Determining Porous-Cup Resistance to Various Ions.

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ABSTRACT

Lack of in-situ instrumentations made difficult to monitor concentration level of various ions in site for specific management of environmental and agricultural practices. A new fast response and low sample volume soil solution collected in stainless steel solution sampler combining with ion selective electrode (ISE) or Fiber-optic wire probe has been developed to determine in-situ ion concentrations in soil solution. However, the ion exchange between stainless steel sampler and surrounding soil solution is dominated by diffusion process. The concentration of ions diffused into stainless steel solution sampler with time needs to be estimated for establishing accurate monitoring schedule. To accomplish such task, a simplified model to predict the time-varying nitrate concentrations in the inner cup can be developed by using simple electric circuit analogies. The slope of the relative concentration inside the stainless steel cup to overall average ion concentration in equilibrium gives overall resistance to ion diffusion. Employing overall resistance, the sensitivity of diffusion on the properties of sampler cup can be investigated. Moreover, this paper describes the relationships between overall resistance and the mass diffusion of examined ions using simplified analytical model.

BACKGROUND and METHODS

Absorbance measurement

The absorbance measurements employed a fiber optic dip probe that was obtained from Ocean Optics. A Heraeus FiberLight UV source was used to provide light for the measurements and a two-channel Ocean Optics SD-2000 UV-VIS spectrometer was used for spectrum analysis. The spectrometer was coupled to a computer for data acquisition and analysis. Deionized water was used as the reference solution. A schematic of the overall optical system is shown in **Fig. 1**.

The dip probe was in the form of a stainless steel cylinder that contained two optical fibers and a lens. UV light from the Heraeus light was directed into the input fiber of the dip probe. This fiber terminated within the probe, and the light that exited from the fiber terminus impinged upon a lens located at the end of the stainless steel tube. This lens directed the light along a path through the liquid (water and ions) and onto a mirror that was held rigidly in place a fixed distance, typically 2 mm or 5 mm, from the lens. The light that was reflected from the mirror returned to the lens, which focused the return light beam onto the return fiber. This fiber carried light back to one of the spectrometer channels, allowing the liquid absorption spectra to be measured. The dip probe had a reference fiber to enable fluctuations in the light source to be taken into account when absorbance values were calculated.
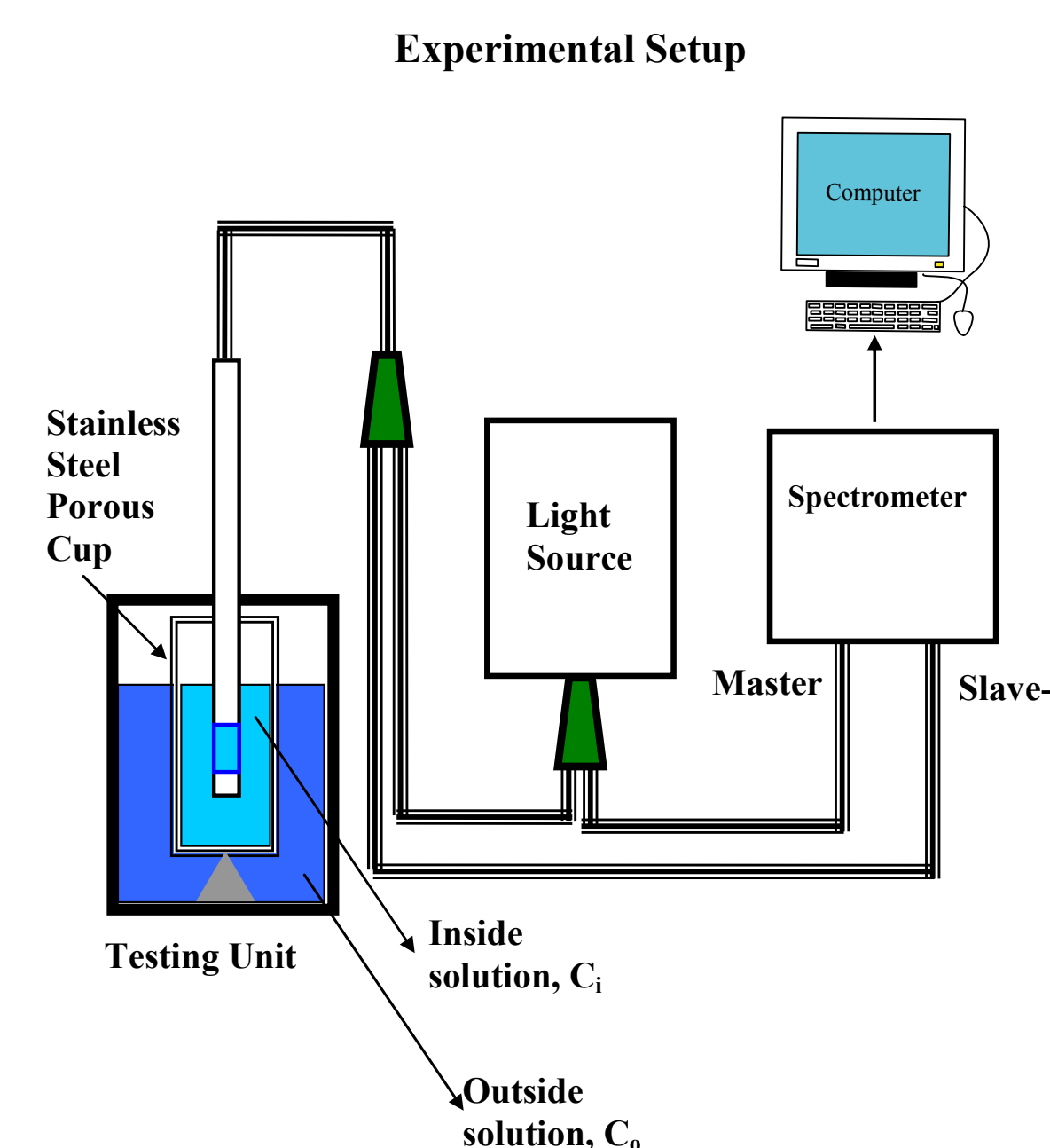

