

Demonstration of environmental chemistry with microscale chemistry and a low-cost four-led based photometer

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Con esta entrega terminan los dos años en los que sus ocho números han contenido los artículos invitados DE ANIVERSARIO. En esta ocasión el tema de estas contribuciones es el de QUÍMICA EN MICROESCALA. Quien por parte de la revista hizo la selección de los invitados ha sido Jorge G. Ibáñez, del Centro Mexicano de Microesca la en la Universidad Iberoamericana. A mí me tocó seleccionar a Jorge como otro de los autores de esta última sección. Habrá que esperar a cumplir los veinte años de la revista para quizá volver a abrir nuevamente una tercera sección DE ANIVERSARIO.

El Director de Educación Química,
Andoni Garriz Ruiz

Abstract

In this article, a four-LED based photometer, in which four LEDs are used as light sources, are demonstrated to be a useful instrument for the study of pollution problems caused by phenols and of their remediation by electrochemical degradation method and the iron (II) catalyzed homogeneous Fenton's reaction. The fate of phenols can be monitored by the photometer via the 4-aminoantipyrine method. The results revealed that the latter method was a superior method to treat the phenolic compounds. Within 60 min, over 99.9% of the phenols can be completely mineralized by the Fenton's reaction while around 65% of the phenols were broken down electrochemically. This study serves as a good case study, enabling the students to know how to quantify organic pollutants exemplified by phenolic compounds and to introduce chemical methods to remediate the pollutants.

1. Introduction

Environmental chemistry has become an integral part of chemistry curriculum not only in universities, but also in high schools (1). The design of curricula with well coverage of important aspects of environmental chemistry has been attracted a wide attention from the education practitioners (2, 3). Moreover, it has been suggested that students cannot gain an adequate appreciation of environmental chemistry without doing laboratory based work (4). To make way for more vigorous investigations on environmental issues, we have developed a low-cost four

LED-based photometer (5). A series of experiments related to environmental analysis has been developed and can be accessed via our website under the auspices of the Federation of Asian Chemical Societies (FACS) (www.hkbu.edu.hk/~iwlcmc). Low cost LEDs have characteristic wavelength emission maxima and band width in the visible light region as shown in Table 1.

As a result of wide coverage of the light source, the instrument can be utilized for essentially all colorimetric experiments (Figure 1). In the article published by us (6), we reported the use of each of the LEDs of the photometer for the analysis of four chemical species from different light sources, viz.,

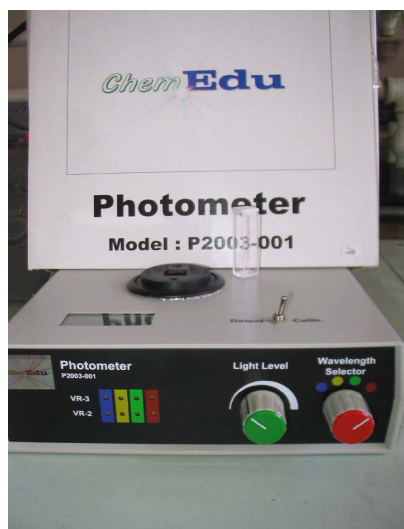
- Analysis of airborne formaldehyde (an indoor air pollutant) by the red-LED source.
- Analysis of NO₂ (an outdoor air pollutant) by the green-LED source
- Determination of copper content in water sample by the yellow-LED source.
- Determination of iron content in commercial minerals tablet by the blue-LED source.

As a continuous effort to develop more "case studies" in teaching environmental chemistry, we describe in

Table 1. Summary of the characteristics of the Four LEDs based photometer.

Color of the LED used	Pea wavelength	Spectral bandwidth
Blue	465 nm	25 nm
Green	525 nm	36 nm
Yellow	590 nm	35 nm
Red	626 nm	45 nm

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To promote the use of the photometer in innovating laboratory teaching, the instrument has now been commercialized by ChemEdu. Model with 110V AC or 220V AC power supplier can be purchased at a cost of USD 320 per piece.

Figure 1. Four LED-based photometer.

this submission our recent work entitled “Phenols as organic pollutants and their remediation by chemical methods”.

Phenolic compounds are ubiquitous in the environment. They occur as natural constituents and are manufactured as useful materials in a wide variety of chemical industries. Phenols are produced as bulk industrial chemicals in the manufacture of plastics, dyes, drugs and antioxidants. In the natural environment, they are the breakdown products from humic substances, lignins and tannins. They are also heavily used in pulp industry to extract cellulose from wood and their derivatives released into the environment as a major pollutant. Their quantification in environmental samples is a major concern of environmental protection agencies (7).

2. Experimental

2.1 Determination of phenols in water samples by the 4-Aminoantipyridine Method

Phenolic compounds react with 4-aminoantipyridine at $\text{pH } 7.9 \pm 0.1$ in the presence of potassium ferricyanide to form a pink colored antipyridine dye as shown in Figure 2. The dye was kept in aqueous solution and absorbance was measured by the green LED of the photometer after 15 min (8).

