td>800</td>
<td>1</td>
<td>0.2992</td>
<td>0.2982</td>
<td>0.0010</td>
<td>0.0011</td>
<td>0.0011</td>
<td>0.0784</td>
<td>0.0864</td>
<td>76.39</td>
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<tr>
<td></td>
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<td>0.3003</td>
<td>0.2991</td>
<td>0.0012</td>
<td>0.0011</td>
<td>0.0011</td>
<td>0.0944</td>
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<td></td>
</tr>
<tr>
<td>1000</td>
<td>1</td>
<td>0.3008</td>
<td>0.3000</td>
<td>0.0008</td>
<td>0.0007</td>
<td>0.0007</td>
<td>0.06295</td>
<td>0.0551</td>
<td>84.94</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.3061</td>
<td>0.3055</td>
<td>0.0006</td>
<td>0.0007</td>
<td>0.0007</td>
<td>0.04721</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Appendix 3 Calculation of corrosion inhibition using weight loss method

- **Calculating corrosion rate of the blank (First trial data)**

Weight loss (W<sub>b</sub>−W<sub>a</sub>) = 0.00465 g

Corrosion rate of the blank (V<sub>corr</sub>) = \( \frac{8.76 \times 10^4 \frac{mm}{y} \times 0.00465 g}{350 mm^2 \times 355 h \times 8.96 \times 10^{-3} c m^{-3} \times \frac{1 cm^2}{1000 mm^2}} \)

\[ = 0.3659 \text{ mm/y} \]

- **Calculating corrosion rate of 1000 mg/L carbon dots (First trial data)**

Weight loss (W<sub>b</sub>−W<sub>a</sub>) = 0.0007 g

Corrosion rate of the blank (V<sub>corr</sub>) = \( \frac{8.76 \times 10^4 \frac{mm}{y} \times 0.0007 g}{350 mm^2 \times 355 h \times 8.96 \times 10^{-3} c m^{-3} \times \frac{1 cm^2}{1000 mm^2}} \)

\[ = 0.0551 \text{ mm/y} \]

Where, mm/y is millimeters per year and h is hours.

Calculating Inhibition efficiency

\[ \eta_w (\%) = \left( \frac{V_{corr} - V_{corr}}{V_{corr}} \right) \times 100 \]

\[ = \left( \frac{0.3659 - 0.0551}{0.3659} \right) \times 100 \]

\[ = 84.94\% \]
Appendix 4 Calculation of corrosion inhibition using the potentiodynamic polarization method at 1000 mg/L carbon dot concentration

Tafel equation: \[ y = ax + b \Leftrightarrow \log|i(mA)| = aE(mV) + b \]

Cathode Tafel equation: \[ y = -0.0059x - 5.9374 \]

Anode Tafel equation: \[ y = 0.0069x + 2.5963 \]

Corrosion potential (E) at \( y_c = y_a \)

If: \[ -0.0059x - 5.9374 = 0.0069x + 2.5963 \]

Then \( x = E = -666.7 \text{ mV} \)

Corrosion current (i)

\[ y = -0.0059x - 5.9374 = -0.0079(-666.7) - 5.9374 = -2.004 \]

Since: \[ \log|i| = y \]

Then: \( i = 10^y = 10^{-2.004} = 0.0099 \text{ mA} \)

Inhibition efficiency (IE)

\[ IE = \frac{i_{\text{blank}} - i_{\text{inhibitor}}}{i_{\text{blank}}} \times 100\% \]

\[ IE = \frac{0.043 - 0.0099}{0.043} \times 100\% \]

IE = 76.98\%

Surface coverage (\( \Theta \))

\[ \Theta = 1 - \frac{i_{\text{inhibitor}}}{i_{\text{blank}}} \]

\[ \Theta = 1 - \frac{0.0099}{0.043} \]

\[ \Theta = 0.77 \]

Corrosion rate

\[ \frac{i_{\text{corrosion}} \times A r}{A \times z \times F \times p} = \frac{0.0099 A \times 63.54 \text{ g mol}^{-1} \times 3.1536 \times 10^7 \text{ s}^{-1} \times 10 \text{ mm cm}^{-1}}{3.34 \text{ cm}^2 \times 2 \times 96500 \text{ As mol}^{-1} \times 8.96 \text{ g cm}^{-3}} \]

\[ = 0.03435 \text{ mm/y} \]