Experimental Setup

Stainless Steel Porous Cup — Computer — Light Source — Spectrometer — Master — Slave-1 — Testing Unit — Inside solution, C_i — Outside solution, C_o

Figure 1. Schematic of the optical set up.

Optical Fibers — Lens — Mirror — Measurement Chamber
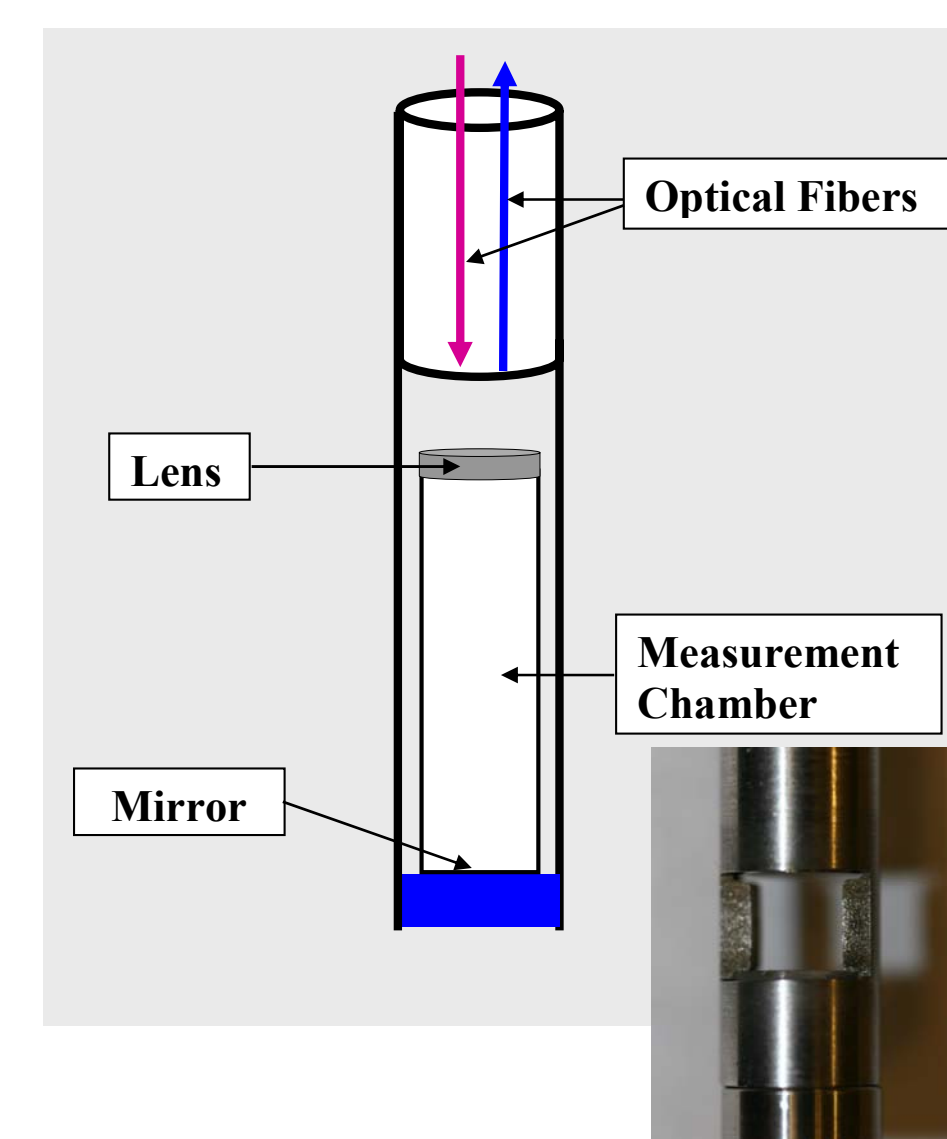
Figure 2. Schematic of Dip Probe.

