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Past, Present, and Future of Waste Cooking Oil (Beyond Biofuel)

Jihyun Kim

CUNY Guttman Community College

Chemistry Laboratory Activity: Research In the Classroom (a 3-week project)

Past, Present, Future of Waste cooking oil (beyond biofuel)

Background

It is reported that U.S. restaurants produce about 25 billion gallons of waste cooking oil per week.[1] This waste cooking oil (WCO) – known as yellow grease - is collected, refined into different types of biofuel.[2] The conversion of WCO to biofuel has extensively been studied , as it has become a ubiquitous undergraduates laboratory activity.[3] However, carbonization of WCO by Yu[4] employing concentrated sulfuric acid as a precursor of Carbon Dots (c-dots) proves there is other use of WCO beyond biofuel.

Carbon Dots (CDs), fluorescent nanomaterials, with size about 10 nm, have emerged since 2004 during separation of multiwalled carbon nanotubes,[5] and then through laser ablation of graphite powder.[6] It is well reported that CDs derived from natural materials are biocompatible and highly fluorescent, and have been employed in biomedical imaging.[7] With the promises in biomedical applications and organic synthesis, recent research interests shift to prepare green CDs from natural carbon precursors, such as orange waste peels, food waste, saccharides, plants, bamboo leaves, milk, garlic, chitosan, etc.

In this project, the students in "General Chemistry" will explore the development of a facile, eco-friendly, and simple preparation method of fluorescent CDs from a mixture of waste cooking oil and orange waste peels. Orange waste peels are one of the most underutilized biowaste residues on earth, therefore, it would make better sense of utilizing a mixture of the two wastes.

Objectives

The main goal of this project is introducing students to Green Chemistry, Nanomaterials, and Sustainability. To implement the goal, the students in General Chemistry will research the conversion of waste cooking oil to carbon nanomaterials, develop facile methods to prepare the nanomaterials. In addition, the project will provide the students an opportunity to learn about how to characterize nanomaterials with limited resources by employing UV lamp, UV/Vis Spectroscopy, and portable Fluorescence Spectrophotometer. In collaboration with the Advanced Science Research Center, Transmission Electron Microscopy (TEM) images will be collected shedding light on the median size and morphology of carbon nanomaterials.

Upon completion of this project, the students will be able to understand a great deal of nanomaterials, environmental issues derived from waste cooking oil and waste orange peels, as well as the utilization of biowastes.

Prelab activity:

1. Reading: read the following two articles regarding the properties of carbon nanomaterials (= carbon dots, carbon quantum dots, and carbon nanoparticles), and work on the prelab questions

and your group presentation. https://en.wikipedia.org/wiki/Carbon_quantum_dots https://www.sciencedirect.com/topics/chemistry/carbon-quantum-dot

2. Videos: the video will describe the applications of carbon nanomaterials in energy, bioimaging and sensor. https://www.youtube.com/watch?v=LlPDyl53rZA

3. Field trip: There will be two field trips prior to the project. The first trip will be touring Newtown Creek Wastewater Treatment in Green Point, Brooklyn. The second is conducting your own field trip around your neighborhood. Visit at least two street vendors, Delis, or restaurants, and find out the disposable methods -how fat and grease leftovers are trapped in their kitchen sink. Interview your family members, friends, or neighbors and find out their awareness of applications of waste cooking oil. Please keep fieldnotes and any videos and photos taken, share them in your group presentation.

4. Prelab questions:
a. Discuss common usages of waste cooking oil.
b. Discuss carbon nanomaterials and their applications
c. In this project, a UV lamp will be employed to see whether as-synthesized carbon nanomaterials are fluorescent or not. Discuss what is fluorescence and what are the safety concerns of using a UV lamp.

5. Group presentation: In the group project, 3-4 students per group, each team member must be assigned responsibilities to work on the project integrating your field trip experience. a 10-15 min group presentation (about 10 slides, photos and short videos are highly recommended) will be peer-evaluated.