2.1.1 Analysis of the concentration of phenol, *o*-chlorophenol and *m*-cresol in water

Blank and 0.2, 0.4, 0.6, 0.8 and 1.0 ppm standard solutions of phenol, *o*-chlorophenol or *m*-cresol were

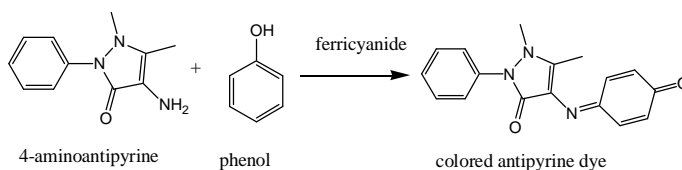


Figure 2. Chemical reaction between phenol and 4-aminoantipyridine.

prepared in a 10 mL volumetric flask from the dilution of 10 ppm phenol standards. Then, 0.25 mL of 0.50M NH_4OH solution was added and adjusted to $\text{pH } 7.9 \pm 0.1$ with phosphate buffer. Afterwards, 0.1 mL of 4-aminoantipyridine solution and 0.1 mL of potassium ferricyanide solution were introduced and mixed well in the solution. After 15 min, the colored solution was transferred to the curvette and the absorbance of samples and standards were read against the blank using the green LED as the light source.

2.2 Remediation by chemical methods

2.2.1 Electrochemical degradation method

3.0 mL of 0.1 M CoSO_4 and 3 mL of 100 ppm phenol, *o*-chlorophenol or *m*-cresol were added into a container and the electrodes were inserted. Besides, the tip of the tubing was introduced into the BaCl_2 solution for transferring of the generated carbon dioxide. The container was then placed in a hot water bath at 40-50°C. Furthermore the wires were connected with alligator clips to the positive (i.e. Pb wire) and negative (i.e. paper clip) ends of a 9 V battery (9). The degradation process was started and ended at different time (i.e. 0, 1, 2, 5, 10, 20, 30 and 60 min respectively). 1 mL of the resultant solution was pipetted and diluted to 10 mL for colorimetric measurements. Three trials were performed for each of the reaction time.

2.2.2 Iron (II) catalyzed homogeneous Fenton's Reaction (10)

For conducting the Fenton's reaction in treating phenolic solutions, to a two-head rounded bottom flask, 100 mL of 100 ppm phenol solution was added. Then 4 mL of 20 ppm Fe (II) solution prepared by dissolving 0.014 g of $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 100 mL of water was introduced. After the addition, the whole rounded bottom flask was immersed into a 60°C water bath. The pH value of the mixed solution was adjusted to around 3 by diluted acid and alkali. Until the temperature of the solution became steady, the sample without any treatment was collected by

withdrawing 1 mL of the solution from the rounded bottom flask for measurements. Afterwards, 10 mL of 35% H_2O_2 was pipetted into the rounded bottom flask and the time was recorded. The reaction was stirred for 60 min. In addition, 1 mL of samples after 1, 2, 5, 10, 20, 30 and 60 min treatment were removed successively. Three trials were performed for consistency

3. Results and Discussion

3.1 Determination of phenolic pollutants in water by the 4-aminoantipyrine method

Based on the calibration graphs obtained from the absorbance of different standard solutions of the three phenols, the dynamic range and the limit of detection of the method can be established (Table 2).

The standard method used for phenol determination is very sensitive, the detection limit of the method was found to be 0.046 ppm. Substituted phenols with a *para*-hydrogen exemplified by the above three phenols respond sensitively to 4-aminoantipyrine. Thus, the method is a rough method to estimate the total phenols as common organic pollutants in water samples.

Table 2. Calibration range of different phenols.

Type of phenol	Calibration dynamic range (ppm)	Linear of the graph
Phenol	0.08-24.00	0.9957
<i>o</i> -chlorophenol	0.04-20.00	0.9976
<i>m</i> -cresol	0.06-25.00	0.9979

3.2 Remediation of wastewater polluted by phenols

To enhance the learning experience of the students on pollution control technologies, two different methods were chosen for comparative studies. The mineralization of phenols was conducted either by electrochemical means or free radical oxidation protocol. In the electrochemical degradation method, the active oxidizing agent Co^{3+} generated *in situ* at the anode served as the powerful oxidant to oxidize phenols giving rise to carbon dioxide. Thus, the extent of degradation of phenols can be monitored semi-quantitatively by trapping the evolved carbon dioxide with barium chloride solution. The residual concentration of the phenolic compounds in the treated solution were determined by the colorimetric method and reported as the function of treatment time (Figure 3).