BACKGROUND and METHODS- continued

The reference fiber was attached to the second channel of the spectrometer. The path length used for the present dip probe configuration was 10 mm. A schematic of the dip probe is shown in **Fig. 2**. Aqueous nitrate ions exhibit two UV absorption peaks. One peak, which is relatively weak, is centered at about 300 nm. The other peak, which is much stronger, is centered at about 210 nm. Both peaks are relatively broad such that useful absorption data can be obtained at wavelengths away from the peaks. The optical system used in these experiments could measure UV-VIS absorption spectra from about 200 nm to 700 nm, and report results from measurements that employed data from the stronger UV absorbance peak for nitrate. However, it was found that for nitrate loadings as high as 100 ppm, the short-wavelength absorbance values were too high to be accurately measured for wavelengths less than about 230 nm. As a result, we focused on obtaining absorbance spectra at wavelengths in the range 235 nm to 240 nm, which provided good results while still allowing strong (but not saturated) signals. **Figure 3** shows absorbance spectra over this range. These spectra were obtained by placing the dip probe into previously-prepared nitrate-water solutions. The reference spectrum in each case was deionized water. By using the data in **Fig. 3**, calibration data were obtained to relate the absorbance at a given wavelength to the amount of nitrate present in the sample. **Figure 4** shows calibration data for the wavelengths 235 nm, 238 nm and 240 nm.
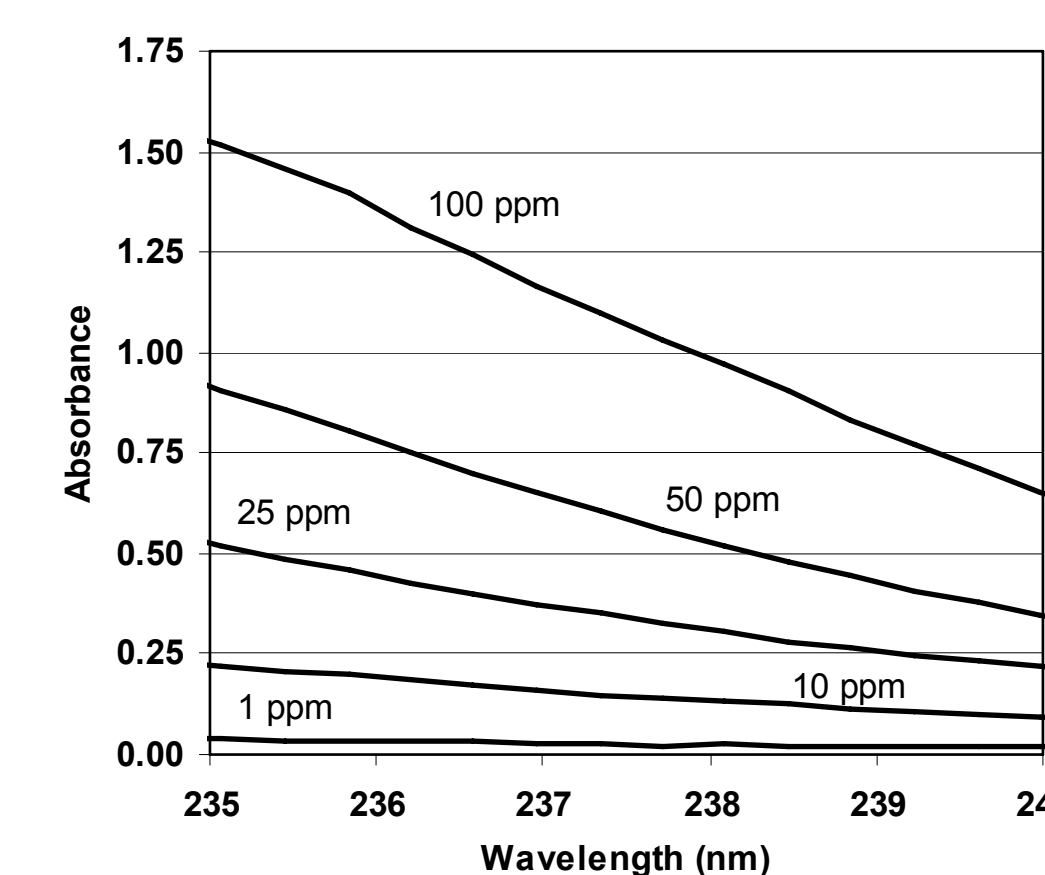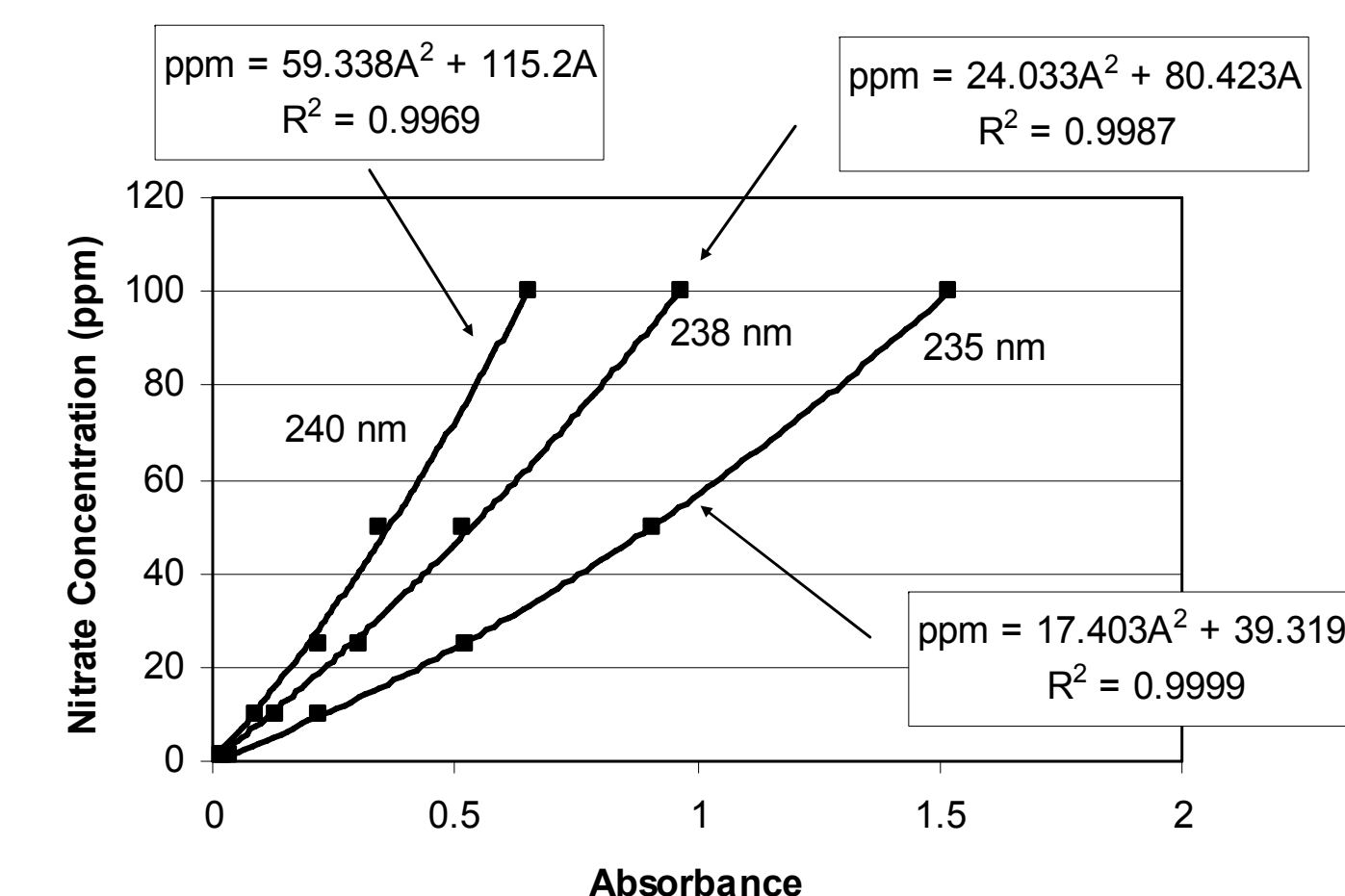

