

**Determining the Electron Storage Capacities of Black Carbon and Humic Acid  
Through Chemical Redox Titration**

by  
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## ABSTRACT

Carbonaceous constituents in soil and sediment play critical roles in biotic and abiotic geochemical redox reactions. In particular, black carbon and humic substances supplying and receiving electrons are of key interest to researchers for their role in facilitating redox transformation of contaminants either directly (i.e., abiotically) or through microbial activity in soil and sediments.

Black carbon (BC) is a category of solid carbonaceous materials formed by pyrolyzing biomass in an oxygen-deficient environment. As a commercially available black carbon that aims to promote soil fertility and microbial activity, it has been hypothesized that redox-active functional groups, such as quinone, are presented in the carbon matrix, and that they can exchange electrons with external bulk reactants. In this work, titanium(III) citrate, a colored, one electron transfer reducing agent, was evaluated as a titrant reducing a commercial black carbon and a standard humic acid. Through a series of batch reduction experiments and continuous monitoring of the UV-Vis absorbance at 400 nm, the measured electron storage capacity (ESC) of the black carbon was  $4.3(\pm 0.1)$  mmol electron/gram at pH 6.4,  $4.1(\pm 0.1)$  mmol electron/gram at pH 5, and  $4.2(\pm 0.4)$  mmol electron/gram BC at pH 7.5.

In addition, to standardize titanium(III) citrate and to demonstrate that it has the capability to fully reduce quinone functional groups (the redox active component

in black carbon and humic acid), 99% purity 1,4-benzoquinone was used to quantitatively titrate titanium(III) citrate stock solution to standardize the exact concentration of titanium(III) used prior to the ESC experiment. We show that the reduction of anthraquinone-2,6-disulfonate (AQDS) and benzoquinone (BQ) are kinetically facile processes; therefore, the slow kinetic of black carbon reduction is ascribed to slow intra-particle diffusion in black carbon particles.

The ESC of humic acid was also estimated using similar titration applied on black carbon. Leonardite humic acid (LHA), one of the most studied standardized humic acid forms, was titrated using a similar approach. By observing the net change of absorbance at 250 nm upon mixing known amounts of titanium(III) citrate and LHA in solution, the electron transfer from titanium(III) citrate to humic acid can be studied. The ESC of Leonardite humic acid was determined to be  $4.7(\pm 0.4)$  mmol/g LHA at pH 6.4,  $3.1(\pm 0.3)$  mmol/g LHA at pH 5 and  $4.1(\pm 0.4)$  mmol/g LHA at pH 8.

An approach of redox reduction of black carbon are hereby proposed, and upon acquirement of additional research progress, a protocol of black carbon titration can be developed and enables researchers to determine the electron storage capacity of black carbon synthesized using various materials and approaches in an efficient and affordable manner.

## Chapter 1

### Research Goal and Background

#### 1.1 Identification of research objective

This research project is initially served as an extension of the work performed by Dr.Saquin, Dr.Yu and Professor Chiu published in early 2016, who investigated and reported the amount of electrons which are able to be deposited and released via one specific microorganism to and from soil reef black carbon (biochar), one of the commercially available black carbons (Saquin et al, 2016). In light of the experimental value of biologically available electron storage/donating capacity, which is the amount of electron (in mmol) being able to stored or donated per units of mass of black carbon (in gram), a more intuitive, and perhaps more complex, hypothesis has been postulated: Can *Geobacter metallireducens*, the microorganism being used in this research, access all of the redox active components (functional groups) in black carbon? If not, what percent of the redox moieties in black carbon can be accessed by microorganism?

Given that the intricate structure of the carbon matrix, biochar can act like a complex network such that much of microorganism cannot easily access the deeper component and grant access to more sites for electron storage/release due to the restriction of size (Saquin et al, 2016), as the TEM image of surface of the char can be found in the cited literature. On the other hand, conventional three-electrode electrochemical titration, in combination with redox active mediators, permits only a small portion (on the order of magnitude of milligram) to be examined (Klöpffel et al,

2014). Moreover, both experimental methods mentioned above require costly and lengthy experimental setups, which add to the difficulty in replication. Recent publication from PrévotEAU et al has made direct titration in bulk scale possible via using ferricyanide complex to oxidize reduce black carbon using rotating disk electrode (RDE) as tool of concentration measurement (PrévotEAU et al, 2016); however, due to different experiential setup and procedure, PrévotEAU et al's work took around two months for the completion of experiment. In both study mentioned above, organic reductant/mediator has been used, which has incorporated organic sorption to the uncertainty of measured value.

## **1.2 Research Objective and significance**

Experimenting on large sample size of black carbon gives quantitative result on the large-scale performance of black carbon upon use on site. To develop an experimental assay that permits the timescale of black carbon titration experiment to be shorten to within hours and with affordable instruments, a small scale redox titration in a batch reactor is promising in terms of investigating the timescale and kinetics of biochar oxidation/reduction. The primary objective of this work is to explore the potential of utilizing reductant/oxidant and UV-Vis technique to establish an approach of estimating the ESC of black carbon in a timely manner. In addition, such study is extended to humic acid to testify and validate this technique in liquid phase carbonaceous compound.

The chemical titration of black carbon, especially soil reef BC used in this experiment, enable researchers to compare not only the magnitude of the amount of biologically accessible electron versus chemically accessible electrons, but also establish a quick reduction method for one who is interested in studying the ESC of

black carbon of interest, in addition to its measuring its numerous physical and chemical properties. Given the wide usability of black carbon proposed in numerous literatures, such measurement provides further insights of the role black carbon play in altering the redox behavior and fostering microbial activity in soil and sediments.

### **1.3 Background of Black Carbon**

Pyrogenic Black carbon, as known as biochar, is the final product of pyrolysis using various biomass feedstock under oxygen deficient environment. In particular, black carbon has gain enormous attention in recent years in terms of its use in agricultural and environmental sector due to its excellent hydraulic conductivity, water retention and contaminant immobilization capacity (Beck et al, 2011). Readers should note that in the scope of this work, black carbon, in general, refers to a commercially available product (Soil Reef Biochar, additional information available at appendix A), which has been artificially further sieved for preparation in experimental work. In addition, it is also known that various feedstock and pyrolysis methods plays a great role in shaping the physiochemical properties of biochar, and the properties of black carbon can therefore be controlled to a significant extent (Ahmad et al, 2014). Similar to the properties of activated carbon, black carbon shows efficacy in immobilization of heavy metal due to various mechanisms, for example, electrostatic attraction and complexation on the surface functional group (Ahmad et al, 2014; Park et al, 2011; Graber et al, 2014). The role of immobilization of organic contaminant and nutrients (N and P containing inorganic anions) has also been demonstrated by various sources, and readers with interested should consult the cited literature for more information (Ahmad et al, 2014; Cabrera Mesa et al, 2014; Wu et al, 2013). It is also noteworthy to mention that black carbon, and in some cases its leachate, supports microbiological

activities to different degrees, and the exact mechanism is currently still unidentified. Some hallmark experimental study includes investigating the biotransformation of azo dye (Van Der Zee et al), microbial reduction of hematite (Xu et al, 2016) and the denitrification experiment conducted by two colleagues in our research lab (Saquing et al, 2016). Recent attention in the research community has shed light on understanding the role that redox properties of black carbon in biogeochemical processes; this work strives to expand our understanding on this aspect of electron storage capacity.

#### **1.4 Electron storage capacity of black carbon**

Previous literature has focused extensively on the physisorption and hydrological impact of black carbon under various conditions (Ahmad et al, 2014; Beesley et al, 2011). Nevertheless, recent research has gained insight into the role played by the redox active component within the carbon matrix of biochar and has suggested that the actual electron content of black carbon can be of the magnitude of  $10^{-3}$  to  $10^{-6}$  moles electrons per gram of black carbon (Klöpffel et al, 2014; PrévotEAU et al, 2016; Saquing et al, 2016). On the other hand, as mentioned in the introduction section, all previous method employ the use of a three-electrode electrochemical system. The actual reproduction of experimental setup and manipulation might be challenging for interested researchers to with the goal to determine the electron storage capacity of other black carbon. We hereby propose using titanium(III) citrate complex as a one-electron reducing agent to carryout black carbon reduction for rapid characterization of electron accepting capacity.

## 1.5 Identification of reducing agent of interest

The oxidation reaction (release of electron from one compound) and reduction reaction (receive of electron from another compound) are necessarily coupled at all-times to retain overall electro-neutrality. In particular, to access the electrochemical properties of black carbon, one can treat black carbon as the reducing agent, where black carbon donates electrons to other chemical/biological species, or as oxidizing agent, where black carbon receives electrons from elsewhere. Given the charcoal-like nature of black carbon, the only approach to access the respective redox processes inside of biochar is via delivering oxidizing or reducing agent into the carbon matrix, and enable the reactant and product freely diffuse into and out of the carbon skeleton until the reaction has reach to equilibrium (i.e., the reaction has reached completion). Considering the coupling nature of the redox reaction, one should expect that the concentration of reactant drops continuously, and approaches an unchanging concentration upon equilibrium. To reduce the complexity of experiment, this work hereby develops the method of using reductant to reduce air-oxidized black carbon to assess the ESC.

Although there is a wide variety of reductants to be selected as the primary reactant for this experiment, several criteria should be met simultaneously due to the specific nature of biochar and experiment, an ideal reductant should have the characteristics discussed below.

- The selected reductant should be inorganic, since organic compounds would tend adsorb on to the surface of black carbon, and the organic carbon/water partitioning coefficient can be estimated by using the combination of Linear Free Energy Relationship and octanol carbon partition coefficient (DiToro, 2015).

- Relatively high solubility in water. The entire experiment is performed in an Erlenmeyer flask, one needs to ensure that the enough reducing agent can be solubilized such that there must be excess reactant left over after the reaction.
- Negatively charged surface (Mukherjee et al, 2011). To successfully and accurately quantify the amount of electron donated to black carbon, the reactant must not be adsorbed or absorbed on the solid. It has been determined that the surface of black carbon is negatively charged at near-neutral pH, and therefore one should select reducing agent that is negatively charged on the surface to avoid electrostatic attraction.
- Concentration should be easily measureable. Oxygen is a universal oxidizing agent, and exposure of oxygen in ambient environment causes significant and unmeasurable intervention to the experimental result. Therefore, an anaerobic environment (anaerobic glovebox) was to be used to perform the experiment. In the case of optical activity using UV-Vis, the extinction coefficient of reductant shall be relatively high and with minimum interference by solution.
- Stable over the range of experimental condition. Although exposure to oxygen is not an immediate concern, the stability of reducing cannot be taken for granted, since a number reducing agents originate disproportionation or reacts with water once aqueous solution has been prepared. In addition, the reagent must be relatively stable at experimental pH. And it shall exhibit no interaction with buffering solution and pH condition. In addition, the reagent must be relatively stable at experimental pH and can co-exist with buffering solution. A preliminary control experiment is needed to screen out and decide the final candidate.

- Preparation of reactant must be simple and safe. Given a large variety of reductant product come in the form of pure organic reagent, inorganic salt or concentrated solution, several reductants have been phased out in the search due to their hazardous nature and high difficulty of reactant preparation.

### **1.6 Titanium(III) citrate complex**

Titanium (III) cation and titanium(IV) cation are two of the most common oxidation state for the element of Titanium (Zehnder et al, 1976). Titanium(III) citrate, which is a brownish-purple colored complex, is widely used as reducing agent for biological research (Zehnder et al, 1976, Moench et al, 1983; Seefeldy et al, 1994; Collins et al, 2005), and it easily undergoes one electron oxidation and converted into colorless titanium(IV) citrate complex (Uppal et al, 2006). Previous study has reported the one electron reduction potential of titanium(IV) citrate to be of -480 mV with respect to standard hydrogen electrode (Zehnder et al, 1976). In-situ measurement has confirmed that as pH change 1 unit, the reduction potential of titanium(III) citrate increases for 59 mV, such Nernstian behavior proves that the reduction is indeed couples with the uptake of one proton as one titanium(IV) citrate is being oxidized to its conjugate oxidation product (See appendix G). In addition, by examining the isosbestic point of the spectrum of Titanium (III)/(IV) complex, it can be shown that conservation mass for Titanium cation can be attained.

### **1.7 Introduction of Lenarodite Humic Acid (LHA)**

The redox titration of black carbon has enable the author to have a better understanding of the electrochemical behavior in terms of the amount of electron

transfer by infusing in reducing agent. Meanwhile, yet another major category of redox active organic component, the measurement of electrochemical properties of humic acid has gain interest in the research communality years before the intense interest of black carbon starts to develop. There are numerous sophisticated techniques developed for measurement, including the use of three electrode cell (working, auxiliary and reference electrode), UV-Vis electrophotography and measurement at inferred wavelength and so forth (Aeschbacher et al, 2009, 2011, 2012; Baigorri et al, 2009; Maurer et al, 2010; Sharpless et al, 2014; Yang et al, 2016). Similar as black carbon, it has been widely considered that function group responsible for the redox reaction is of various type of quinone, and microbial activity can also be supported by such (Jiang et al, 2008), and the electron exchange capacity of LHA has been measured to be of 3 mmol/g at pH 7 (Aeschbacher et al, 2011).The rationale of this work is to: First, validate the data from black carbon work by using titanium(III) citrate to titrate a known natural organic component with widely known ESC. Second, evaluate the potential of using such reducing agent to titrate colored natural redox active constituent (humic acid).

## Chapter 2

### Materials and Methods

#### 2.1 Standardization of reducing agent

Titanium(III) citrate complex appears to be one of the promising option in the search, and sodium citrate is used as buffering agent ( $pK_a=6.4$ ). Since Titanium(III) cation comes in the form of relatively dilute titanium(III) chloride solution in 2 N hydrochloric acid, the protocol of preparation will simply be the mixing of several solution to achieve the objective solution for experiment.