<u>Materials:</u>

Waste cooking oil
Waste orange peels
Blender
Sand
Hot plate
Stir bar
Glass rod
pH paper
Conc. Sulfuric acid
TLC plates
UV lamp
UV/Vis spectroscopy
Portable fluorometer (LED 300, 350, 375, 400, 450, 500 nm)
0.1 M Fe^{3+}, 0.1 M Cr^{3+}, 0.1 M Cu^{2+}solutions

Experimental:

Part A: Synthesis of carbon nanomaterials

a. C dots from WCO and sulfuric acid: Pour 10 mL of waste cooking oil into a flask, add one scoop of molecular sieves to the flask, and stir for 10 mins to remove water. If necessary, add more molecular sieves, and stir the mixture for another 10 mins. After stirring, filter the oil. Record color change, the volume of filtered oil, and viscosity. Slowly add about 1 mL of concentrated sulfuric acid to the filtered oil, and heat it up in the hood for 10 mins at 100 ^{0}C while stirring vigorously. Caution: hot oil is dangerous. Please carefully monitor the temperature of the mixture. Record any color change. After 10 mins heating, cool the solution at room temperature, add about 10 mL of distilled water. And add NaOH pellets to neutralize the solution. The amount of NaOH needed will be varied, thus, add small amounts of base, stir it, measure the pH using pH paper. Centrifuge the solution for 10 mins at 4900 rpm to remove heavy particles. Collect the supernatant, irradiate the solution under UV light 365 nm. Caution: don't look at the light directly, protect your eyes and hands. Record the color of fluorescence, be prepared for UV/Vis and Fluorescence spectrophotometers.

b. C dots from a mixture of WCO and waste orange peel (1:1): the same method will be applied for this part except that a mixture of waste cooking oil and waste orange peel (1:1; dried, and grinded; recommend this process a week prior to the project.) without sulfuric acid. It would be of interest to investigate whether the addition of orange peels could be a suitable replacement for sulfuric acid.

Part B: Characterization

The as-prepared carbon nanomaterials solutions from Part A will be measured by UV/Vis and Vernier Fluorescence spectrophotometers. Students are required to be familiar with using spectrophotometers, calibration, and sample preparation.

UV/Vis measurement

1. Measure and record in your data sheet the absorbance of the as-prepared solution over 280 nm to 600 nm range three times, and plot Absorbance vs wavelength using Excel.

Fluorescence Spectrophotometer

1. Measure and record the fluorescence emission and intensity from 300 nm to 700 nm with excitation at 350 nm, 375 nm, 400 nm, 450 nm, 500 nm, and 525 nm, respectively.

2. Plot Fluorescence Intensity vs emission wavelength using Excel. And plot emission spectra at different excitation wavelength to observe whether the emission is dependent of excitation.

Transmission Electron Microscopy (TEM) images

As the College lacks advanced instrumentation, TEM images will be collected at other research facilities. However, students in lower-level chemistry courses will prepare TEM samples by dropping 5 microliter on a 300 mesh copper grid. The data, the size and shape of carbon nanomaterials, will be discussed as a group in class.

Infrared Spectroscopy (IR)

Likewise, the sample will be measured at other facilities. It is expected to identify functionalities on the carbon nanomaterials.

Part C: Application:

Sensor for detecting heavy metal ions

In order to further investigate the feasibility as metal sensors, the as prepared carbon nanomaterials will be tested with several cations, including Cu^{2+}, Fe^{3+}, and Cr^{3+}. Mix 1.0 mL of your solution from Part A with 0.1 mL of each of the 0.1 M cation solution, see it under UV lamp, measure its fluorescence intensity at 350 nm excitation. If the solution were nonfluorescent, the carbon nanomaterials could be employed to sense

pH probes

Furthermore, fluorescent carbon nanomaterials would be evaluated as pH sensors. A series of fluorescent carbon nanomaterials prepared in Part A will be treated in different pH values, the spectrofluorimeter will monitor its fluorescence intensity. The as- prepared solution is itself acidic due to the presence sulfuric acid, add pea size of NaOH pellet to raise the pH to 5, and measure its fluorescence intensity at 350 nm excitation, add more NaOH to the solution you just adjusted to reach pH 7, and measure its intensity. Repeat this process as you raise to pH 9, 11, respectively.

