ESTIMATION OF ALGAE CONCENTRATION IN WATER SOLUTIONS USING SPECTROPHOTOMETRIC MEASUREMENTS AND ABSORBANCE FIRST DERIVATIVE

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ABSTRACT

The monitoring and detection of algae in wastewater and surface solutions is important in controlling the quality of surface water and wastewater, yet there is currently no quick and simple method to achieve this. The present work illustrates a new method to determine the concentration of algae in different water samples using spectrophotometric measurements and the absorbance first derivative. The relationship between algal concentration and absorbance for three types of water solution (distilled, surface, and wastewater) was established in the 200–800 nm wavelength range, and the effect of using the absorbance first derivative on improving algal concentration detection limit was estimated.

In the distilled water samples, the lowest detection limits, using absorbance measurement and the absorbance first derivative, were 0.53 mg TVS/L and 0.47 mg TVS/L, respectively. In samples collected from surface water and wastewater treatment plants, the detection limits varied between 0.56 to 3.84 mg TVS/L depending on the NOM in the water sample. Higher detection limits were possible with the chlorophyll extraction methods.

Keywords: Algea, detectoin limit, derivative, absorbance

1 INTRODUCTION

The presence of algae in both surface and wastewater is one of the main causes of water quality deterioration [1, 2]. Algal growth in different parts of conventional wastewater treatment plants or aerated lagoon systems can result in false indications in the final effluent parameters, such as TSS, CBOD5 and COD [3-5]. In surface water, the presence of algae creates nuisance surface scum, poor water clarity, and noxious odors [6, 7]. In order to set up an efficient control and treatment process to minimize algal concentration in water samples, it is necessary to have access to a concentration measurement method which is quick, simple, and accurate, and which can detect low algal concentrations in different types of wastewater. The methods currently used to determine algal concentration such as algal number, chlorophyll extract concentration [8, 9] are time-consuming, require much laboratory preparation, expensive and inaccurate.

The present work aims to examine and test the performance and sensitivity of spectrophotometric measurements in determining the concentration of algae in different water and wastewater samples (distilled, surface, and wastewater), and to test the effect of using the concept of the absorbance first derivative to improve the detection limit of algae in the same water samples.

2 MATERIALS AND METHODS

2.1 Cultivation of microalgae

Chlorella vulgaris was used in this study and purchased from the UTEX Culture Collection of Algae (UTEX # 265) (University of Texas at Austin, USA). The algal strain was sterilized in an autoclaved grown in 500 mL Erlenmeyer flasks using a temperature-controlled incubator maintained at 25 °C at 25 °C.

2.2 Preparation of microalgae samples

The cultivated algal culture was separated from the media by centrifugation at 10,000 rpm for 15 min; the collected algae was then washed with distilled water for 3 min. and centrifuged at 10,000 rpm for 15 min. The washing step was repeated three times to ensure the removal of growth media and other impurities from algae. Afterwards, selected quantities of the concentrated algae was mixed in 500 mL water sample, tested for TS (total solids) and TVS (total volatile solids), and used in the experiments. Three different water samples were used: distilled water, surface water from Rideau River (Ottawa, ON), and secondary effluent from the ROPEC (Ottawa, ON) municipal wastewater treatment plant. The final algae concentration in samples ranged from 0.9 to 56 mg TVS/L.

2.3 Absorbance measurements

Absorbance measurements were used to quantify the microalgae in the wavelength range of 380 nm to 800 using a UV-vis spectrophotometer (Cary 100, Varian).

2.4 Calculation of the first derivative of absorbance spectra

The derivative of the absorbance spectra can be defined as the rate of change in absorbance with respect to wavelength ($\frac{dA(a.u)}{d\lambda}$). The first derivative technique was used in this study to improve the detection limit of the algae by minimizing the background noise from other water constituents. First derivatives were computed by dividing the difference between successive absorbance values by the wavelength interval separating them (i.e. $\frac{\Delta A}{\Delta \lambda}$).

