Quantification of polymer concentration in water using UV-Vis spectroscopy

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ABSTRACT

The goal of this study was to develop a method that uses UV-Vis spectroscopy for the determination of residual polymer concentration water and environmental samples. UV-Vis absorbance measurements are quick and simple and can be usefully applied in research and practice. Five different polymers exhibiting a wide range of polymer characteristics were tested in the UV range of 200–300 nm. The incremental increases in polymer concentrations corresponded to incremental increases in absorbance measurements, and a strong linear relationship was established between the polymer concentration and the absorbance values. The method was successfully used in the determination of polymer concentrations in water samples, as well as in centrate samples collected from a wastewater treatment plant.

Key words | concentration, measurement, UV-Vis absorbance, water-soluble polymers

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INTRODUCTION

Water-soluble polymers are used in many industrial processes, including treatment of water, wastewater, municipal and industrial waste, and in agriculture, mining and oil field applications. These polymers are expensive and are used in large quantities. Therefore, it is important to use polymers in a cost-effective manner, and this requires the ability to measure and adjust polymer concentrations to keep the polymer dose at optimum levels during a treatment, mining, manufacturing or industrial process. In some cases, it is also necessary to measure the residual polymer concentration in effluents before discharge to the environment, and this has been a main challenge, particularly for effluents containing low polymer concentrations (0–10 mg/L).

There is a wide range of methods available for characterization of polymers (Hunt & James 1993; Pethrick & Viney 2003; Hiemenz & Lodge 2007). Some of these methods are suitable for extraction, separation, identification and quantification of polymers in water-based environmental and industrial samples, but the accuracy and reproducibility of these methods heavily depend on the polymer and sample characteristics.

In general, analytical methods for polymers include gas chromatography, high-performance liquid chromatography, mass spectrometry and a combination of these methods. In addition, the starch-triiodide method (Scoggings & Miller 1979), viscosity (Jungreis 1981), calorimetry (Hansen & Eatough 1987), turbidimetry (Clapper et al. 1989), fluorescence spectrometry (Arryanto & Bark 1992), colloid titration (Gehr & Kalluri 1983), radioactive labeling (Nadler et al. 1994), flow injection analysis (Taylor et al. 1998), size exclusion chromatography (SEC) (Lu et al. 2003), nuclear magnetic resonance (NMR) spectroscopy (Chang et al. 2002), fluorescence tagging (Becker et al. 2004) and spectrophotometric determination using cationic dyes (Chmilenko et al. 2004) were previously used for detection of polyacrylamide in surface water, wastewater, soil water and oilfield brines. The presence of salts, cations, anions, oil, humic acids, dissolved organic substances, and pH and temperature conditions has been shown to interfere with the sensitivity of these methods (Lu & Wu 2003).

Analytical methods that are available for the measurement of polymers are complex and require advanced research instrumentation, trained personnel, and

pretreatment and processing of samples that may take several days. Simpler methods such as those that rely on colorimetric methods, titration, turbidity, and viscosity lack specificity and sensitivity, particularly at low polymer concentrations. Therefore, neither the advanced nor the simpler methods are suitable for practical applications in the field or process optimization. There is also no available method that can be used in-line and that can provide real-time information on measured polymer concentrations; such a method would be very valuable for industrial applications. Overall, a simple and sensitive method for determining polymer concentrations in water is currently lacking. The goal of this study was to develop an appropriate method for measuring a wide range of polymer concentrations in water and environmental samples using UV-Vis spectroscopy.

MATERIALS AND METHODS

Polymers

Five cationic polymers, commonly used in sludge dewatering, were used in the experiments. The polymers and their characteristics, including approximate charge densities and molecular weights, are listed in Table 1. The Zetag polymer was chosen since it is the polymer used for sludge dewatering at the local wastewater treatment plant. The SNF polymers were chosen in order to represent cationic polymers with a range of charge densities and molecular weights.