It has come to the attention of both the author and research advisor that although the titanium (III) chloride solution is purchased from the same vendor, same company and with the same product specification, the actual concentration of product does fluctuate from one batch to another. Although the certificate of analysis does gives some parameter on the product concentration upon examination of product following the manufacture, the author has decided standardize the titanium(III) chloride solution using 1,4-Benzoquinone, which is a pure (99%) and stable surrogate of the postulated redox active quinone functional group as proposed in the literature, given the uncertainty of solution density and titanium(III) content. It is worthwhile mentioning that quinoic compounds are two electron acceptors. Upon successfully receiving two electrons, two carbonyl bond converts to two hydroxyl bond, where two additional electrons are stored in the carbon connecting to the oxygen atom (change in oxidation state of carbon atom from +2 to +1)

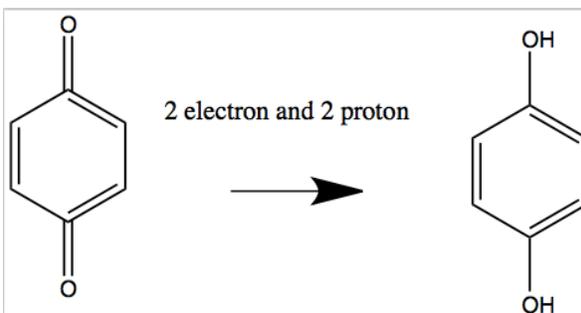


Figure 2.1. Schematics of oxidation of 1,4-benzoquinone, which is a widely used oxidation agent in study of redox properties of geochemical reducing agents (note the transfer of two electrons and protons).

Akin to the figure presented above, benzoquinone, which is a one benzene ring compound sharing the same bonding configuration with AQDS, exhibits the same oxidation property, and the color change is also coupled to oxidation of molecule due to the change in conjugated  $\pi$ -bond.

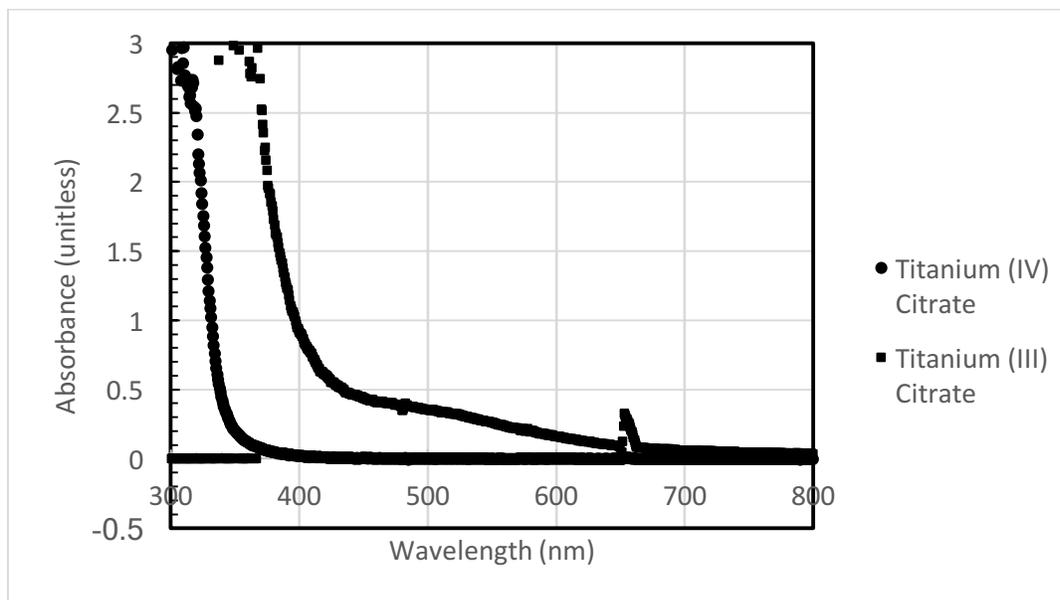


Figure 2.2. UV-Vis Spectrum of titanium(III) citrate and titanium(IV) citrate at total Titanium concentration of 10 mmol/L at pH 6.4.

In figure 2.2, the UV-Vis spectra of titanium(III) citrate and titanium(IV) citrate are shown. Note that in the black carbon titration experiment, the wavelength selected for measurement is 400 nanometers, and the absorbance changes pronouncedly upon oxidation of titanium(III) cation. In spectrophotometry, the ideal range of absorbance for use is from 0.05 to 1 in absorbance, since absorbance is calculated by taking the  $\log_{10}$  of the ratio of light intensity of the receptor to the light source. In other words, an absorbance of zero stands for no light has been diffracted by the solution with respect to blank, and an absorbance of 1 represents that 90% light intensity is diminished upon the diffraction/absorption by solution/colloidal species presented in cuvette. Visually, titanium(III) citrate solution at experimental condition is of brownish purple color, and titanium(IV) citrate, which is the oxidation product of titanium(III) citrate, is completely transparent in consistent with the spectrum presented above.

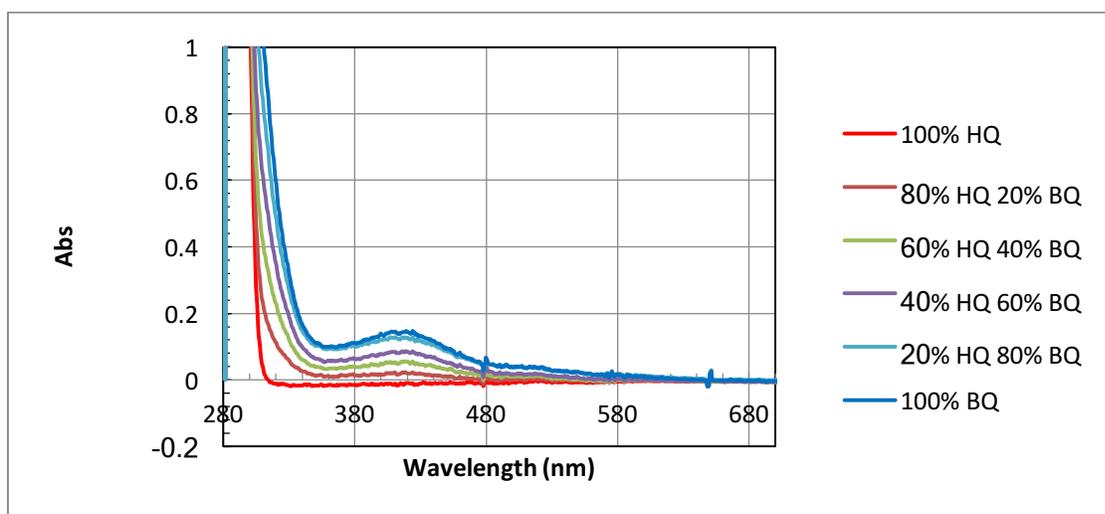


Figure 2.3. UV-Vis spectrum of of 1,4-benzoquinone (BQ)/1,4-bydroquinone (HQ) of various ratio after 10 minutes of incubation. Total quinone concentration 5 mM under 100 mM citrate buffer, pH 6.4 +/- 0.1.

On the other hand, benzoquinone solution, which is the oxidizing reagent to be used to oxidize titanium(III) citrate, is of light green color upon preparation from solid crystals. However, it has been observed by both the author and coworker from other laboratory that freshly prepared benzoquinone solution has the tendency to visually darken with time (on the order of hours), such that the UV-vis spectrum rises upon sitting on the bench top in both aerobic and anaerobic environment. Literature suggests that such phenomenon is due to the formation of quinhydrone (adduct of 1,4-benzoquinone and 1,4-hydroquinone). This suggests that benzoquinone prepared in-situ needs to be used upon preparation, and the duration of experiment must be short enough such that the extinction coefficient of 1,4-benzoquinone does not change with time in short-term.

In a well-mixed reactor containing solution of titanium(III) citrate of sufficient concentration, one can observe the following color change (qualitatively) upon slow addition of benzoquinone solution.

- First, discoloration of purplish color happens due to increasing consumption of titanium(III) citrate while all benzoquinone has been reduced to hydroquinone
- Second, solution turned entirely clear where benzoquinone is further added into the solution. At this point, the amount benzoquinone added into the system is completely consumed by titanium(III) citrate and there's no titanium(III) citrate left over at the absorbance at 400 nm.
- Finally, the solution subsequently turned yellow upon continuous addition of benzoquinone, where all titanium(III) citrate has been consumed and benzoquinone is in excess.

If one monitors the change of at 400 nm during such experiment (at constant total volume by setting up numerous batches), where both benzoquinone and titanium citrate both absorbs strongly, one will be able to observe a linear decrease in absorbance with additional of benzoquinone, and the absorbance will increase lineally due to further addition of benzoquinone. The extinction coefficient of all four species are tabulated below.

Table 1.1 Extinction coefficient of experimental reagent used for calibration experiment at pH 6.4.

Compound	Extinction coefficient at 400 nm at pH 6.4	unit
Titanium(III) citrate	91.5	1/(M*cm)
1,4-Benzoquinone	32.4	1/(M*cm)
Titanium (IV) Citrate	3.2	1/(M*cm)
1,4-Hydroquinone	0.8	1/(M*cm)

By investigating the intercept of the two line by setting up numerous batch tubes with different proportion of titanium(III) citrate and 1,4-Benzoquinone solution added and maintaining the total volume constant, the intercept of these two lines represents the point where titanium(III) citrate and 1,4-Benzoquinone have both been reacted in completion, and there's no reactant in excess.

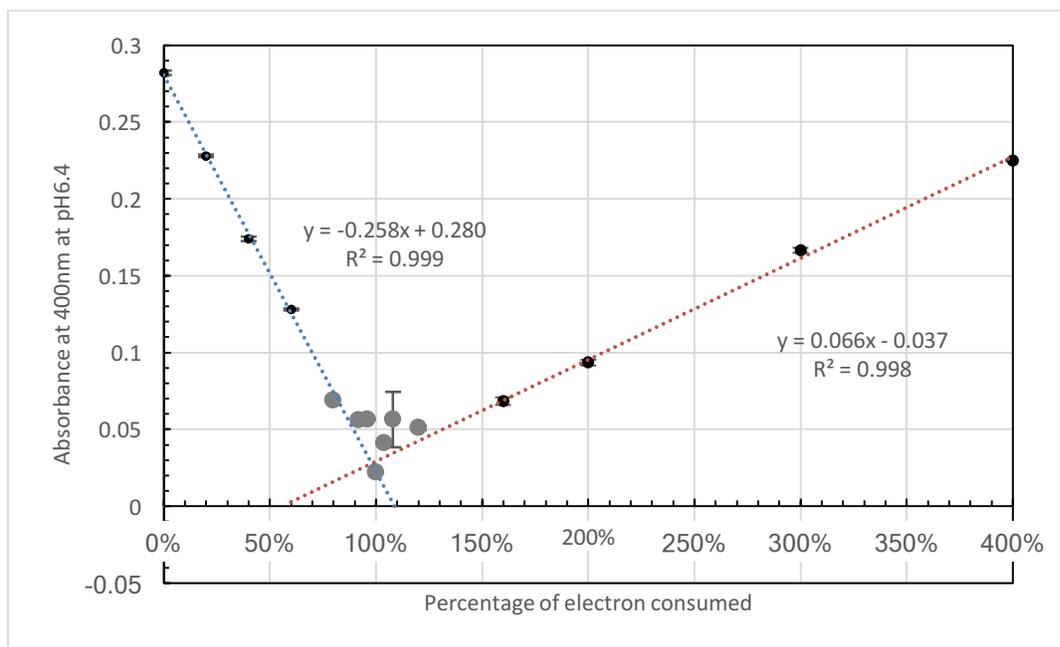


Figure 2.4. Final absorbance after 10 minutes of incubation as a function percentage of electron receiver added in the system. (Error bar: 1 standard error)

By performing a preliminary experiment, the exact concentration of Titanium (III) cation in stock solution is now known. In Fig 2.4, the two lines intercepts at 100%, which represent the fact that upon careful preparation of solution, titanium(III) citrate solution of any concentration can now be prepared with confidence, and their extinction coefficient at various acidity can be obtained by measuring their UV-Vis spectrums. A list of extinction coefficient has been presented below as the complex is to be prepared under different pH value, benefited by the standardization experiment.

Table 1.2 Extinction coefficient of titanium(III) citrate complex at pH 5, pH 6.4 and pH 7.5 under 100 mM Sodium Citrate buffer.

pH	Extinction coefficient	Unit
5	0.00869	1/(M*cm)
6.4	0.00915	1/(M*cm)
7.5	0.00990	1/(M*cm)

## 2.2 Black carbon and titanium (III) chloride

Soil Reef Biochar was obtained via pyrolysis at 550°C using Southern Yellow hardwood Chip, and the method of preparing experimental black carbon was described in Saquing et al. In short, the particle diameter is of less than 100 µm after sieving from the original material, and is air-oxidized in deionized water for 60 hours (Saquing et al, 2016). 20% titanium (III) chloride (w/v) was acquired from ACROS organics, and titanium(III) citrate was prepared by mixing calculated amount of 200 mmol/L sodium citrate (Sigma-Aldrich) stock solution and titanium(III) chloride solution in a 500 ml Erlenmeyer flask, and pH was adjusted to desired value, subsequently.

## 2.3 Black carbon ESC measurement

The entire experiment is performed in an anaerobic glove box (5% H<sub>2</sub>; 20% CO<sub>2</sub>; balance Nitrogen) to ensure the stability of reducing agent. UV-Vis spectrophotometer (Vernier Software & Technology, LLC) is used to quantify concentration of residual titanium(III) citrate at 400 nm. Solution was filtered using 0.22 µm syringe filters prior to measurement. To eliminate mass transfer limitation, magnetic stir bar at 350 RPM of rotation speed is used to promote agitation of fluid along with the black carbon particles. However, it is noteworthy to mention here that

due to the constraint of intricate porous structure of black carbon and particle size, it is of great difficulty to have direct control of the internal transport limitation, which will be discussed extensively in the following chapter.

#### **2.4 The ESC measurement of humic acid**

Leonardite Humic Acid (LHA) are acquired from the International Humic Substance Society, and 200 ppm stock solution is prepared and purged with air for six hours using air stone. The materials used for preparing titanium(III) citrate is identical with that of used in last section.

Pretreatment of humic acid was done by purging 200 ppm of LHA solution using compress air for 6 hours in ambient environment, then nitrogen is used to de-air the solution for two hours before transferring into the glovebox.

2.5, 5, 7.5 and 10 ppm of LHA is prepared at experimental pH under to 10 mmol/L of titanium(III) citrate solution, and the spectrum are measured using UV-Vis spectroscopy. 50 mL centrifuge tubes are used for experimental container, and these centrifuge tubes are placed on a rotator for constant rotation throughout the experiment (30 RPM). Solution spectrum are measured every hour and the experiment is terminated at the sixth hour. The extinction coefficient at wavelength 250 nm are provided in the appendix for interested readers.