3. RESULTS AND DISCUSSION

3.1 Measurements in distilled water

The absorbance spectra of *C. vulgaris* at different concentrations (measured as mg TVS/L) was determined for distilled water in three concentration ranges: 0.11–0.90 mg TVS/L, 0.9–5.6 mg TVS/L, and 5.6–56 mg TVS/L. These concentration ranges allowed for the determination of the sensitivity of the method at low, medium, and high algal concentrations. Figures 1a and 1b show an example of the absorbance spectra for algae concentration in the ranges 0.9–5.6 mg TVS/L and 5.6–56 mg TVS/L in the wavelength range of 380–800 nm. Four absorbance peaks were observed in these spectra at 455, 515, 675 and 695 nm, with the highest absorbance values measured at 695 nm. Incremental increases in algal concentrations in distilled water resulted in incremental increases in absorbance values and indicated a linear relationship between algal concentration and the absorbance of the samples. The absorbance values measured ranged from 0.001 to 0.866 (A.U.).

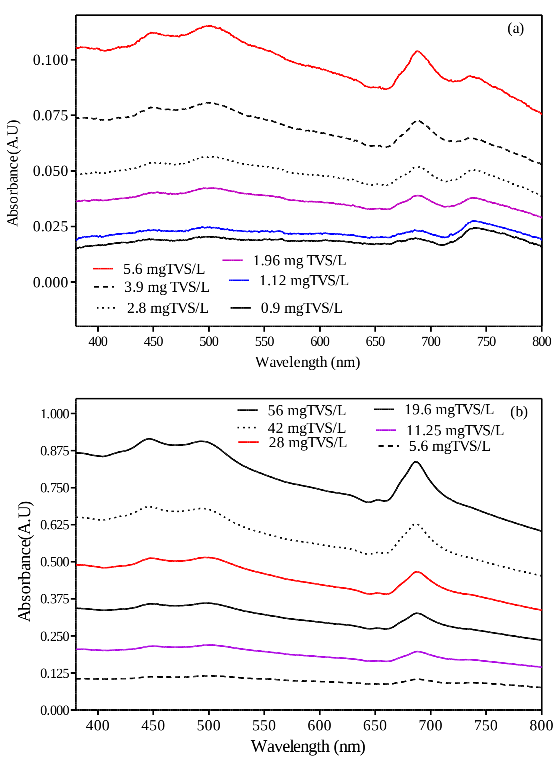

Figure 1: Absorbance of *Chlorella vulgaris* in distilled water at different concentration ranges (a) 0.9-5.6 mgTVS/L and (b) 5.6-56 mgTVS/L

A calibration curve between the algal concentration and the sample absorbance was constructed to determine the unknown algal concentrations in water using absorbance A strong linear relationship between algal concentration and sample absorbance at 695 nm was found (R^2>0.99 @95% C.I). The linear relationship between algal concentration and absorbance also held at 515 and 455 nm, but the slopes of the regression lines were lower, indicating that the method would be less sensitive at these wavelengths. Statistical analysis of absorbance data showed that a detection limit as low as 0.53 mg TVS/L.

Figures 2a and 3b show the first derivative of sample absorbance with respect to wavelength for algae concentrations of 0.90 - 5.6 mg TVS/L and 5.6 - 56 mg TVS/L. Taking the first derivative of the sample absorbance generated large peaks that are easy to detect. As the algal concentration increased, the most noticeable changes in the plotted derivatives also occurred at these specific wavelengths, indicating that the first derivative of absorbance is directly related to the concentration of algae in the sample. The relationship between the first derivative of absorbance and the algal concentration showed a strong linear relationship (R^2 > 0.98) between the first derivatives of absorbance and algal concentrations confirms that the algal concentration can be determined by using the derivative value. The detection limit of algae concentration using the absorbance first derivative can be as low as 0.47 mg TVS/L.