Table 1 | Characteristics of cationic polymers

Polymer name	Charge density	Molecular weight	Physical form
CIBA Zetag 7,587	High	High	Free-flowing microbead
SNF Flo Polymer CA 475	High	Ultra-high	Granular solid
SNF Flo Polymer CA 4,400	Low	Very-high	Granular solid
SNF Flo Polymer CA 4,600	High	Very-high	Granular solid
SNF Flo Polymer CA 4,800	Very-high	Ultra-high	Granular solid

Polymers were prepared to a concentration of 0.05% for use in the experiments. The polymers were prepared using a jar test apparatus (Phipps and Bird, USA) by mixing dried polymer in 500 mL of deionized water at a speed of 200 rpm for 5 min, followed by mixing at a speed of 125 rpm for 55 min to ensure that the solution was well mixed. After the initial 1-h of mixing, the solutions were mixed with a hand-held blender for 10 s, and left to sit for 1 h before use in the experiments. This procedure produced a homogeneous and well-mixed polymer solution for all of the polymers used in the experiments. Polymer stock solution was prepared daily.

Samples

Two water matrices were analyzed in the experiments. The first was deionized water (Millipore Direct Q UV 3, Millipore, USA); the other was the centrate of anaerobically digested sludge collected from a wastewater treatment plant. The centrate was used in the experiments as collected and also after filtration through a 0.45 μm filter. Centrate samples were diluted before absorbance measurements such that the final samples had 10 and 25% centrate in them.