Figure 3. Nitrate absorption spectra.

Figure 4. Absorbance calibration data.

SIMPLE MODEL and EXPERIMENTS

Predicting the time-varying concentration

A simplified model to predict the time-varying nitrate concentrations in the inner cup can be developed by using simple electric circuit analogies. In this model, average nitrate concentrations inside the cup are denoted as C_i and average nitrate concentrations outside the cup, i.e., in the outer container, as C_o. In addition, the liquid volumes inside and outside the cup are denoted as V_i and V_o, respectively. For simplicity, the volume of liquid contained within the porous wall material is assumed to be negligible. The rate, J, that nitrate ions diffuse from the outer volume into the cup is given by Eq. (1)

$$ J = \frac{C_0 - C_i}{R_{tot}} \qquad (1) $$

where R_{tot} is the overall resistance to mass transfer. In addition, J can be related to the time-rates-of-change of the average concentrations in the inner and outer zones, as shown in Eq. (2).

$$ J = V_i \frac{dC_i}{dt} = -V_o \frac{dC_o}{dt} \qquad (2) $$

For development of the model, we will also require that mass is conserved (Eq. (3))

$$ C_i V_i + C_o V_o = C_{ave} V_{tot} \qquad (3) $$

SIMPLE MODEL and EXPERIMENTS - continued

By combining Eqs. (1) – (3) a ordinary differential equation can be developed with subjecting to the initial condition $C_i(0) = 0$, leading to $C_{ave} = C_o(0) / (1 + V_i / V_o)$, where $C_i(0)$ and $C_o(0)$ are the nitrate concentrations at the time t = 0. After rearranging the solution of ordinary differential equation, Eq. 4 was obtained

$$ \ln\left(1 - \frac{C_i}{C_{ave}}\right) = -at \qquad (4) $$

such that a plot of $ln(1 - C_i / C_{ave})$ as a function of time should yield a straight line with the slope $-a$.

Diffusion experiment

The concentration of ions diffused into stainless steel solution sampler with time needs to be estimated for establishing accurate monitoring schedule. To accomplish such task, simple liquid diffusion experiment was started by adding deionized water where $C_i(0) = 0$, into stainless steel (SS) porous cups and a solution at predetermined concentration into a outside reservoir. At t=0, the stainless steel cup filled with de-ionized water was immersed into the reservoir filled with nitrate or sugar solution. The changes in concentration with time were measured continuously with UV-VIS fiber optic dip probe during nitrate (NO_3^-) or sugar diffusion from outside solution into sampler solution **(Figure 5A and 6A)**. These experiments was repeated for two types stainless steel porous cups having different resistance to diffusion of ions .