#### **2.5 Operational safety**

Laboratory safety is of key concern in the search of appropriate reagent of use. Titanium (III) Chloride and titanium(IV) Chloride stock solution contains higher than 2 N of hydrochloride acid in the original packaging, and all operation involving the manipulation of volatile acid and organic compound are to be performed in a fume

hood for safety. When manipulating volatile acid in the glove box, the exposure of hydrochloric acid is to be minimized by shortening the time of opening the bottle to less than 10 second. Due to the small particle size of black carbon, handling of biochar has been done in fume hood to prevent inhalation of black carbon particles in the atmosphere. All residual Titanium (III) cation has been air oxidize to completion by compressed air prior to disposal to waste container.

## Chapter 3

### Measuring Electron Storage Capacity(ESC) of Black Carbon

#### 3.1 Experimental result and general discussion

It has been known that the brownish color of titanium(III) citrate fades away as it has been oxidized as shown in Fig 2.1 and Fig 2.2. In this work, we used the change of absorbance of titanium(III) citrate to quantify the degree of reduction of black carbon and utilize the extinction coefficient at 400 nm to determine the amount of electron that has been transferred from titanium (III) to titanium(IV) citrate. In other words, using the absorbance at certain wavelength as the yardstick to probe the progress of the reaction.

By mixing titanium(III) citrate and titanium(IV) citrate solution of the same concentration but of various ratio. The absorbance of at 400 nm can be plotted as a function of percentage of titanium(III) citrate within the sum of titanium concentration. A linear pattern can be observed, and the slope of the linear regression is essentially the extinction coefficient of titanium(III) citrate as in the appendix and chapter 2, and additional info can be found thereof.

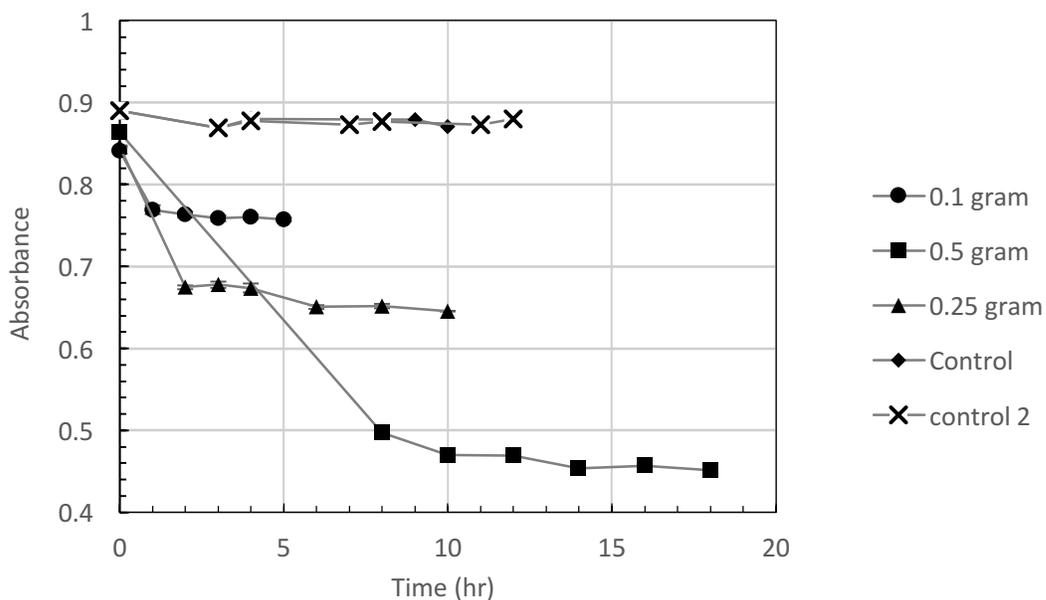


Figure 3.1. Sample raw data for black carbon reduction experiment at pH 6.4, 500 mL of reaction volume and 10 mmol of titanium(III) citrate concentration.

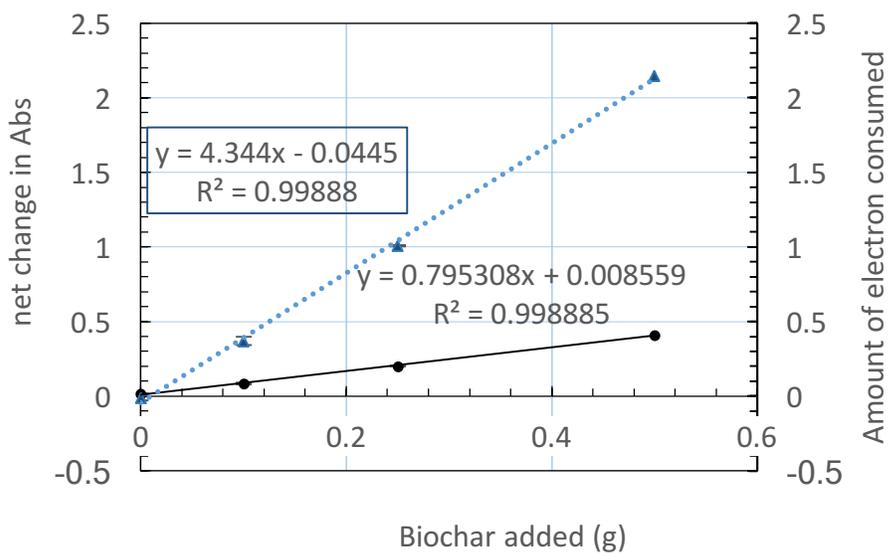


Figure 3.2. Calculation of Electron storage capacity via linear regression for pH 6.4.

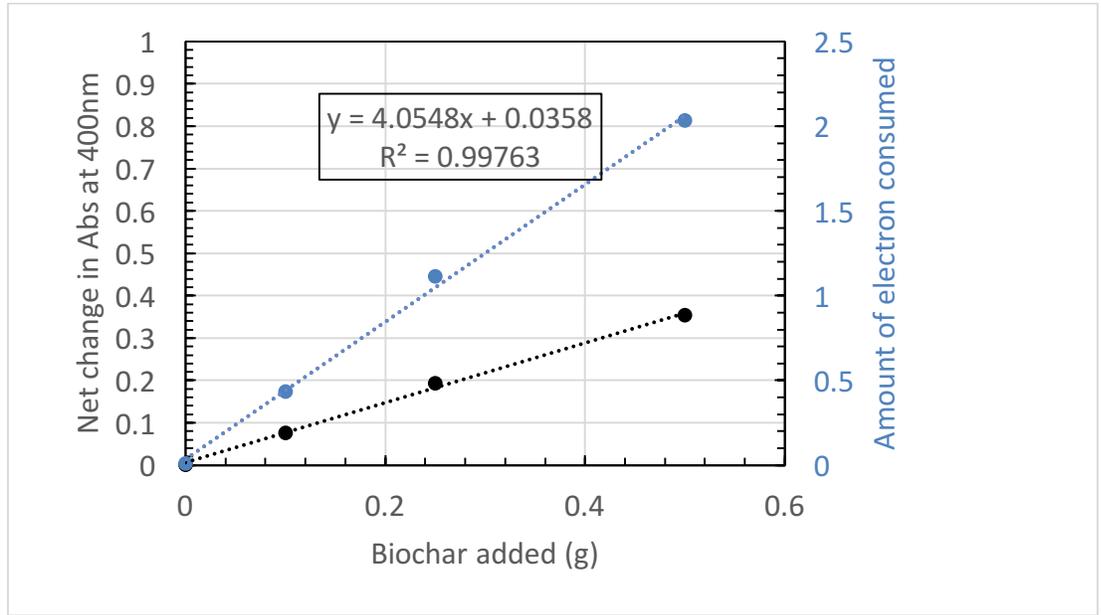


Figure 3.3. Calculation of Electron storage capacity via linear regression for pH 5.

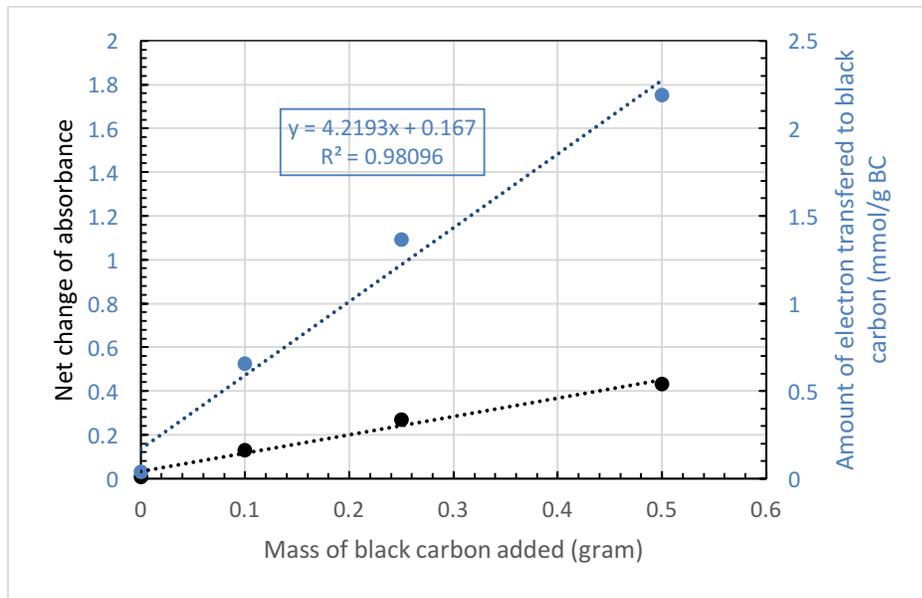


Figure 3.4. Calculation of Electron storage capacity via linear regression for pH 7.5.

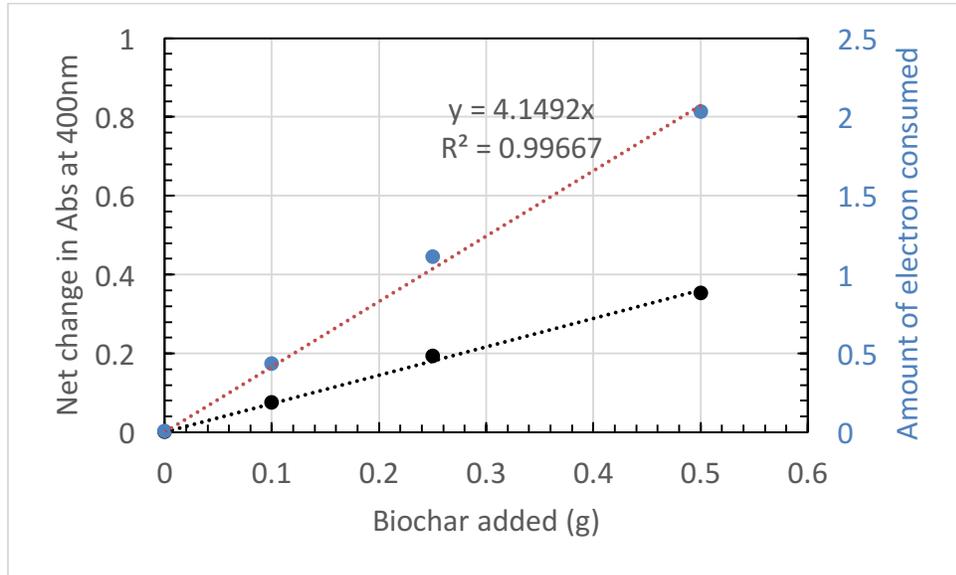


Figure 3.5. Calculation of Electron storage capacity via linear regression (setting the origin as intercept) for pH 5.

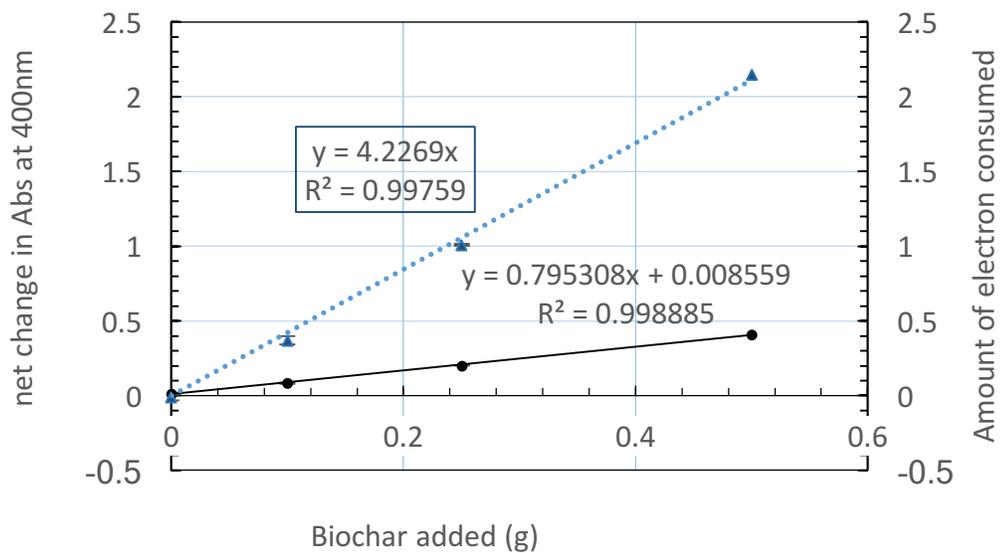


Figure 3.6. Calculation of Electron storage capacity via linear regression (setting the origin as intercept) for pH 6.4.

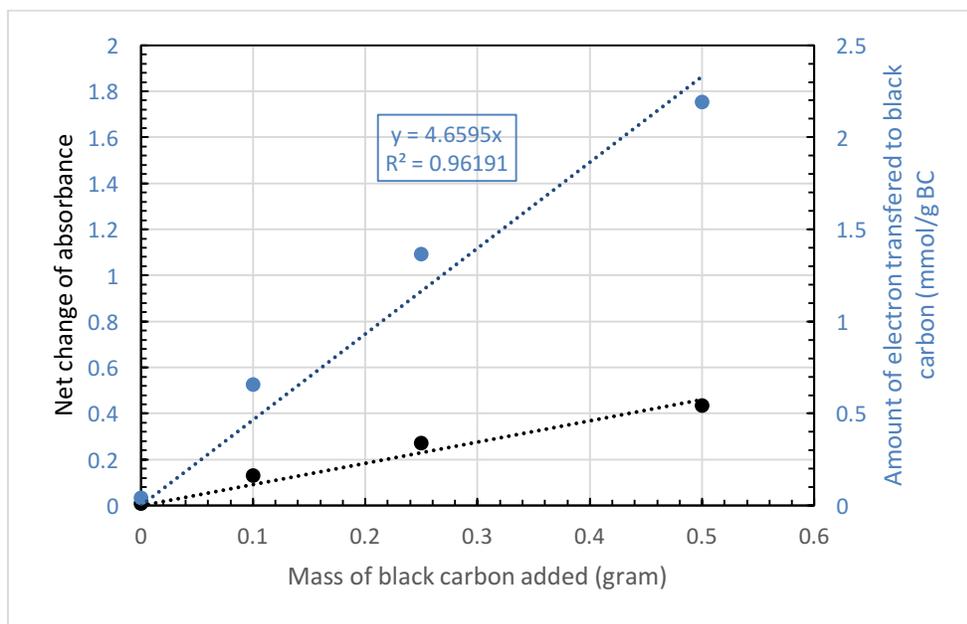


Figure 3.7. Calculation of Electron storage capacity via linear regression (setting the origin as intercept) for pH 7.5.