Absorbance measurements

Absorbance measurements were performed with a UV-Vis spectrophotometer (Cary 100 Bio UV-Vis Spectrophotometer, Varian Inc./Agilent Technologies, Canada) using a 1-cm quartz glass cell (HellmaCanada Ltd, Canada). Deionized water was used as a blank during calibration. Initial scans showed no change in the absorbance measurements between 300 and 800 nm, and the 200–300 nm wavelength range was used in the experiments. Each measurement was repeated three times, and the reported absorbance measurements are the average of three replicates. Eight replicates were used to determine the method detection limit (MDL) as explained in Berthouex & Brown (2002). The MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analyte.
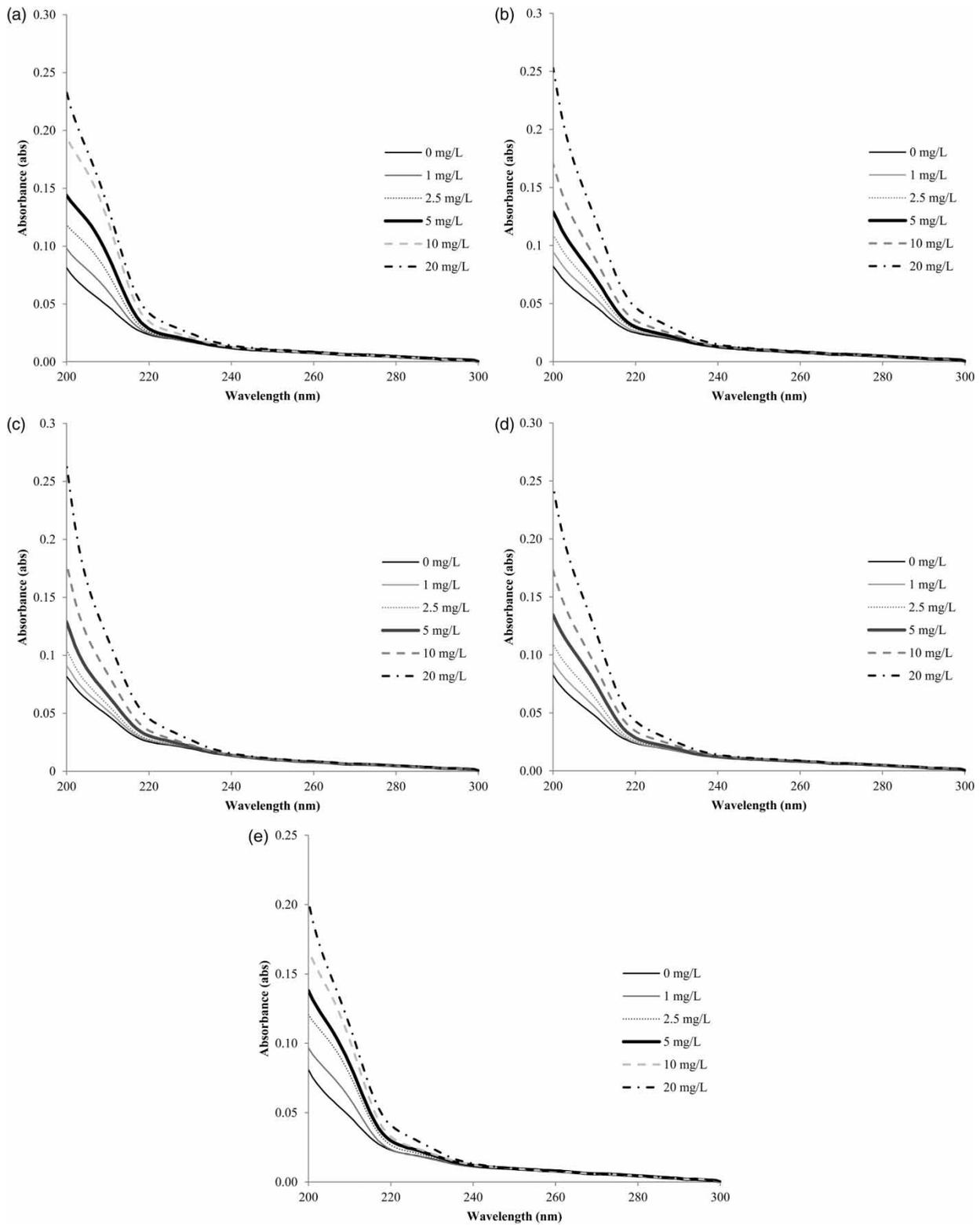
Figure 1 | (a) Zetag polymer in water (0–20 mg/L), (b) SNF 475 polymer in water (0–20 mg/L), (c) SNF 4,400 polymer in water (0–20 mg/L), (d) SNF 4,600 polymer in water (0–20 mg/L), (e) SNF 4,800 polymer in water (0–20 mg/L).
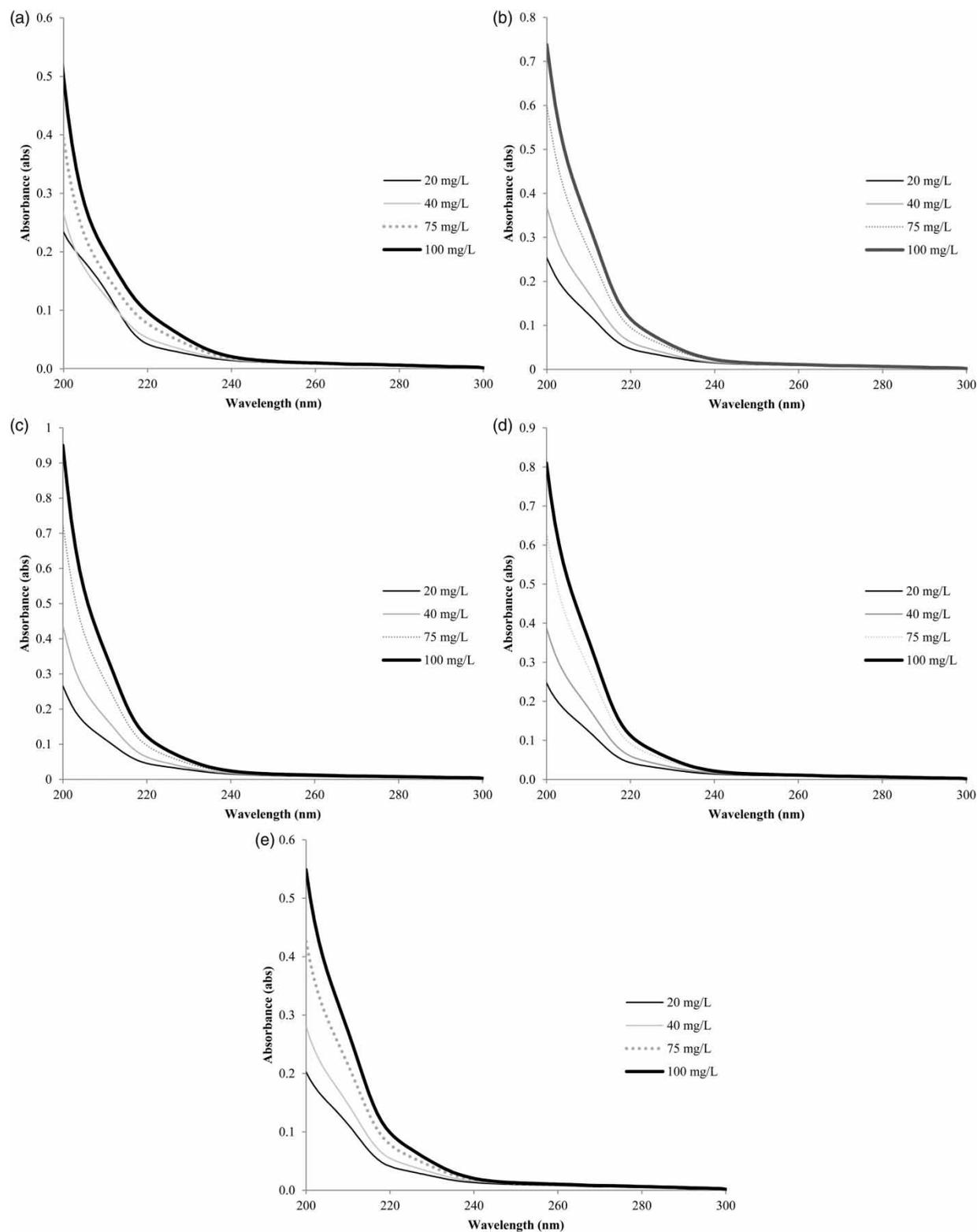
Figure 2 │ (a) Zetag polymer in water (20–100 mg/L), (b) SNF 475 polymer in water (20–100 mg/L), (c) SNF 4,400 polymer in water (20–100 mg/L), (d) SNF 4,600 polymer in water (20–100 mg/L), (e) SNF 4,800 polymer in water (20–100 mg/L).