RESULTS

The Experimental data from a diffusion experiment with the inner cup initially filled with pure deionized water, i.e., with $C_i(0) = 0$, are shown in **Fig. (5B and 6B)**. The data in **Fig. 7** show that $ln(1 − C_i / C_{ave})$ varies linearly with time. By measuring the slope of the data, which determines the variable a, the overall resistance to nitrate diffusion, i.e., R_{tot}, can be found by using definition of slope a. This overall resistance can be related to parameters such as the porosity and thickness of the cup wall material and the mass diffusion coefficient of nitrate.
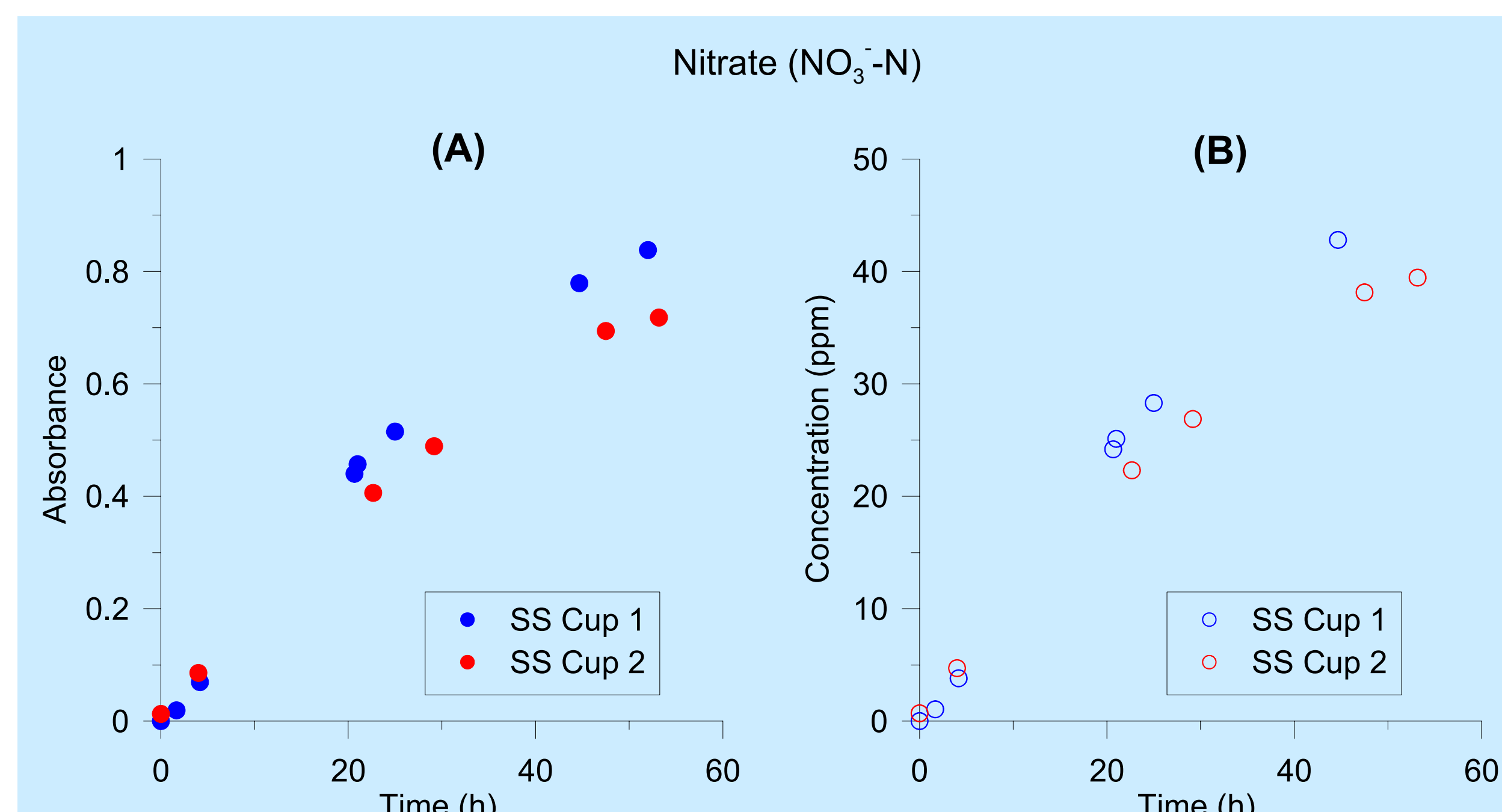