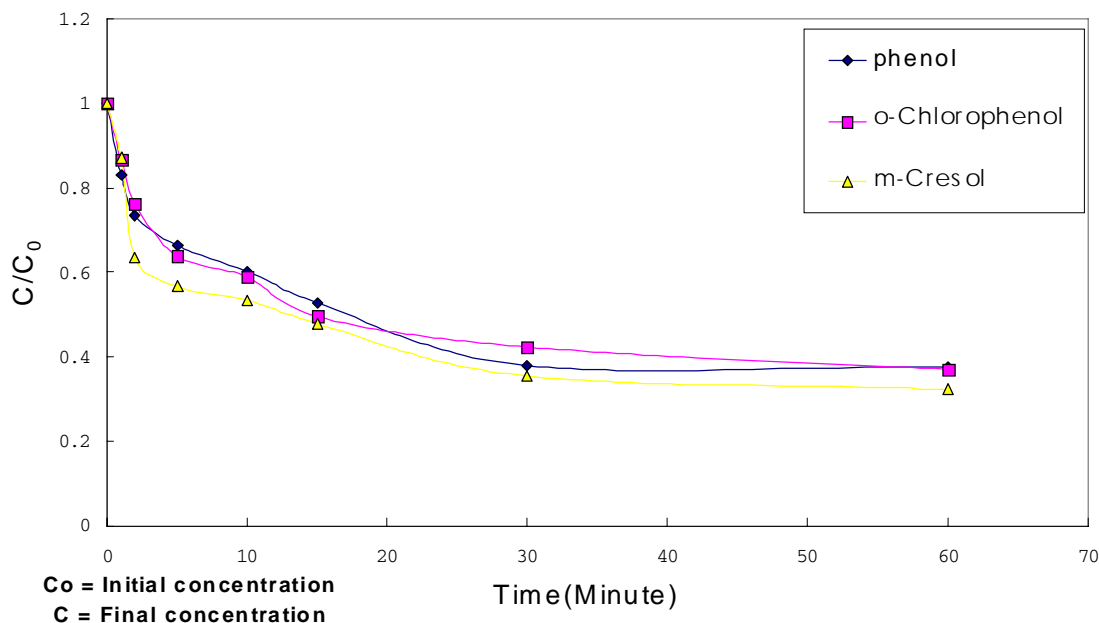


Figure 3. The amount of phenol removed from each phenols against time by Electrochemical Degradation Method.

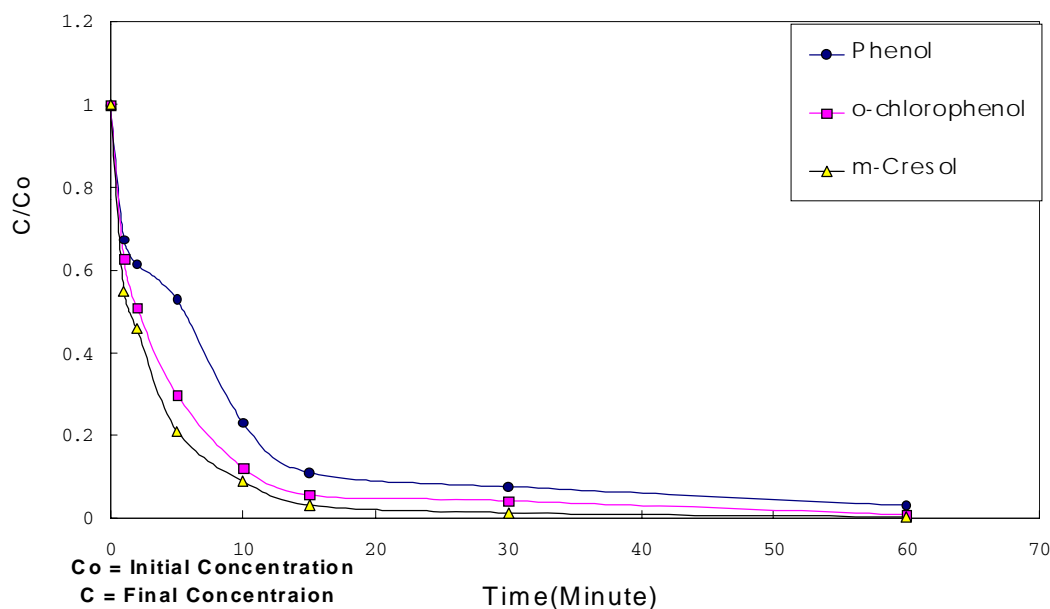


Figure 4. The amount of phenol removed from each phenol solutions against time by the Iron(II) Catalyzed Homogenous Fenon's Reaction.

The results revealed in Figure 3 indicated that most the removal efficiency of the electrochemical method is around 65% irrespective of the types of phenols. In contrast, the active per-hydroxyl radicals generated by the Fenton's reaction were found to be very effective to destroy phenols. The degradation profile illustrated in Figure 4 impressively showed that within 60 min, up to 99.9% all phenols were being destroyed. It is noteworthy that not only the overall efficiency of the latter method is better, but also the degradation rate is much faster than that of the former method. From the kinetic profile graph, it is apparent that the radical method induced by the Fenton's reaction could be removed nearly 70% pollutants in the first 5 min.

4. Conclusion

The Four LED-based photometer developed by our laboratory is a very versatile instrument which is suitable for most photometric measurements. Through its utilization, we have developed several case studies in environmental chemistry. Environmental chemistry can be presented in more quantitative way. Students may acquire more in depth understanding of pollutant problems caused by common organic pollutants such as phenols. Most importantly, the reported work also demonstrated that chemists

have the solution to improve our environment by incorporating adequate remediation technology. ■

5. References

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