RESULTS AND DISCUSSION

Measurement of polymer concentration in water

The relationship between polymer dose and UV absorbance was evaluated using five different polymers spiked to different concentrations in deionized water. Absorbance scans are shown in Figure 1(a)–(e) (0–20 mg/L) and Figure 2(a)–(e) (20–100 mg/L) for the five polymers. Overall, the shapes of the absorbance scans were similar between the different polymers. For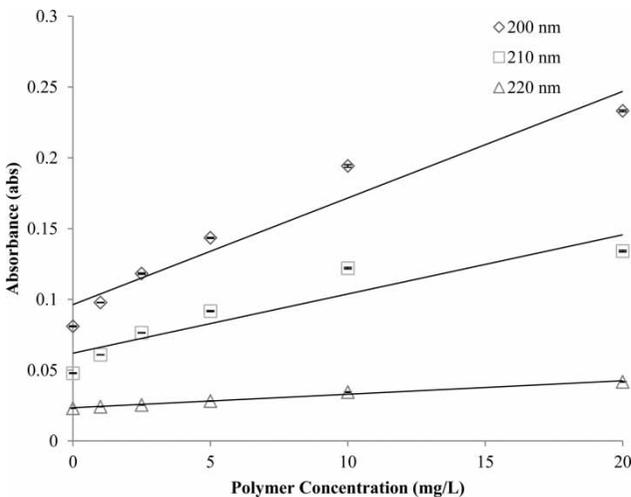 all polymers, increasing the polymer concentration resulted in an increase in the absorbance values, and the highest absorbance values were measured at 200 nm within the wavelength range tested. When higher wavelengths were used, it was found that absorbance values dropped substantially at 220 nm and there was no significant difference between the absorbance values beyond 240 nm between different polymer concentrations. The difference between absorbance values after each incremental polymer increase was highest at 200 nm. The absorbance values measured at 200 nm were similar for each polymer; at a polymer concentration of 20 mg/L, the absorbance was between 0.2 and 0.3.

Based on the results shown in Figures 1 and 2, it appeared that a linear relationship between absorbance and polymer concentration could be established at wavelengths 200, 210 and 220 nm. When absorbance values were plotted against polymer concentrations, a strong linear relationship was observed between absorbance and polymer concentration for each polymer (Zetag polymer shown in Figure 3) in the low concentration range (0–20 mg/L). R^2 values and slopes for the regression lines for all polymers are provided in Table 2. The slopes of the regression lines were highest at 200 nm indicating that this would be the wavelength that is most sensitive to changes in the polymer dose. A majority of the R^2 values were >0.9, and the lowest R^2 value was 0.816.

A strong linear relationship between absorbance and polymer concentration was also observed in the high

Figure 3 | Calibration curve for Zetag polymer in water (0–20 mg/L).