Figure 5. (A) Absorbance and (B) corresponding concentrations of nitrate as a function of time at two different SS cups.
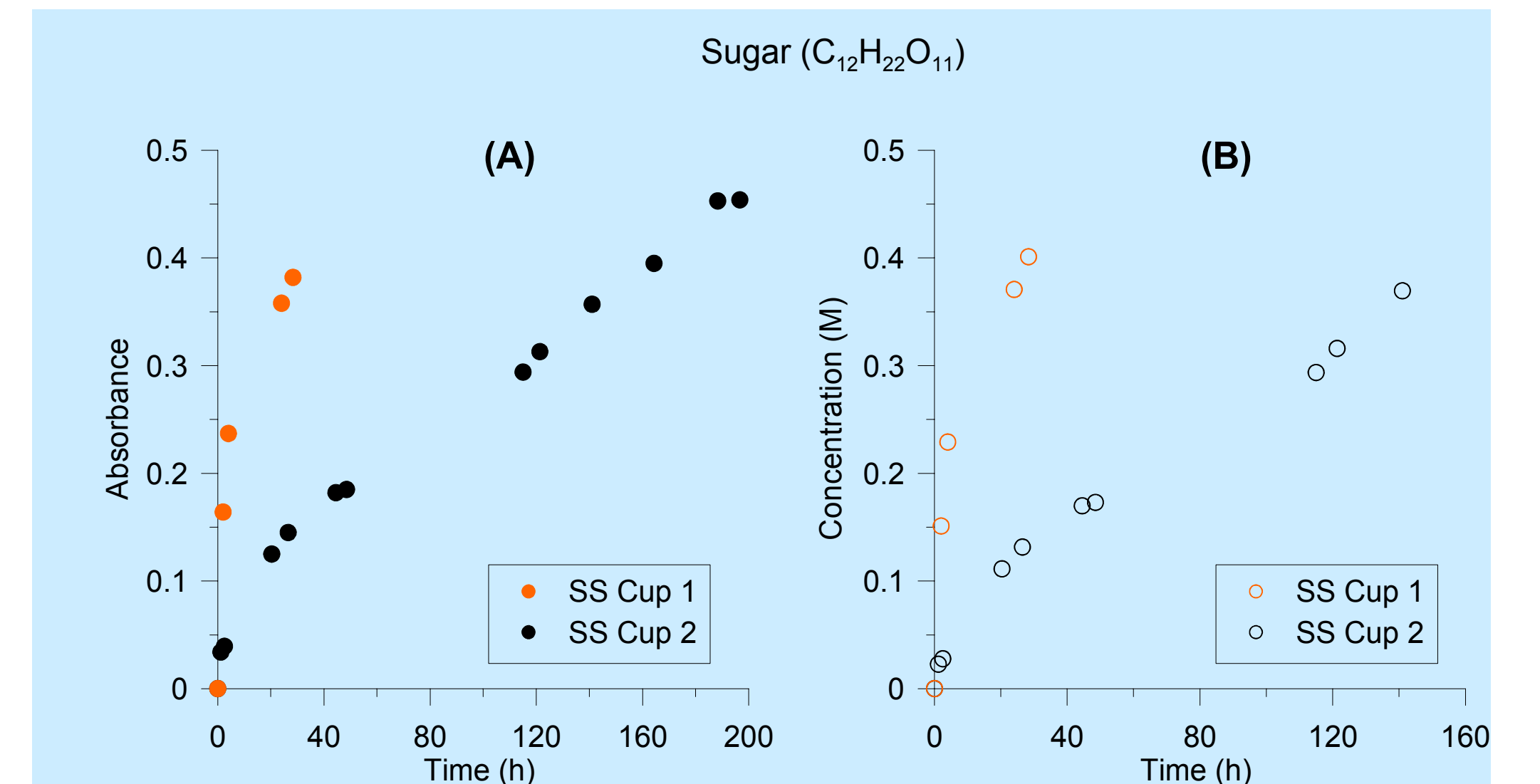
RESULTS - continued