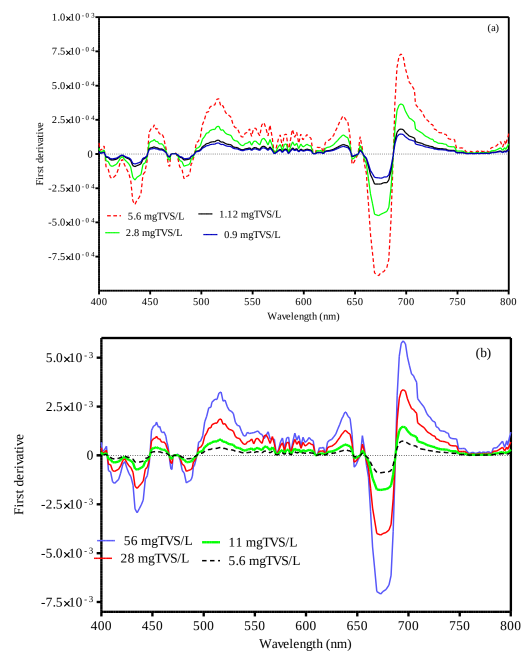

Figure 3: First derivative value of Chlorella vulgaris absorbance in distilled water in different concentration ranges. (a) 0.90 to 5.6 mgTVS/L and (b) 5.6 to 56 mgTVS/L.

3.2 Measurements in surface water and wastewater

Spectrophotometric determination of algal concentration was also carried out in surface water. The aim of this part of the study was to determine whether organic and inorganic constituents present in surface water, such as natural organic matter (NOM) and particles, would affect the spectrophotometric detection of algae using the first derivative of absorbance. The river water and the secondary wastewater were characterized for their COD (chemical oxygen demand) and turbidity, and found to have a COD value of 29 and 72 mg/L and turbidity of 0.595 and 3.8 NTU, respectively.

As in the case of distilled water, the absorbance–concentration data for algae in these water samples showed a good linear relationship ($R^2 \geq 0.9$) between the algal concentration and the corresponding absorbance at 695nm. Tables 2 shows the method used in algal concentration measurements with corresponding minimum detectable concentration. It can be seen in table 2 that both the absorbance and the absorbance first derivative give significant detection ranges. The detection limits of algae concentration in distilled water were estimated to be 0.53 and 0.47 mg TVS/L, respectively, using absorbance and absorbance first derivative.

Tables 2: Minimum Algae concentration range obtained from different methods of measurements

Type of water	Method	Detection limit (mg TVS/L)
Distilled	Absorbance	0.53
	Absorbance first derivative	0.47
Surface water	Absorbance	0.62
	Absorbance first derivative	0.56
Secondary wastewater	Absorbance	3.84
	Absorbance first derivative	1.96

Same trends were observed other water samples suggesting that the proposed methods are more accurate than chlorophyll extraction. Moreover, taking into consideration the simplicity of the procedure involved in carrying out the absorbance and absorbance first derivative measurements—in comparison with the other algae measurement—the suitability of the proposed methods (Absorbance and absorbance first derivative) is clear. Table 2 also shows that the lowest detection limit can be achieved by the use of the absorbance first derivative as a results of improving the spectra shape and removing the noise and background effect.

Conclusion:

A new simple, quick and accurate methods to monitor and detect algae concentrations in different water samples (distilled, surface and wastewater) are presented in this study. The new methods involve the use of spectrophotometric measurements and the absorbance first derivative to determine algae concentration in the previous water samples..

Overall, the results from this study indicate that A strong correlations between algae concentration and absorbance, and algal concentration and absorbance first derivative were established for the three types of water solutions (distilled, surface, and wastewater) at 695 nm with a coefficient of determination R^2 >0.95. The use of absorbance first derivative improved algal concentration detection limits, reduced the effect of background, improved the spectrum resolution and eliminate overlapping in spectra. A detection limit as low as 0.53 mg TVS/L and 0.47 mg TVS/L was reported for distilled water samples using absorbance and the absorbance first derivative measurements. The detection limit for algae concentration in samples collected from surface water and wastewater treatment plants varied between 0.56 to 3.84 mg TVS/L depending on the NOM in the water sample.

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