Table 2 | Linear regression values from calibration curves

	Concentration range (mg/L)	R^2			Slope		
		200 nm	210 nm	220 nm	200 nm	210 nm	220 nm
Zetag	0–20	0.938	0.864	0.988	0.007	0.004	0.001
	20–100	0.981	0.851	0.995	0.003	0.001	0.001
SNF 475	0–20	0.999	0.993	0.997	0.008	0.004	0.001
	20–100	0.999	0.999	0.999	0.006	0.003	0.001
SNF 4,400	0–20	0.999	0.999	0.999	0.009	0.003	0.001
	20–100	0.999	0.999	0.999	0.008	0.003	0.001
SNF 4,600	0–20	0.995	0.981	0.996	0.008	0.004	0.001
	20–100	0.999	0.999	0.999	0.007	0.003	0.001
SNF 4,800	0–20	0.922	0.816	0.979	0.006	0.003	0.001
	20–100	0.998	0.997	0.998	0.004	0.002	0.001
Composite	0–20	0.953	0.865	0.964	0.008	0.004	0.001
	20–100	0.731	0.749	0.931	0.006	0.002	0.001

concentration range (20–100 mg/L) for each polymer at wavelengths 200, 210 and 220 nm. A majority of the R^2 values were >0.9, and the lowest R^2 value was 0.851 (Table 2). The results indicated that the most sensitive absorbance measurements at 200 nm could be used to measure the polymer concentrations at both low and high polymer

residuals. In contrast, there was less variability between the absorbance values at a wavelength of 220 nm.

Although a strong linear relationship between polymer concentration and absorbance of samples exist in the concentration range of 0–20 mg/L, the sensitivity or the detection limit of the method at very low concentrations also needs to
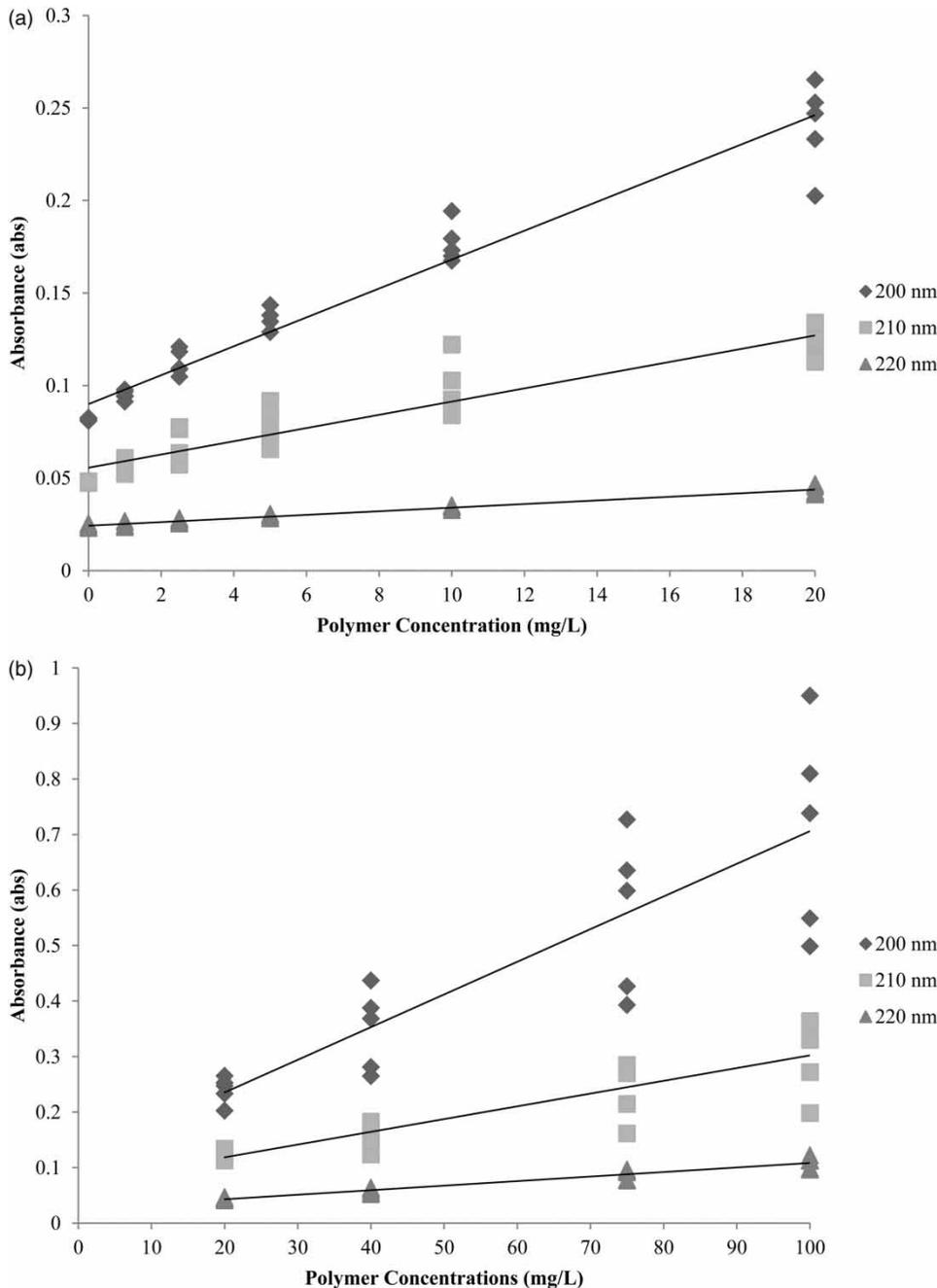