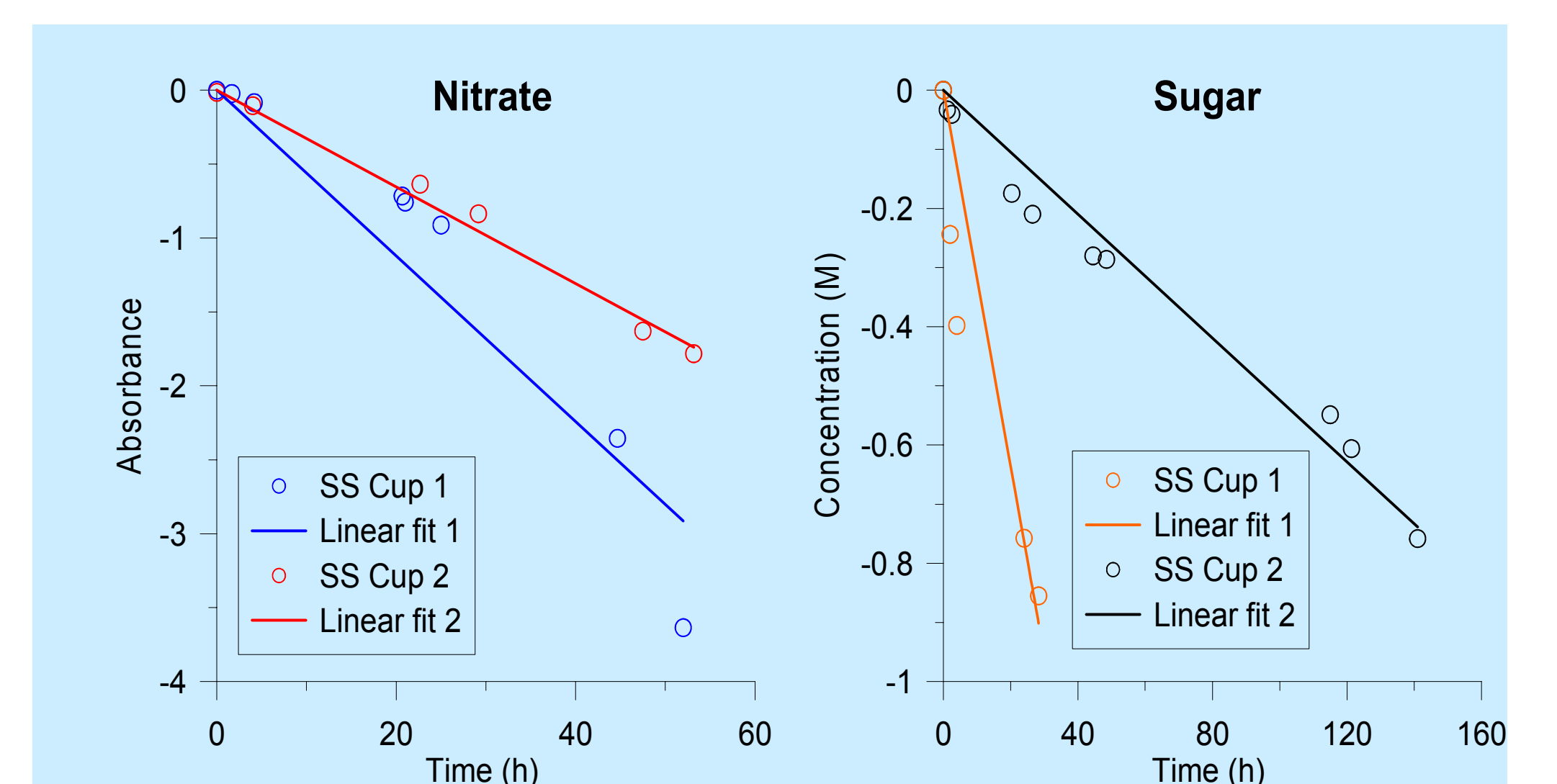**Figure 6. (A) Absorbance and (B) corresponding concentrations of sugar as a function of time at two different SS cups.**

Figure 7. Plot of ln(1 - C_i/C_ave) as a function of time.

Table 1. Linear equations for data and calculated total resistance of the SS cups .

Solution	Cup	Equation	R^2	RSS	R_{tot}
Nitrate	SS Cup 1	y = -0.05603 x	0.89904	1.18073	3.339
Nitrate	SS Cup 2	y = -0.03270 x	0.98785	0.03372	2.926
Sugar	SS Cup 1	y = -0.03180 x	0.78707	0.10783	6.385
Sugar	SS Cup 2	y = -0.00523 x	0.97007	0.01850	20.076

CONCLUSIONS & FUTURE WORK

- Resistance of SS cups are found to be similar for nitrate diffusion, although the diffusion of nitrate ion in solution as a function of time for the different SS cups showed discrepancy (Figure 5B and Table 1).
- Resistance of SS cups are quite pronounced for diffusion of sugar (Table 1).
- This overall resistance of porous cups to ion diffusion will be related to mass diffusion coefficient.