Where \( A \) is area of the electrode, \( z \) is number of electrons involved in the redox reaction, \( F \) is Faradays constant, \( \rho \) is density of copper, \( i_{\text{corrosion}} \) is corrosion current and \( Ar \) is atomic weight of copper.
Appendix 5 Fluorescence intensities of carbon dots at different concentrations of lead (ii) ions at 505 nm

<table>
<thead>
<tr>
<th>Concentration of Pb$^{2+}$ (µg/L)</th>
<th>Fluorescence Intensity (a.u)</th>
<th>$F_0/F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>54636.91</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>36039.3</td>
<td>1.516</td>
</tr>
<tr>
<td>10</td>
<td>29195.25</td>
<td>1.871</td>
</tr>
<tr>
<td>15</td>
<td>27026.66</td>
<td>2.022</td>
</tr>
<tr>
<td>20</td>
<td>24678.88</td>
<td>2.214</td>
</tr>
<tr>
<td>50</td>
<td>16151.81</td>
<td>3.383</td>
</tr>
</tbody>
</table>

Where $F_0$ is the fluorescence intensity of the blank and $F$ is the fluorescence intensity of the carbon dot solution plus the different concentrations of Pb$^{2+}$ ions.

Slope = 0.44179

(Blank signals; 54636.91, 54636.89, 54636.87)

Standard deviation of blank signals (n=3) = 0.02

Limit of detection = \( \frac{3 \times Sd}{\text{slope of calibration line}} \)

Limit of detection = \( \frac{3 \times 0.02}{0.044179} \) = 1.358 µg/L

Where $Sd$ is standard deviation.

Appendix 6 Fluorescence intensities of carbon dots at different concentrations of copper (ii) ions at 505 nm

<table>
<thead>
<tr>
<th>Concentration of Cu$^{2+}$ (mg/L)</th>
<th>Fluorescence Intensity (a.u)</th>
<th>$F_0/F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>54636.91</td>
<td>1</td>
</tr>
<tr>
<td>0.1</td>
<td>42099.67</td>
<td>1.298</td>
</tr>
<tr>
<td>0.5</td>
<td>30619.38</td>
<td>1.784</td>
</tr>
<tr>
<td>1</td>
<td>29008.78</td>
<td>1.883</td>
</tr>
<tr>
<td>5</td>
<td>23413.75</td>
<td>2.334</td>
</tr>
<tr>
<td>10</td>
<td>13836.78</td>
<td>3.949</td>
</tr>
</tbody>
</table>

Where $F_0$ is the fluorescence intensity of the blank and $F$ is the fluorescence intensity of the carbon dot solution plus the different concentrations of Cu$^{2+}$ ions.

Slope = 0.134181

Standard deviation of blank signals (n=3) = 0.02

Limit of detection = \( \frac{3 \times Sd}{\text{slope of calibration line}} \)

Limit of detection = \( \frac{3 \times 0.02}{0.134181} \) = 0.447 mg/L

Where $Sd$ is standard deviation.
I Kalema Christopher was born on 27th October 1991 in Mubende district Uganda. I completed my primary school education at Kaweeri primary school in 2004. I completed my ordinary level secondary education in 2008 at St Charles Lwanga SS Mubende and also completed my advanced level at the same secondary school in 2010. I pursued my Bachelor’s degree in chemistry from Uganda Martyrs University in 2014. I then worked as a chemistry teacher at St Charles Lwanga SS Mubende from 1st August 2014 to September 2016.

I then got Indonesia Government developing countries partnership (KNB) Scholarship in September 2016. I got admitted for a master study in Chemistry, IPB University. The research paper entitled “Versatile coffee carbon dots as lead (ii) and copper (ii) ion detectors and copper corrosion inhibitors” has been submitted to the International Journal of Research in Science, Engineering and Technology (IJSRSET) and the paper is accepted and published by the journal.