<u>References:</u>

(1) "World Used Cooking Oil Market." Reuters, April 23, 2018. (2). Leung, D. Y. C.; Wu, X.; Leung, M. K. H. A review on biodiesel production using catalyzed transesterification. Appl. Energy 2010, 87, 1083−1095. (3) Bladt, D.; Murray, S.; Gitch, B.; Trout, H.; Liberko, C. Acid catalyzed preparation of biodiesel from waste vegetable oil: An experiment for the undergraduate organic chemistry laboratory. *J. Chem. Educ.* 2011, 88, 201−203. (4) Hu, Y.; Yang, J.;Tian, J.; Yu, J. Waste frying oil as a precursor for one-step synthesis of ulfur-doped carbon dots with pH-sensitive photoluminescence. Carbon 2014, 77, 775-782. (5) Li, L.; Wu, G.; Yang, G.; Peng, J.; Zhao, J.; Zhu, J.-J. Focusing on luminescent graphene quantum dots: Current status and future perspectives. Nanoscale 2013, 5, 4015−4039. (6) Li, H.; Kang, Z.; Liu, Y.; Lee, S.-T. Carbon nanodots: Synthesis, properties and applications. J. Mater. Chem. 2012, 22, 24230−24253. (7) Ding, C. Q.; Zhu, A. W.; Tian, Y. Functional Surface Engineering of C-dots for Fluorescent Biosensing and in vivo Bioimaging. Acc. Chem. Res. 2014, 47, 20−30.

Data sheet

Name:
Team members:
Date:

Part A: Synthesis of carbon nanomaterials

1. Waste cooking oil and sulfuric acid:

Mass of waste cooking oil:
Volume of sulfuric acid:

Observation:

Color of as-prepared carbon nanomaterials at daylight:
Color of as-prepared carbon nanomaterials under 365 nm UV:

2. A mixture of waste cooking oil and waste orange peels

Mass of waste cooking oil:
Mass of waste orange peels:

Observation:

Color of as-prepared carbon nanomaterials at daylight:
Color of as-prepared carbon nanomaterials under 365 nm UV:

Part B: Spectroscopic Characterization

1. UV-vis spectra

Table 1: Absorbance vs wavelength

Wavelength (nm)	Absorbance of Carbon nanomaterials from waste cooking oil and sulfuric acid	Absorbance of Carbon nanomaterials from a mixture of waste cooking oil and waste orange peels
280		
300		
320		
340		
360		
380		
400		
440		
480		
520		
560		
600		
650		
700		

Plot Absorbance vs wavelength using Excel and attach it

2. Fluorescence spectra

Excitation (nm)	Max. Emission (nm)	Fluorescence intensity of carbon nanomaterials from waste cooking oil and sulfuric acid	Fluorescence intensity of carbon nanomaterials from a mixture of waste cooking oil and waste orange peels
300 350 400 450 500 525			

Plot Fluorescence Intensity vs emission wavelength using Excel. And plot emission spectra at different excitation at 350 nm, 375 nm, 400 nm, 450 nm, 500 nm, and 525 nm, respectively. Attach your graph.

3. TEM images

	Carbon nanomaterials from waste cooking oil and sulfuric acid	Carbon nanomaterials from a mixture of waste cooking oil and waste orange peels
Avg. size (nm)		

4. IR

	Carbon nanomaterials from waste cooking oil and sulfuric acid	Carbon nanomaterials from a mixture of waste cooking oil and waste orange peels
Functional groups observed		

Part C: Application

Metal sensors

fluorescence intensity to ion	Carbon source WCO + H_2SO_4	WCO + WOP
Cu^{2+}		
Fe^{3+}		
Cr^{3+}		

pH sensors:

fluorescence intensity to pH	Carbon source WCO + H_2SO_4	WCO + WOP
pH 3		
pH 5		
pH 7		
pH 9		

<u>Post lab questions</u>:

1. In part A, you have synthesized carbon nanomaterials from the two different carbon sources. Discuss which carbon sources provide better results in terms of fluorescence intensity and its application.

2. In part B, UV-vis spectra are collected, find the maximum absorbance wavelength, and discuss what kinds of functional groups can be found on carbon nanomaterials. Further elaborate your findings with IR spectra.

3. It is reported that some carbon nanomaterials show excitation-dependent fluorescence behavior. Do your as-prepared samples show excitation-dependent emission? If so, what cause this particular behavior?

4. Molecular sieves are used in part A. Describe any changes happened after adding molecular sieves to the waste cooking oil. What other alternatives could be employed? And what would happen if you forgot to add them?

Student survey and reflections:

Please share your experience and feedback by answering the following questions. We need your honest feedback to modify the project, if necessary, and to promote student success. (note: this part should be done separately and anonymously.)

a. Did the project help develop positive attitudes toward the learning of chemistry?

b. Did the project help develop a confidence in learning and using chemistry?

c. Did the project satisfy your expectation of learning chemistry?

d. Did the project promote your interest in learning and doing chemistry?

e. Did you learn new ways of presenting your findings, communication skills?

f. What did you find most valuable about doing the project?

g. What do you like least about the project?

h. What was your overall experience working on the project?

i. Any comments?