Figure 4 | (a) Composite calibration curve for 0–20 mg/L, (b) composite calibration curve for 20–100 mg/L.

be established. The MDL for the Zetag polymer in deionized water was calculated using the US Environmetal Protection Agency method presented in Berthouex & Brown (2002). Among the five polymers tested, Zetag polymer was chosen as the most challenging polymer as it showed the lowest linearity ($R^2 = 0.938$ at 200 nm, $R^2 = 0.864$ at 210 nm and $R^2 = 0.988$ at 220 nm) compared to other polymers. The MDLs were found to be 0.55 mg/L at 200 nm, 0.61 mg/L at 210 nm and 1.98 mg/L at 220 nm. It should be noted that the detection limits may vary with different polymers, and using the specific absorbance maxima for each polymer would increase the sensitivity of the method and lower the detection limit. Although the detection limit of 0.55 mg/L at 200 nm is higher than the detection limits reported using more sophisticated methods (i.e. NMR analysis or SEC analysis), the detection limit may be adequate for measuring residual polymer concentrations, depending on the application.

Combining the results from all five polymers, a composite calibration curve was determined for the low concentration range (Figure 4(a)) and the high concentration range (Figure 4(b)). The composite curve was more accurate between 0 and 20 mg/L polymer concentration at the wavelengths of 200, 210 and 220 nm, with R^2 from 0.86 to 0.94 (Table 2); in comparison, the composite curve was less accurate between 20 and 100 mg/L polymer concentration with R^2 ranging from 0.73 to 0.91. Therefore, the composite curve could provide a reasonable estimation when the polymer concentration is expected to be in the range 0–20 mg/L for a variety of polymers.

Measurement of polymer concentration in sludge centrate

The method was also evaluated using sludge centrate which was collected from a wastewater treatment plant. Centrate was selected as it represents a challenging wastewater sample that is highly concentrated. The centrate sample was spiked with Zetag polymer.

The centrate exhibited very high absorbance exceeding the working range suggested for the instrument (above 4 absorbance units). For the next experiments, centrate was first filtered through a 0.45 μ filter and then diluted by deionized water to 10 and 25% centrate before polymer addition. A very low concentration range of 0–10 mg/L