0.1, 0.25 or 0.5 grams of black carbon were added into the reactor while the reaction volume and titanium(III) citrate concentration remains constant, meanwhile, the net change of absorbance at 400 nm was recorded (Figure 3.1) and subsequently converted to the electron transferred to black carbon as in Figure 3.2. It is worthwhile to note that the slow kinetics of the reaction might not due to the intrinsic kinetic of the reduction of redox-active functional group, but impeded by the internal transport inside of the carbon skeleton of black carbon itself. This phenomenon is further escalated by the increase biochar mass causing even lower flux of titanium(III) citrate being able to diffuse across the surface of the black carbon in later phase reaction, the kinetic aspect of such phenomenon will be further elaborated in later chapter in this document.

Table 3.1 Summary of ESC from black carbon titration result

pH	Regression	Regression (constant set at zero)
5	4.1 ( $\pm 0.1$ )	4.1 ( $\pm 0.1$ )
6.4	4.3 ( $\pm 0.1$ )	4.2 ( $\pm 0.1$ )
7.5	4.2 ( $\pm 0.4$ )	4.7 ( $\pm 0.3$ )

Three number of electron storage capacity has been attained from these experiments, but what implication does it give and how can reader gain an appreciation on the order of magnitude of these data? Imagine 1 mole ( $\sim 6.02 \times 10^{23}$  molecule) of 1, 4-benzoquinone molecules are being reduced into 1, 4-hydroquinone by some reducing agent. Given that 1 mole of benzoquinone molecule can accept 2 moles of electrons, each gram of benzoquinone can obtain 18.36 milli-mole of electrons, in other words, this tested black carbon can hold up about 22% of electron as of benzoquinone for the exact same mass! From the standpoint of electrochemical energy engineering, utilizing black carbon as medium of energy storage might not be an ideal option given the low electron density per gram (compare to lithium and other organic fuel, for example), relatively slow kinetic of reaction and uncertainty in the conductivity of the carbon skeleton. From the viewpoint of the voltage of the reaction, the redox potential of aerated natural water is around 0.775 V assuming partial pressure of air is of 0.21 atm, and the reduction potential of titanium(III) citrate is of the range -380 to -350 mV. Unless a stronger oxidizing agent is to be used and the conductivity of black carbon can be significantly improved, the ease of applying black carbon as medium of energy storage might not be as promising as current technology, for example proton exchange fuel cell or lithium polymer battery. After all, black carbon is an intricate mixture as an outcome of biomass pyrolysis, and one should not expect such to outweigh the electron storage capacity of artificially refined chemical compound.

On the other hand, in the sector of environmental engineering and pollution mitigation, the presence of such discovery has gain attention in recent decades in terms of its potential of increase in water retention, pollutant sorption, and potential facilitation of microbial activity in soil as discussed in chapter 1. However, compared to the previous hallmark studies which utilized various approach to determine the ESC of black carbon, are the consistency and discrepancy between this work and other literature comparable? In this chemical titration work, the black carbon was taken from Saquing et al's work from the same batch, which makes the number determined from this work comparable to the biological accessible portion (0.85 to 0.87 mmol electron/gram GC) of black carbon (Saquing et al), and it is concluded that the biological accessible portion of electron of black carbon is of around 20% compare to that of determined by titanium(III) citrate titration, since it can be expected that microorganism resides on the surface portion of the biochar and therefore the electron accessibility is limited. Such ratio has given significant insight on the biological utilization of such redox active component on black carbon by environmentally relevant organisms and might be able to serve as a hub for temporal storage of electron near soil.

On the other hand, the ESC data attained from other literatures are limited, and the table below summarizes the reported value.

Table 3.2 Tabulation of ESC value from literature and this work

HTT temp C	EDC mmol/g	EAC mmol/g	ESC mmol/g	Source
400.0	7.0	0.2	7.2	PrévotEAU et al, 2016 (Rotating disk electrode for measurement, different reagent)
500.0	3.7	0.4	4.1	
600.0	1.4	0.1	1.5	
400.0	0.2	0.2	0.4	Klüpfel <i>et al</i> , 2014 ( <i>electrochemical oxidation/reduction</i> )
500.0	0.0	0.5	0.6	
600.0	0.0	0.0	0.1	
550.0	N/A	4.2	4.2	This work (unpublished value)

In PrévotEAU et al's work, both value from Saquing et al's work and Klüpfel's work are to be compared with their experimental value, and it has been claimed by the authors that the electron storage capacity (in their case electron exchange capacity) of black carbon is "dramatically underestimated" as their electron donating capacity of black carbon are much higher than Klüpfel's research work. Are the consistency and discrepancies comparable in these works? Fairly, due to the very limited availability of ESC data of various black carbon currently available in the literature search, it is worthwhile to compare the result obtained from various work using different char and methods, and get an appreciation of the possible range of what ESC should be expected when someone is reproducing the experiment with the goal of identifying the ESC for black carbon of interest. However, a direct comparison and conclusion drawn from such the discussion from data across different experiment are discourage by the author of this paper, since the material used in these tests are from different sources and prepared via various pyrolysis conditions. As it is commonly known that the distribution of organic functional groups and other physical properties are of strong dependence of feed stock type, pyrolysis method and other production aspects (Chen et al, 2014; Sun et al, 2014). Unless the same batch of black carbon is to be used with in short period to perform different experiment, no conclusion can be arbitrarily drawn

directly from the comparison of using diverse type of black carbon and measured by various techniques.

The major variable in this work is the change in pH. When performing linear regression with intercept set as zero, the ESC increases monotonically with pH, but not in a substantial manner. It has been demonstrated by both in lab experiment and in literature (Zehnder et al, 1976) that titanium(III) citrate complex donates one proton upon reduction, and the redox potential decreases (more reductive) upon increase in pH. However, in terms of redox functional group, it is still unclear that whether, or to what degree is the functional group is redox reversible. Since functional group with full reversibility (typically quinone) couples with proton exchange, and the potential of redox pair changes with pH and cancel out the increase the reduction capacity of titanium (III) citrate. However, if some function groups do not couple with pH change, there should be no impact of the redox potential upon the change in pH. Upon increase in pH, titanium (III) citrate complex becomes more reducing, function groups with low redox potential that is unavailable to be reduce at low pH (for example) can be consumed at this point. Another observation is that when performing titration at higher pH, a decrease in pH is observed at pH 7.5, such that the author need to add sodium hydroxide to maintain the solution pH to make it consistent. Such phenomenon clearly indicates the presence of non-proton exchange function group. However, the limited data shown in this work does not justify any of these speculations above, and more work is needed to prove such hypothesis.

### **3.2 Discussion in reaction kinetic perspective**

Like heterogeneous solid-fluid catalyst that facilitates reversible/irreversible reaction, which is well-covered in the reaction engineering class in a typical chemical

engineering curriculum, black carbon shares many of similarities in terms of the transport phenomenon occurred during the course in this study. The typical rate of reaction in solid-liquid is not only dependent on the intrinsic kinetics, which is the collision of reactant molecules and structural transformation to form product, but also faces limitation of internal transfer (conductive and convective diffusion of reactant in the carbon matrix), and external transfer (concentration of reactant on the surface is not the same as the concentration in the bulk fluid due to boundary layer theory). Since the reactor was being stirred using a stir bar at 350 RPM ( $D/T=0.25$ ), the surface of black carbon is constantly being refreshed with bulk fluid, therefore the limitation of surface double layer is greatly reduced due to the fast fluid motion in reaction, such that the limitation of external transport can be hereby phased out (see Appendix F).

When it comes to the discussion on internal transport phenomenon, the diffusive flux across an infinitesimal and spherical control volume is defined by:

$$J_{A,r} = -D_{A,eff} \left. \frac{\partial C_A}{\partial r} \right|_r \quad (1)$$

where A represents the reactant, and  $D_{A,eff}$  stands for effective diffusivity.

Assumed that the reactive function group remains active after reacting with titanium(III) citrate, the following differential equation describes the change of concentration profile with respect to radius:

$$\frac{\partial}{\partial r} \left( r^2 D_{A,eff} \frac{\partial C_A}{\partial r} \right) = r^2 (-R_{A,v}) \quad (2)$$

If the reaction is of first order reaction kinetics, the differential equation can be further simplifying to:

$$\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} = \frac{k_v C_A}{D_{A,eff}} \quad (3)$$

And Thiele modulus, concentration profile and effectiveness factor (which is used to describe the difference between true kinetic and diffusion controlled kinetics) can therefore be calculated upon integration.

Unfortunately, for the reaction taking place inside of black carbon, such simplified model cannot account for what has indeed occurred during the reaction, and isn't sufficient to model the kinetics. Since in this work, black carbon does not serve as catalyst, but in turn, the redox active functional groups are serves as the reactant and to be reacted with titanium(III) citrate in fluid.

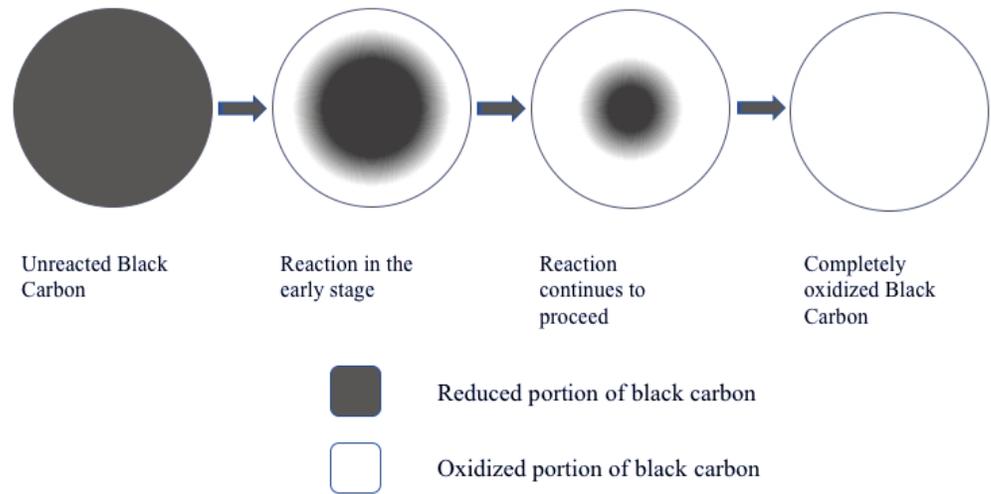


Figure 3.8. Schematic of progress in reaction with respect to the unreacted-core-shrinking model proposed in Wen, 1968.

The late Professor C.Y. Wen, who used to be the chair of the Department of Chemical Engineering in West Virginia University, has proposed solution to account for heterogeneous and non-catalytic solution with respect to reaction kinetic controlling, diffusion controlling (internal transport) and fluid film controlling (external transport) kinetics, which has been widely acknowledged as an applicable solution (Wen, 1968). The analytical solution in this model has also been used in Perry's Handbook of Chemical Engineering as explanation of reaction kinetic in spherical and porous solid-fluid reaction system. In Fig 3.8, a schematic of Wen's model has been drawn. In short, assume that reactive sites are evenly distributed on the throughout the black carbon, the spherical particles will experience a "Shrinking-unreacted-core" as the reaction proceed. Where in the figure, the white portion represented the reaction site has been completely exhausted by reaction, and the dark portion represent that the part that has not yet been reached by the reactant due to slow diffusion kinetics. As the reaction progresses, the reacting part shrinks in a radial direction and subsequently the black sphere is getting smaller and smaller, and eventually disappear.

The differential equation representing the reacted sphere (white portion in Fig 3.8) in an infinitesimal spherical control volume is:

$$D_{A,eff} \left( \frac{d^2 C_A}{dr^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right) = 0 \quad (4)$$

The form of this differential equation is essentially the same as given above for heterogeneous catalyst, except the reaction rate term is dropped, since this equation represents the flux of reactant travelling through the reacted portion of black carbon that has already reacted.

To solve this second order differential equation, two boundary conditions and one initial condition are needed, which are,

$$D_{A,eff} \left( \frac{\partial C_A}{\partial r} \right) = aK_s C_{so} C_{Ac} \quad (5)$$

which relates the flux of reactant over the control volume to the rate of reaction, where  $K_s$  is kinetic constant,  $C_{so}$  is concentration of reaction site on the solid, and  $C_{Ac}$  is the concentration of titanium(III) citrate on the surface of the reacting core, in addition,

$$-D_{A,eff} \left( \frac{\partial C_A}{\partial r} \right) = aC_{so} \left( \frac{dr_c}{dt} \right) \quad (6)$$

where the change of radius of unreacted core ( $r_c$ ) are also related to the flux across the spherical control volume, lastly, the initial condition is of

$$r_c = R \text{ at } t = 0 \quad (7)$$

If one assume the reaction order is of first order with respect to titanium(III) citrate and of zero order with respect to the reaction site on the surface, the analytical solution obtained by Wen is

$$t = \frac{aR^2 C_{so}}{6D_{A,eff} C_{AO}} [1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X)] \quad (8)$$

where  $X$  is the extent of reaction,  $t$  is reaction time,  $C_{AO}$  represent the liquid concentration of titanium(III) citrate at any time,  $a$  is the stoichiometric constant, and  $R$  is the particle diameter. (Wen, 1968)

However, it is still unclear that whether the slow kinetics is due to slow reaction or diffusion in biochar. Although in experiment with relatively small biochar mass (less than 0.25 grams), the reaction can reach an equilibrium within two to three

hours, but one cannot phase out the possibility that the fast kinetics is due to the relatively high residual concentration remained in the flask gives a higher mass flux of titanium(III) citrate across the boundary of black carbon surface. And Wen has also provided a handy approach on determining whether the reaction is of kinetically limited or internal mass transfer limited:

$$t = \frac{aR^2C_{SO}}{2D_{A,eff}C_{AO}} [1 - (1 - X)^{\frac{1}{3}}]^C \quad (9)$$

If the constant C is of 1, and give a reasonable fit to the data, the reaction is of kinetically limited, however, if the constant C is 2, the experiment will be internal diffusion limited. From a preliminary fit to the 0.5 gram data assuming liquid concentration is constant, the following expression gives a good fit.

$$t = \frac{aR^2C_{SO}}{2D_{A,eff}C_{AO}} [1 - (1 - X)^{\frac{1}{3}}]^2 \quad (10)$$

Unfortunately, since the titration of black carbon is done in a batch setting, the concentration decreases as titanium(III) citrate continues to be consumed. For experiments using 0.1 and 0.25 gram BC, one might argue that the change of concentration is negligible and can assume liquid concentration is a constant, however, there's insufficient data point in the first two hours to display a decent kinetic profile. Therefore, rearranging the above equation, one might express the concentration term as a function of extent of reaction.

$$t = \left( \frac{aR^2C_{SO}}{2D_{A,eff}C_{AO, ini}} \right) * \left\{ \left( \frac{1}{1 - \frac{C_{AO, end}}{C_{AO, ini}}(1-X)} \right) * [1 - (1 - X)^{\frac{1}{3}}]^2 \right\} \quad (11)$$

where  $C_{AO, ini}$  represents initial liquid concentration, and  $C_{AO, end}$  represents the end-point concentration of each experiment, and the unit for the terms in the above equation are of:

Table 3.3 Unit and value for model fitting.

Terms in equation	Unit	Value
a	Dimensionless	1
R	meter	$50 \cdot 10^{-6}$
$C_{SO}$	Mole/m <sup>3</sup>	$4.2 \cdot 10^{-6}$
$C_{AO, ini}$	Mole/m <sup>3</sup>	$10 \cdot 10^{-6}$
$C_{AO, end} / C_{AO, ini}$	Dimensionless	0.58
$D_{A, eff}$	m <sup>2</sup> /s	-

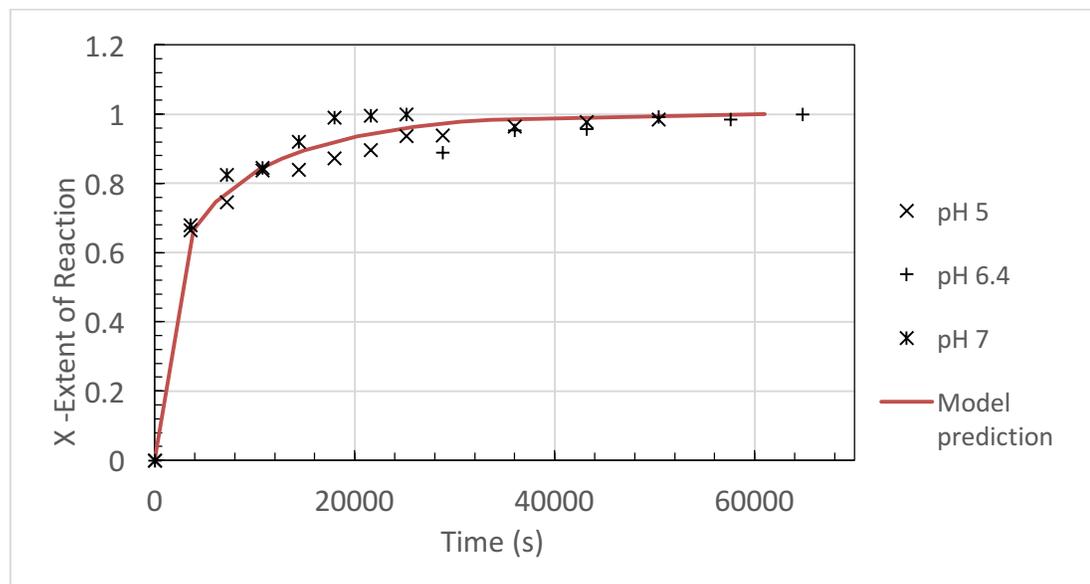


Figure 3.9. Model prediction for black carbon titration data at mass load of 0.5 gram in the direction.

All three 0.5 gram experiments are fitted to the above model assuming ESC is of 4.2 mmol/g and final solution concentration is 5.8 mmol/L, and the effective diffusivity for titanium(III) citrate in black carbon particle calculated is of  $2 \cdot 10^{-14}$  m<sup>2</sup>/s ( $2 \cdot 10^{-10}$  cm<sup>2</sup>/s) using the constant obtained from the fitting and solver from excel, and the standard error obtain from the above number is of 8.3% as estimated by the solveraid add-in in excel. Compare to the common diffusivity in liquid, which is often of the order of magnitude of  $10^{-9}$  m<sup>2</sup>/s (Russel et al, 2008), the low effective diffusivity gives an appreciation on the rate of reaction is essentially diffusion limited.

In this analysis, the particle size is assumed to be 100 micrometer; however, given that the particle distribution is unknown, there might be a vast difference in particle size distribution that might invalidate the assumption in this model and causes erroneous result. Extreme precaution should be given when dealing with particle with unknown particle size distribution.

Further more, the effective diffusivity and true diffusivity in solution can be related by:

$$D_{A,eff} = D(r)_{A,P} \frac{\varepsilon}{\tau_p} \quad (12)$$

Where  $\varepsilon$  represents intra-particle porosity and  $\tau_p$  represents the tortuosity inside of particle, which represents the how torturous of the carbon skeleton is for reactant to access the center (Roberts, 2009). Assume that the intra particle porosity is of 0.5, and pore diffusion coefficient is of  $1 \cdot 10^{-10}$ ,  $\tau_p$  is calculated to be of around 500, where for industrial catalyst, the  $\tau_p$  is often of the range of 2 to 10 (Roberts, 2009). Note that the  $D_{A,eff}$  is calculated under the scenario where particle has the maximum diameter (100 micron), in the case where the particle size is smaller, the

effective diffusivity calculated will be smaller, which indicates a larger tortuosity in reality.

Readers should also note that this solution solved by Wen is obtained under pseudo-steady-assumption to simplify calculation. And it is crucial to have the precaution that the author who had derived this solution has warned that the solution is applicable preferably to solid-gas and solid-liquid system at low reactant concentration in liquid. Given that the concentration of titanium(III) citrate is of 10 mM throughout the set of experiment, this model is used for calculation with extreme care, and a 10% of error for model estimation is expected. Additionally, the pH value might have effect in changing the zeta potential of the surface such that it might cause deviation of the model as well.

It should be noted that the purpose of such modeling effort, although not as significant as the ESC of black carbon itself, conveys information about the intrinsic mechanism and kinetics of the titration process. And an effective diffusion coefficient, which carry on info on the rate of diffusion of reactant in the carbon matrix, can be attained from such analysis and be compared with the other resources. Unfortunately, due to the time scale of sampling is not sufficiently small, there is insufficient short term kinetic information can be attained (especially from the first hour of experiment), and modeling fitting of data might suffer from high uncertainty and gives rise to a large confidence interval.

## Chapter 4

### Measuring Electron Storage Capacity of Leonardite Humic Acid

The change of spectrum upon oxidation of humic acid of low concentration (0.1 mmol/L) is drastically different compare to that of high concentration (10 mmol/L). The absorbance at the visible regime is minimal, and the absorbance at far UV regime increases with oxidation of titanium(III) citrate complex. It has been shown in literature that the spectrum of LHA at UV region does not depend on the oxidation status of itself down to 250 nanometers (Maurer et al, 2010; Aeschbacher et al, 2012). And it is hereby assumed that any redox change in the spectrum upon mixing of titanium(III) citrate and LHA is solely due to the oxidation of titanium(III) anion.

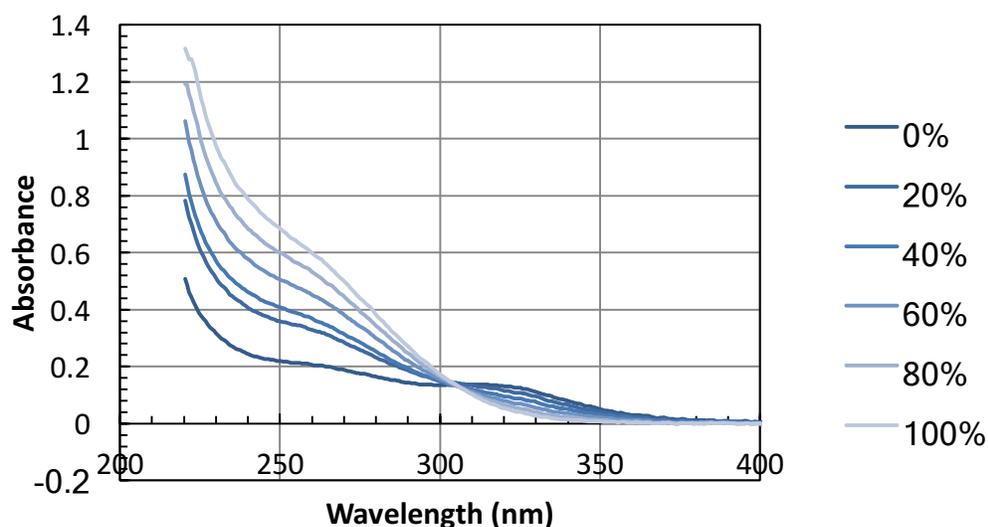


Figure 4.1. Absorbance of Titanium (III)/(IV) Citrate complex mixture at 0.10 mmol/L and at pH 6.4 (percentage represent fraction of titanium(IV) Citrate)

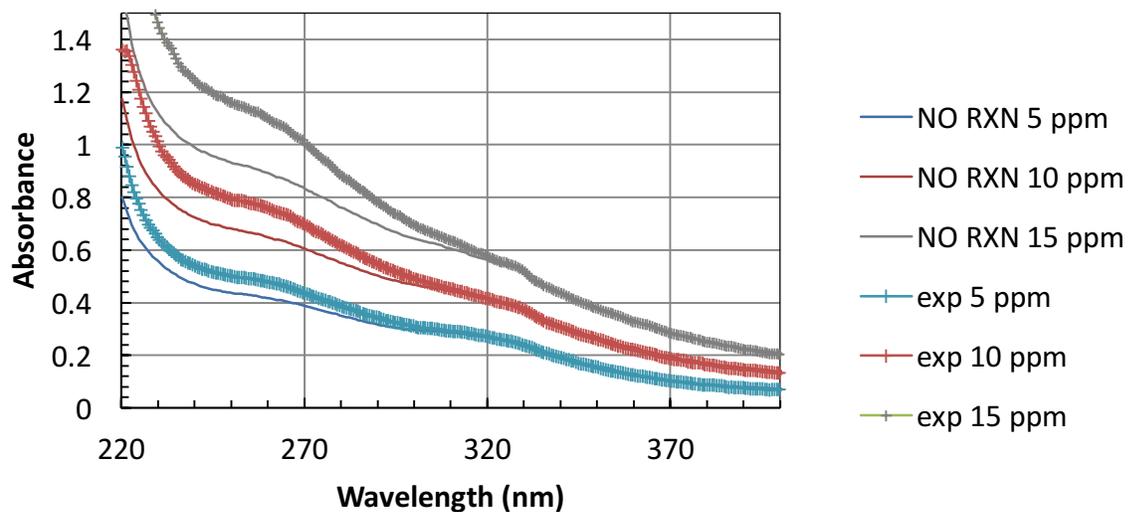


Figure 4.2. Spectrum of mixture of Humic acid of various concentration and 0.10 mmol/L LHA of absorbance as compare to the stoichiometric sum of two spectrums

As shown in figure 4.2, it has been clearly shown absorbance increased with mass of LHA added to the system at 250 nm. By monitoring such change of absorbance, one can analyze how much electron has been transferred into LHA.

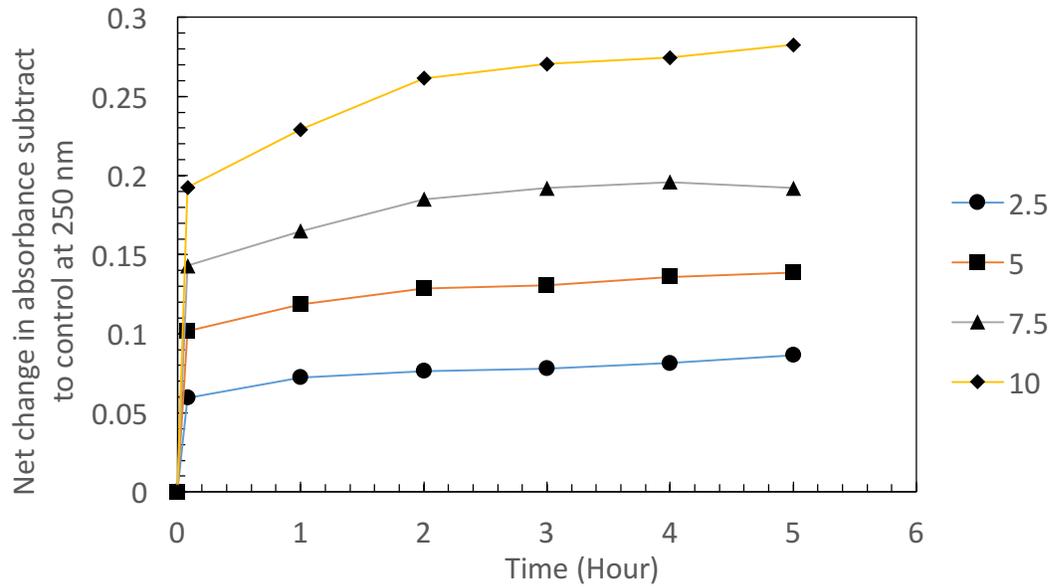


Figure 4.3. Sample data collected during experiment for data analysis at pH 6.4 (Legend concentration in ppm).