was chosen since this is the most challenging concentration range that would show the sensitivity of the method. The resulting absorbance scans are illustrated in Figure 5(a) for 10% centrate and in Figure 5(b) for 25% centrate. Similar to the results previously observed (Figure 1), increasing the polymer dose incrementally increased the measured absorbance and the highest absorbance was measured at 200 nm. The presence of dissolved organic matter in the centrate did not appear to interfere with the measurements. Dissolved organic matter strongly absorbs UV light around 254 nm which is not likely to interfere with the polymer
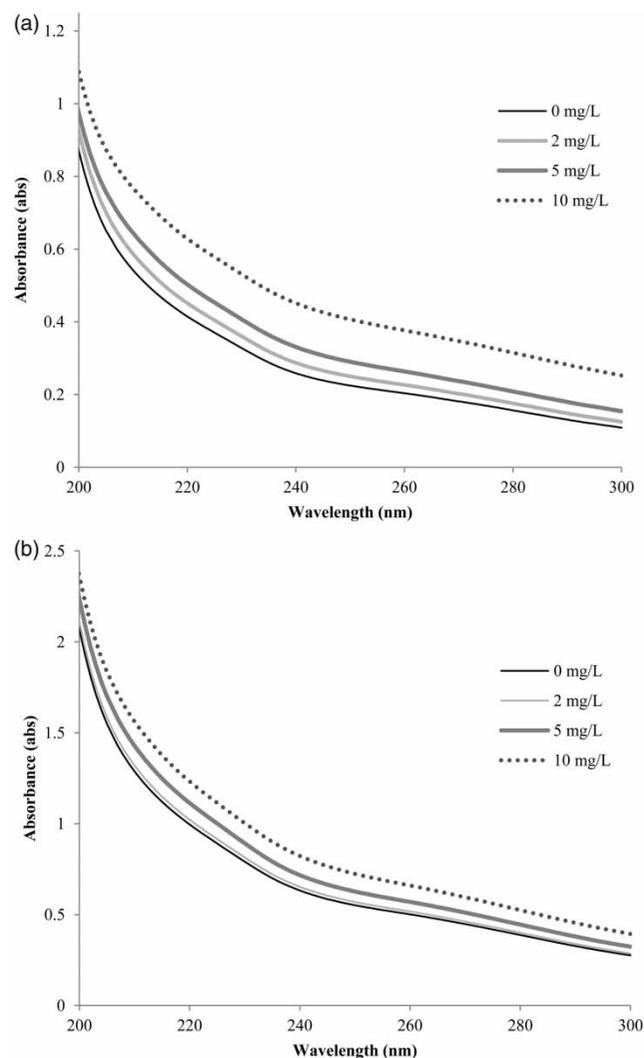

Figure 5 | (a) Filtration and dilution of centrate (10% centrate) for 0–10 mg/L Zetag, (b) filtration and dilution of centrate (25% centrate) for 0–10 mg/L Zetag.

Table 3 | Linear regression values for Zetag polymer in filtered and diluted centrate

	Concentration range (mg/L)	R^2			Slope		
		200 nm	210 nm	220 nm	200 nm	210 nm	220 nm
10% centrate dilution	0–10	0.995	0.997	0.991	0.021	0.022	0.021
25% centrate dilution	0–10	0.988	0.992	0.992	0.03	0.028	0.024

absorbance measurements at 200 nm. When absorbance values were plotted against polymer concentrations, a strong linear relationship was observed for both the 10 and 25% centrate samples. The R^2 values at 200 nm were 0.995 and 0.988 respectively (Table 3). These results showed that the method could also be used successfully in centrate samples after filtration and dilution.

Practical applications

As stated in the introduction, a quick and simple method for detecting low polymer concentrations does not exist. UV spectrophotometry is commonly used as an in-line measurement in drinking water and wastewater treatment plants, and a new generation of inline UV-Vis spectrophotometers that cover the full wavelength range 190–800 nm are now available. With pilot testing, the method described in this paper could be used to measure inline polymer concentrations at wastewater treatment plants. Factors that would require further work in pilot testing include suitability of the centrate or filtrate matrix, measurement of different polymers, quality assurance and quality control, calibration and seasonal changes, among others.

CONCLUSIONS

UV-Vis spectroscopy was successfully used in determining polymer concentrations in water and centrate samples collected from a wastewater treatment plant. Five different polymers were tested and the highest absorbances were measured at 200 nm. A strong linear relationship was observed between absorbance values and polymer concentrations in the low (0–20 mg/L) and high (20–100 mg/L) polymer ranges. The method was also sensitive at low polymer concentrations (<10 mg/L), and the MDL for the Zetag polymer was determined as 0.55 mg/L at 200 nm in

deionized water. It should be noted that the detection limits may vary with different polymers, and using the specific absorbance maxima for each polymer would increase the sensitivity of the method and lower the detection limit.

The method provides a quick and simple tool for measuring polymer concentrations, and it is useful for both research and practice. It may find future applications in various fields and industrial processes that require measuring and controlling the polymer concentration both in-line and off-line. The method would be useful in preventing the excessive use of polymers, which would not only save money but would also help to reduce the adverse effects of polymers on aquatic ecosystems.

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