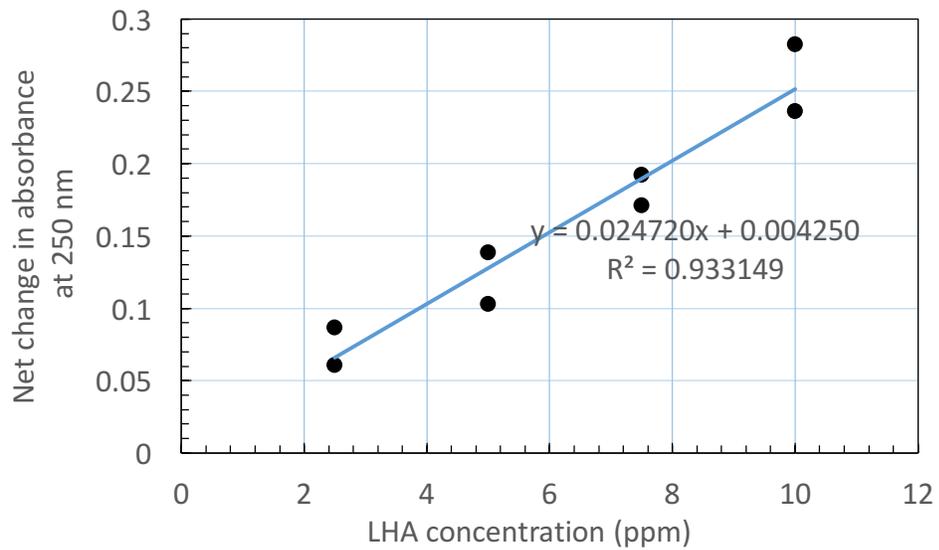


Figure 4.4. Change of absorbance a function LHA concentration at pH 5.

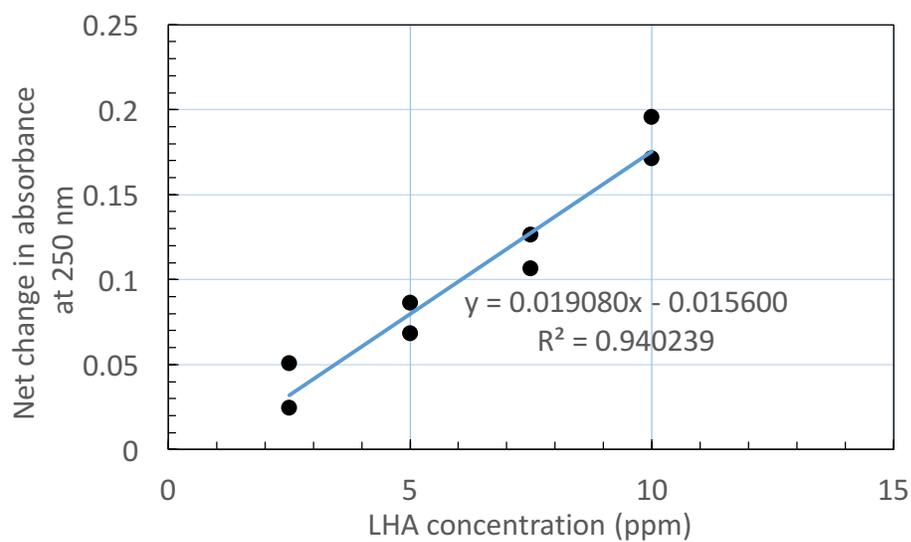


Figure 4.5. Change of absorbance a function LHA concentration at pH 6.4.

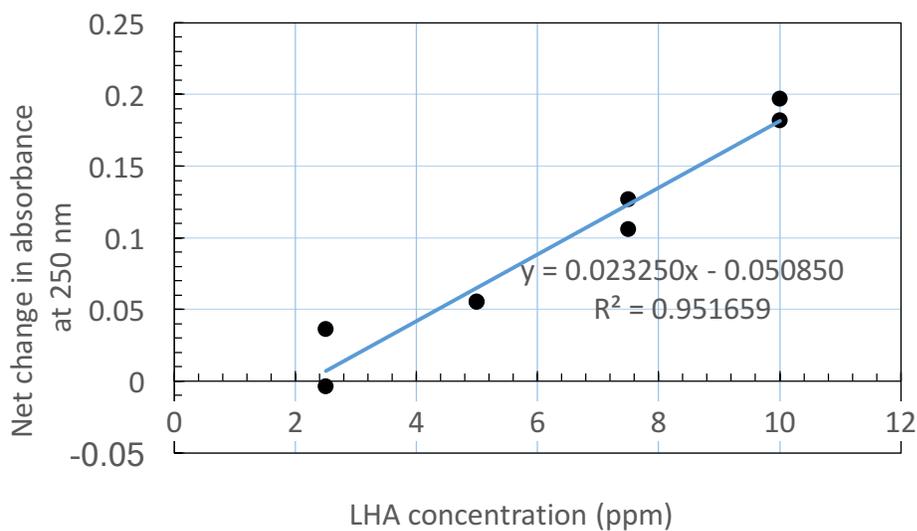


Figure 4.6. Change of absorbance a function LHA concentration at pH 7.5

Sample data analysis and experimental data is shown above. By performing a linear regression and back-calculate the electron transfer using the extinction

coefficient from the calibration curve (see appendix), one can determine the electron transfer from reducing agent to LHA per unit mass.

Table 4.1. Tabulation of experimental result for Leonardite humic acid titration

<b>pH</b>	<b>ESC (mmol electron/ gram)</b>
5	4.7 ( $\pm 0.4$ )
6.4	3.1 ( $\pm 0.3$ )
7.5	4.1 ( $\pm 0.4$ )

The standard error attained from regression analysis is large, primarily because the extremely low concentration of LHA and Titanium (III) used in this work give rise to the insensitivity of this approach. Overall, the concentration of reductant used in the black carbon work is of a hundred times higher than that used in this experiment, and the black carbon is shaken every time before the experiment to ensure uniformity. In humic acid titration work, although the same jar of stock LHA solution is used, the concentration of experiment is too low such that a high degree of dilution might lead to the inconsistency in the properties LHA used every time.

Low molecular weight portion of humic acid contains about an order of magnitude higher of electron donating/accepting content compare the untreated LHA (Yang et al, 2016), which accounts for the relatively rapid kinetics at the beginning of the experiment and slow kinetics as time progresses. In that work, the bulk reducing capacity is determined to be of 1.44 mmol/g LHA using the method of hydrogen reduction on platinum catalyst (Yang et al, 2016). On the other hand, Aeschbacher et al has tested a selection of natural organic matter, humic acid, fulvic acid and industrial humic acid, and the ESC for LHA is determined to be of around 3 mmol/g

LHA with uncertainty of around 0.3 mmol/g (Aeschbacher et al, 2012). The data from this work is of close consistency as that of Aeschbacher's work, and reader should treat the method from this work as a chemical counterpart of the electrochemical titration (w/mediator) experiment.

## Chapter 5

### Conclusion, Implication and Future Work

The redox active site contributes to the electron accepting behavior of air oxidized black carbon, and the amount of electron stored by them can be probed by carrying out a redox titration utilizing titanium(III) citrate complex and UV-Vis spectroscopy, and it has been proved to be an cost effective approach to determine the ESC of small particle size black carbon (less than 100 micrometer). A ESC of around 4 millimoles per gram suggest that synthesized wood chip black carbon of this type possesses considerable capacity as an electron sink (and donor if oxidation is taken in to account) in soil and sediment, and gives insight into justifying the additional role black carbon plays. For example, the application of black carbon on rain garden and bioretention site for enhanced in-situ pollutant mitigation. Future research effort is needed in terms of studying the short time kinetic of the reaction via increase measurement frequency, and the reversibility of the charging/discharging of electron stored by black carbon can be probed by oxidizing the black carbon via other oxidation approach.

The methodology used in black carbon applies to LHA as well; however, readers should treat using such method with care when titration liquid phase natural organic compound, as the UV-Vis spectrum for other compound might not be constant as a function of the redox state of the material of interest. Additionally, the relatively large uncertainty from this approach gives a rough estimate on the ESC. In the case that high-quality data with small uncertainty is needed, the electrochemical

oxidation/reduction of liquid phase compound will be a more ideal solution. Yet, the consistency of these value with literature has strengthen the confidence for black carbon data developed in section three, and provide an avenue for another affordable approach for fast redox titration for humic acid.

Commercially, black carbon is advertised as beneficial additive to soil for gardening and farming purposes. On the other hand, it has been tested in roof top rain garden and storm water bioretention site for contaminant remediation. While the sorption capacity

This work presents a set of redox titration experiment with the primary goal to estimate the electron storage capacity of black carbon. In the laboratory setting, the contribution of this work enables researchers to utilized identical or similar approach to determine the ESC of black carbon being synthesized in various way, for example various feed stock or pyrolysis method. And it is foreseen it can be applied to black carbon with relatively small particle size (<100 micron) and low leachate content. For black carbon with larger particle size, it is expected that the time scale of titration will be lengthened to a couple days. The authors and co-workers in lab are currently conducting further development of the titration approach. The combination of this low-cost titration approach and additional experimental work can become a sample protocol for one who is interested to study the electrochemical properties of black carbon of interest.

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## Appendix A

### Properties of Soil Reef biochar used in this work

	Value <sup>a</sup>	Units	Method
pH	8.71 <sup>b</sup>		1:20 w/v in DI water, 24 hr
Electrical Conductivity (EC 20 w/w)	283	mmhos cm <sup>-1</sup>	4.11 USCC:dil. Rajkovich
Total Ash	21.4	% of total mass	ASTM D-1762-84
Particle Density	1.816 <sup>b</sup>	g cm <sup>-3</sup>	
BET Surface Area	391±10 <sup>b</sup>	m <sup>2</sup> g <sup>-1</sup>	N <sub>2</sub> adsorption
Organic Carbon (org-C)	74.2	% of total mass	Dry Combustion-ASTM 4373
Total Nitrogen (N)	0.59	% of total mass	Dry Combustion-ASTM 4373
Hydrogen/Carbon (H/C) Ratio	0.26		Dry Combustion-ASTM 4374
Liming (neutral value as CaCO <sub>3</sub> )	14.7	% CaCO <sub>3</sub>	Rayment & Higinson
Total Potassium(K)	3566	mg/Kg dry mass	Enders & Lehman
Available K	4034	mg/Kg dry mass	Wang after Rajan
Total Phosphorous(P)	2528	mg/Kg dry mass	Enders & Lehman
Available P	1608	mg/Kg dry mass	Wang after Rajan
Total N	0.59	mg/Kg dry mass	KjN
Ammonia (NH <sub>4</sub> -N)	4.1	mg/Kg dry mass	Rayment & Higinson
Nitrate (NO <sub>3</sub> -N)	63	mg/Kg dry mass	Rayment & Higinson
Organic (Org-N)	5800	mg/Kg dry mass	
Volatile Matter	79	% dry mass	ASTM D-1762-84
Arsenic (As)	1.4	mg/Kg dry mass	EPA 3050B/EPA 6010
Cadmium (Cd)	<0.01	mg/Kg dry mass	EPA 3050B/EPA 6010
Chromium (Cr)	11	mg/Kg dry mass	EPA 3050B/EPA 6010
Cobalt (Co)	1.3	mg/Kg dry mass	EPA 3050B/EPA 6010
Copper (Cu)	24	mg/Kg dry mass	EPA 3050B/EPA 6010
Lead (Pb)	3	mg/Kg dry mass	EPA 3050B/EPA 6010
Molybdenum (Mo)	0.22	mg/Kg dry mass	EPA 3050B/EPA 6010
Mercury (Hg)	<0.2	mg/Kg dry mass	EPA 7471
Nickel (Ni)	5.1	mg/Kg dry mass	EPA 3050B/EPA 6010
Selenium (Se)	<0.3	mg/Kg dry mass	EPA 3050B/EPA 6010
Zinc (Zn)	15	mg/Kg dry mass	EPA 3050B/EPA 6010
Boron (B)	40	mg/Kg dry mass	TMECC
Chlorine (Cl)	325	mg/Kg dry mass	TMECC
Sodium (Na)	465	mg/Kg dry mass	EPA 3050B/EPA 6010

<sup>a</sup>Data provided by The Biochar Company unless otherwise noted.

<sup>b</sup>Measured at the University of Delaware.

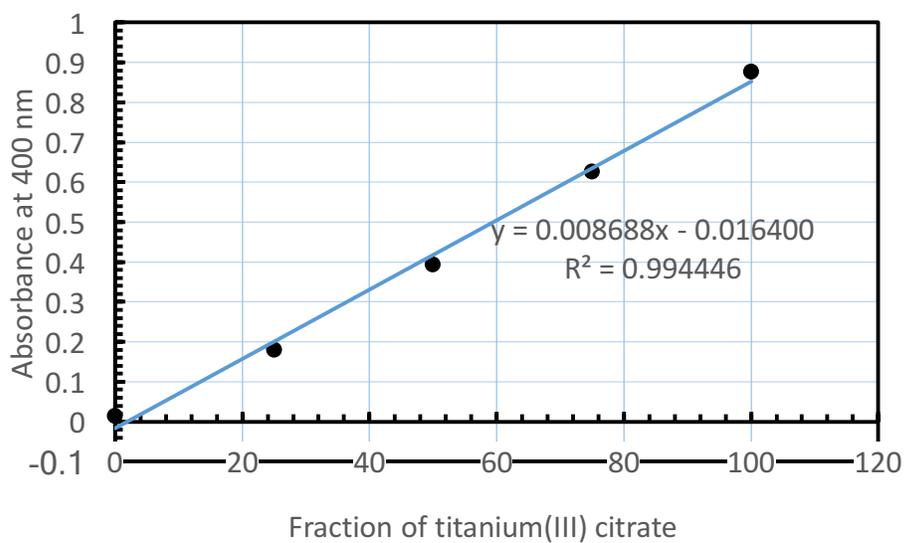
Courtesy of Dr. Pei C. Chiu from University of Delaware.

## Appendix B

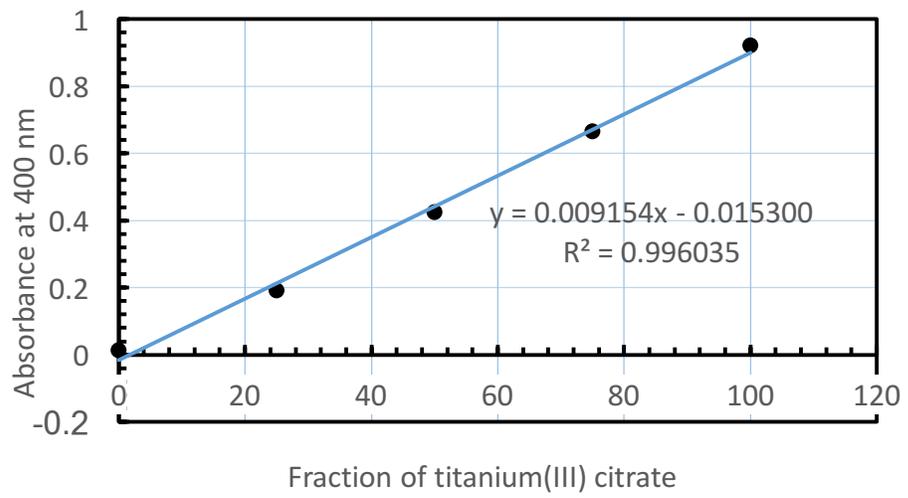
### Calibration curve for titanium(III) citrate solution developed for black carbon reduction experiment

Buffer: 100 mmol/L of sodium citrate

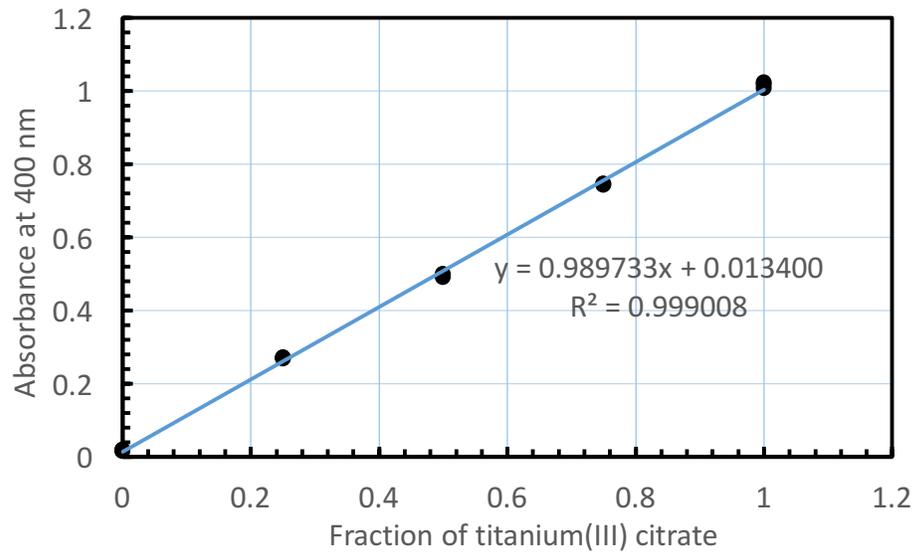
Titanium (III) cation concentration: 10 mmol/L



pH 5



pH 6.4



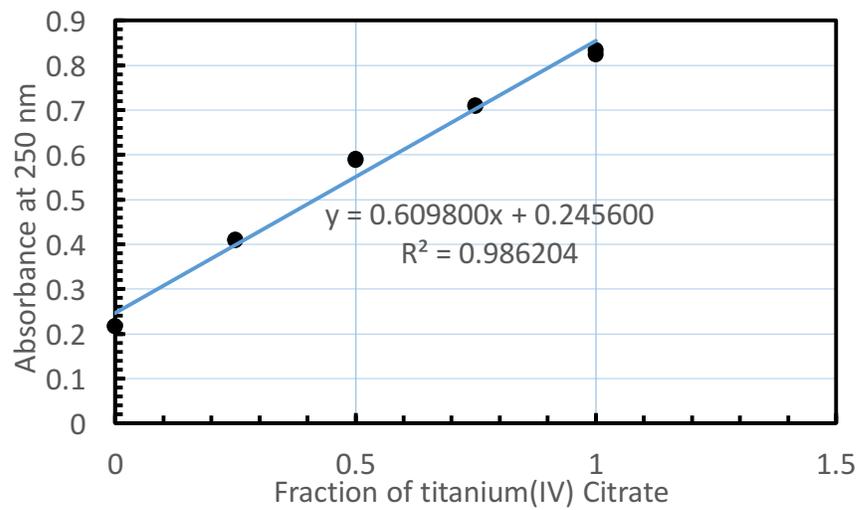
pH 7.5

## Appendix C

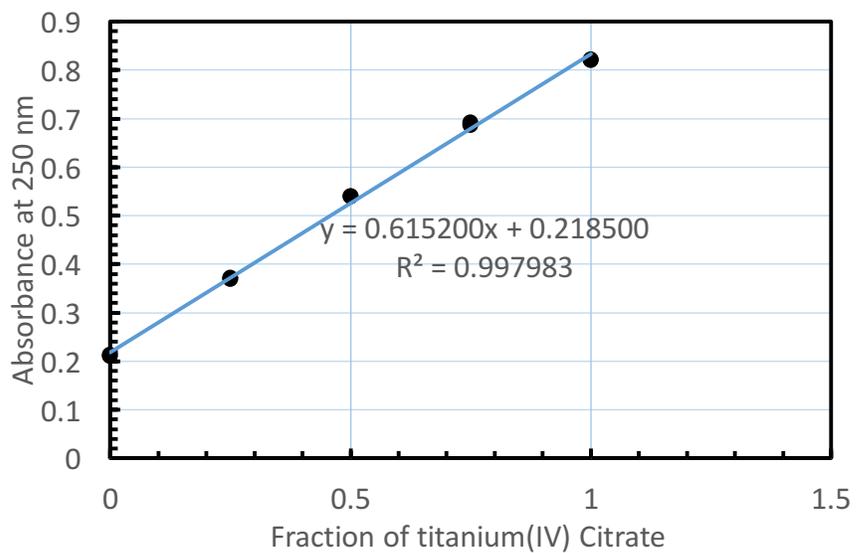
### Calibration curve of titanium(III) citrate solution developed for Leonardite Humic Acid (LHA) reduction experiment

Buffer: 10 mmol/L of sodium citrate

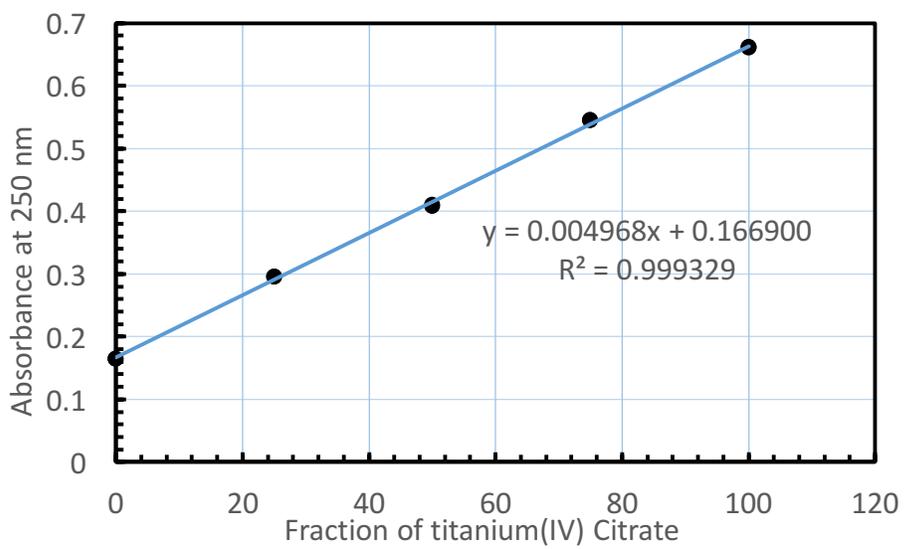
Titanium (III) cation concentration: 0.10 mmol/L



pH 5



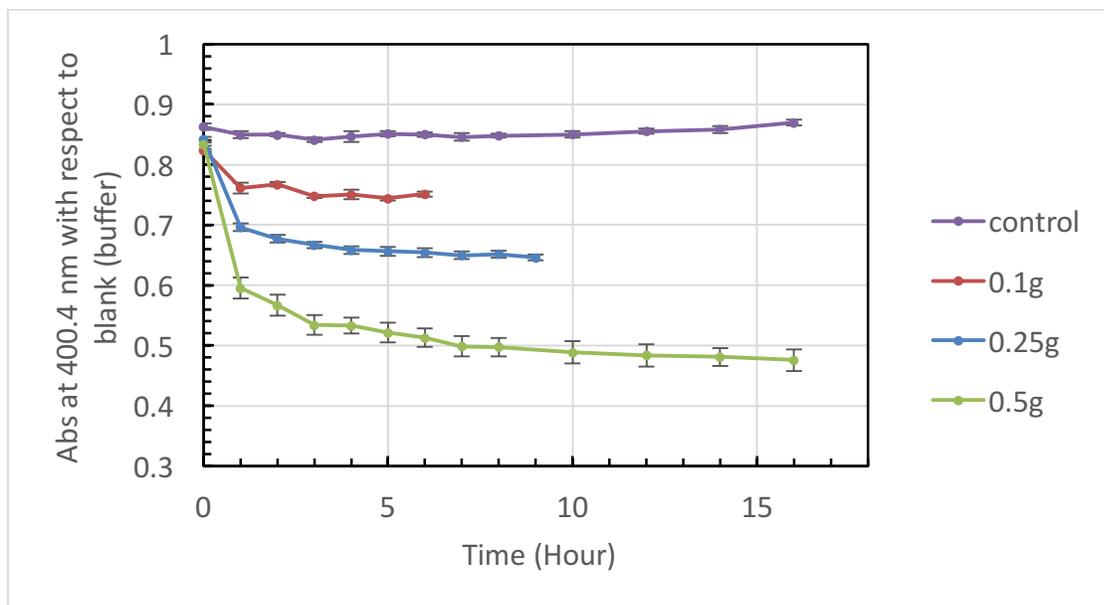
pH 6.4



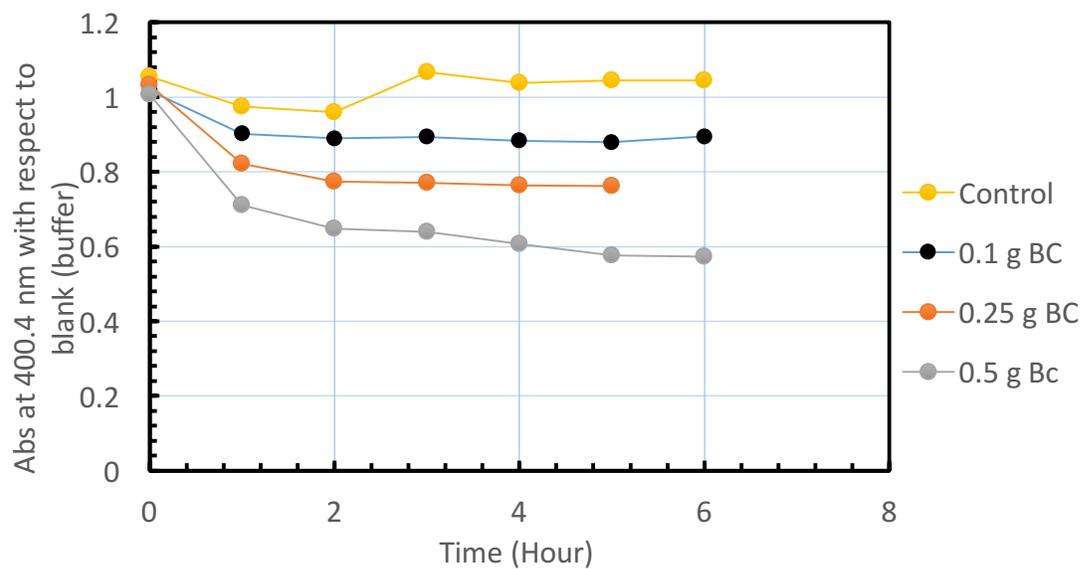
pH 7.5

## Appendix D

### Addition kinetic data for black carbon titration experiment at pH 5 and pH 7.5



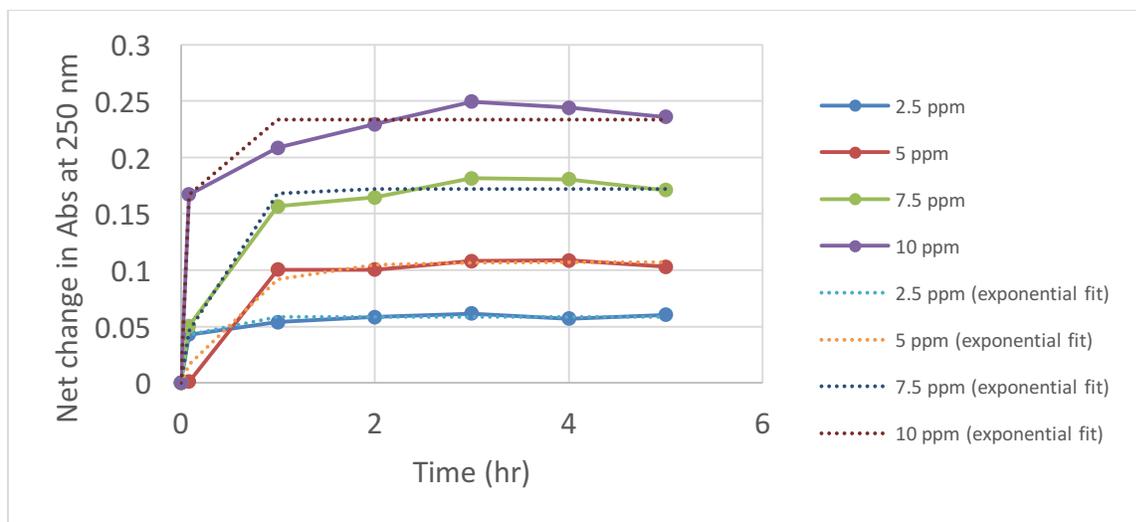
Change of absorbance at 400 nm with time at pH 5. Error bar represents one standard deviation. No error bar is shown for control since the time for sampling are different.



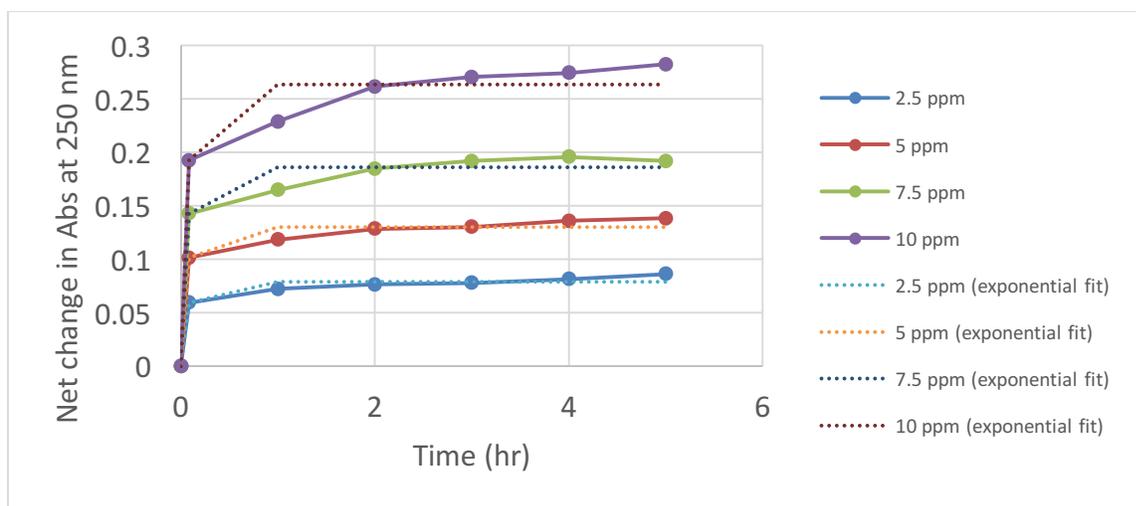
Change of absorbance at 400 nm with time at pH 7.5. Error bar represents one standard deviation.

## Appendix E

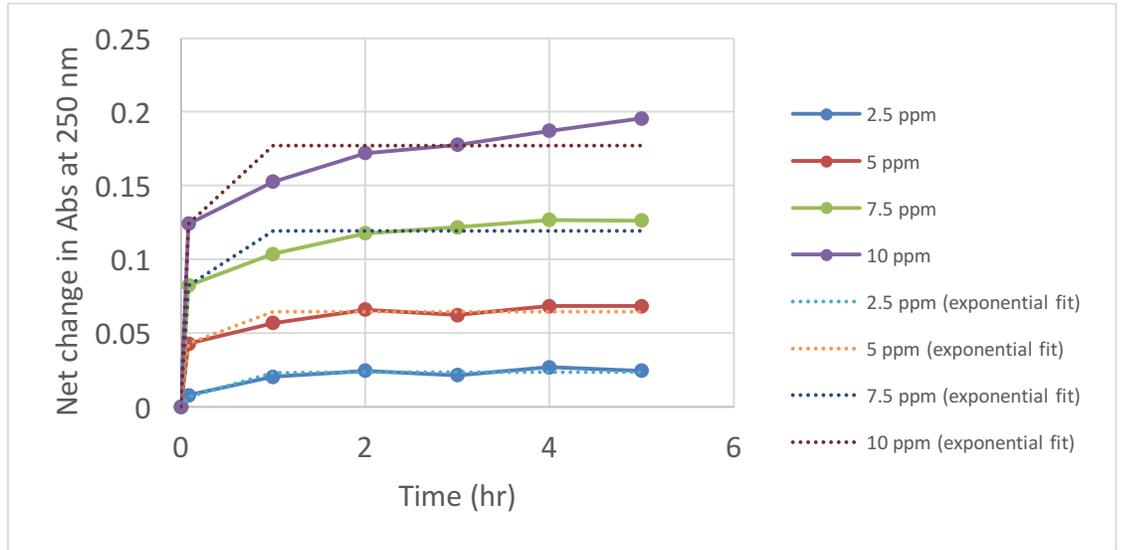
### Addition kinetic data for Leonardite humic acid (LHA) titration experiment at pH 5, pH 6.5 and pH 7.5 with exponential fitting



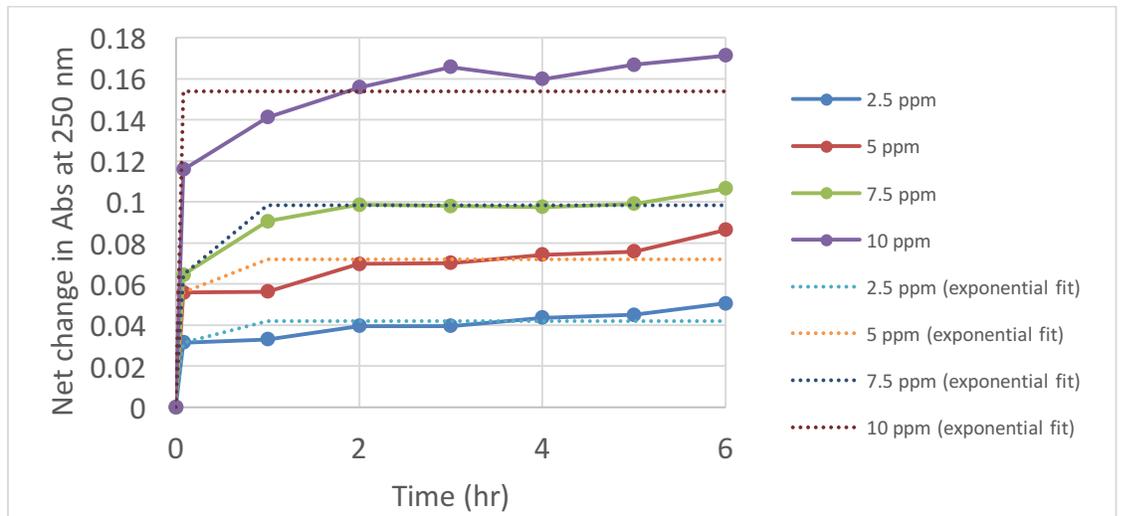
pH 5 (experiment 1)



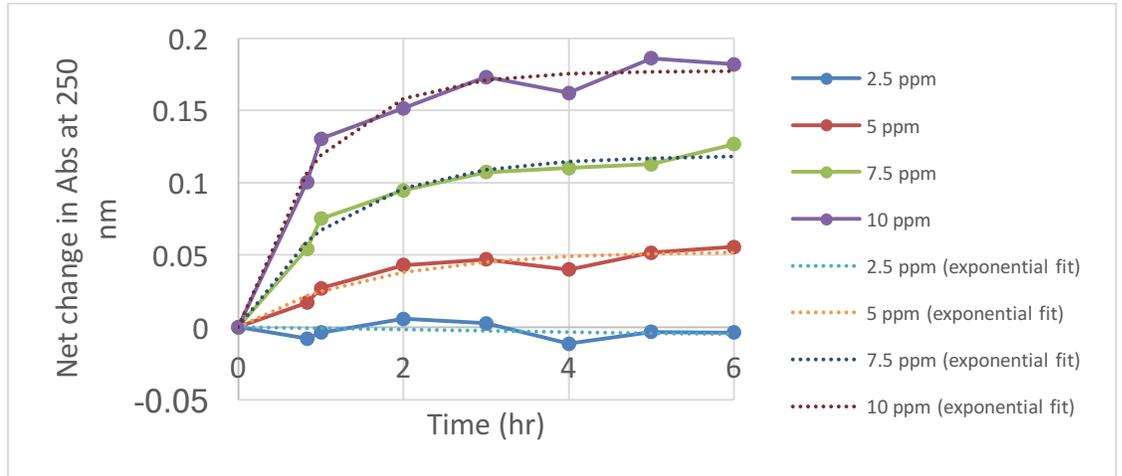
pH 5 (experiment 2)



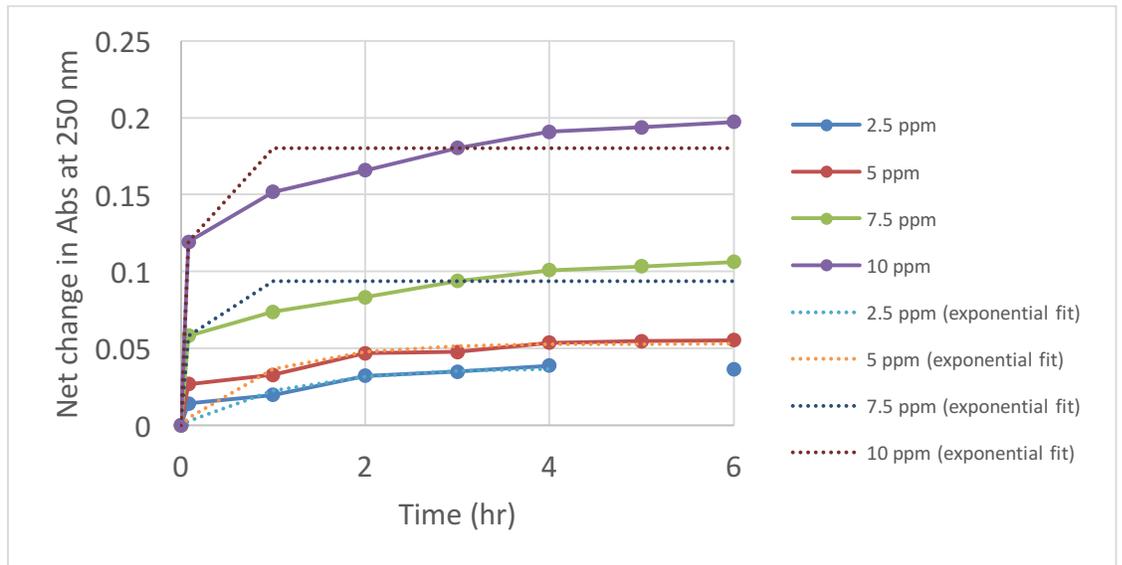
pH 6.4 (experiment 1)



pH 6.4 (experiment 2)



pH 7 (experiment 2)



pH 7.5 (experiment 1)

## Appendix F

### Justification of Off-Bottom Solid Suspension and Calculation of Surface Mass Transfer Coefficient ( $K_L$ ) in Black Carbon Titration Experiment

It has been assumed that off-bottom suspension of solid is achieved and surface mass transfer coefficient is large in the main body of this work. The following calculation justifies such assumption.

Assume:

- The diameter of 1L Fisher Scientific Erlenmeyer flask is 15 cm
- The diameter of cylindrical stir bar is of 3 cm
- The shape of cylindrical stir bar can be model as a pitched blade (radial) turbine,  $Po=1.3$ ,  $Z=1.528$
- Off bottom clearance is of 0.05 cm (since stir bar technically does not has off bottom clearance)
- Black carbon is of spherical and of 100 micrometer in diameter
- Particle skeletal density is of  $1.8 \text{ g/cm}^3$  (particle itself)
- Black carbon bulk density is of  $0.5 \text{ g/cm}^3$  (particle + void) (not used in this calculation)
- Density of solution is of  $1 \text{ g/cm}^3$  at ambient temperature and gravitational acceleration is of  $9.8 \text{ kg/s}^2$
- Rotation speed is at 350 RPM
- Viscosity of solution is of 1 cP
- Mass diffusivity of reducing agent in water is of  $1 \cdot 10^{-9} \text{ m}^2/\text{s}$

The rotation speed ( $N_{JS}$ ) such that solid can be “just suspended” from the bottom can be estimated by the GMB correlation :

$$N_{JS} = \frac{z}{Po^{0.333}D^{0.667}} d^{0.167} X_V^{0.154} \left( \frac{g\Delta\rho}{\rho} \right)^{0.5} \left( \frac{c}{D} \right)^{0.1}$$

Where  $X_V$  is volume fraction in percentage,  $c$  is clearance.

The minimum rotation rate calculated is of 5.7 NPS (340 RPM), in which the actual rotation rate (~350 RPM) is sufficient for solid suspension.

And the surface mass transfer coefficient can be calculated by the correlation below:

$$\text{Average power input per mass: } \epsilon = \frac{PoN^3D^5}{\left(\frac{\pi}{4}\right)T^3} = 0.0022 \text{ W/ kg}$$

$$\text{Sherwood number: } Sh = \frac{v}{D_{AB}} = 1000$$

$$\text{Mass transfer coefficient: } k_L = 2 \frac{D_{AB}}{d} + 0.16(v\bar{\epsilon})^{0.25} (Sh)^{-0.666} = 0.0000310 \text{ m/s}$$

Where  $v$  is kinematic viscosity and  $T$  is tank diameter.

Biot number for mass transfer

$$Bi = \frac{k_L L}{D_{eff}} = \frac{0.0000310 * 100 * 10^{-6}}{2 * 10^{-14}} = 155,000 \gg \gg 1$$

Therefore, the external transport phenomenon is negligible compare to internal diffusion resistance.

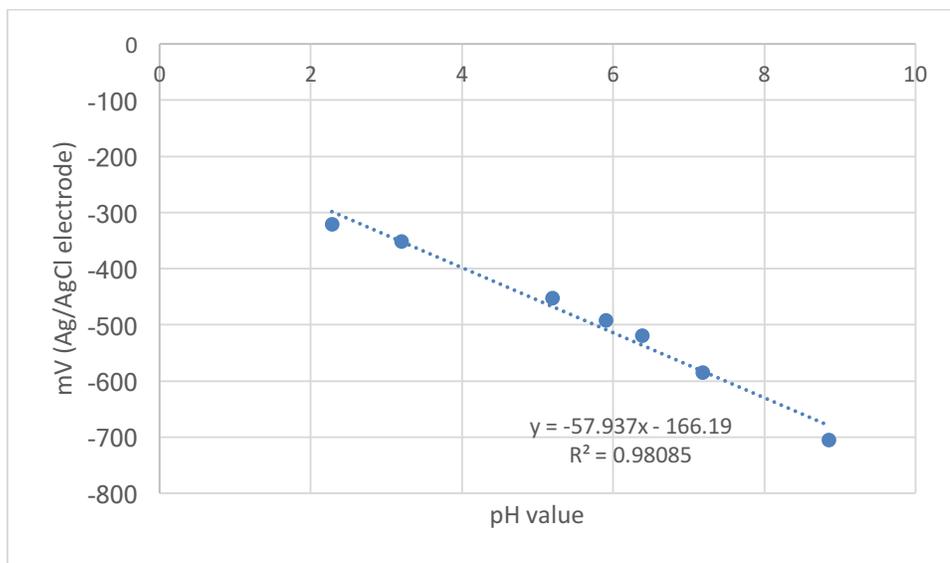
Reference:

Paul, Edward L., Victor A. Atiemo-Obeng, and Suzanne M. Kresta. (2004) Handbook of industrial mixing science and practice. Hoboken, NJ: Wiley-Interscience, Print.

Russell, T. W., Robinson, A. S., & Wagner, N. J. (2008). Mass and heat transfer: analysis of mass contactors and heat exchangers. Cambridge: Cambridge University Press

## Appendix G

### Change of redox potential of titanium(III) citrate solution as a function of pH



Condition: 10 mmol titanium(III) citrate solution, 100mmol citrate buffer. Nerestian behavior is observed since the slope of the curve is around 0.059mV with respect to change in 1 pH unit.