THE APPLICATION OF WHOLE OYSTER SHELLS IN STORMWATER TREATMENT REMOVING HEAVY METALS

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ABSTRACT

Oyster shells are normally applied in wastewater treatment in the form of a powder; but the possibility of whole oyster shells removing metal ions in stormwater has not been investigated. The objectives of this research are to assess the application of whole oyster shells for removing metals in low concentration solutions and to explore the influence of the following factors: surface area of shells, initial concentration and exposure time, on removal efficiency.

Experimental results demonstrated very good removal efficiency by oyster shells for removing copper, followed by cadmium and zinc; but was not effective in hexavalent chromium removal. Up to 70% removal can be reached in just one hour for copper with initial concentrations of 0.2ppm with 550cm^2 of surface area (SA) of shells in a beaker experiment treating two-liter solutions (with an accompanying pH increase from 5 to 6.42). A removal efficiency (RE) of 57.7% and 33.3% was found for cadmium and zinc, respectively, with one day contact using shells of 300cm^2 SA treating one liter of the lowest concentration solution; while only 14.3% was achieved for chromium under the same conditions. Mid-scale experiments with continuous inflow based on the 6-hour Saanich Design Storm demonstrated an 85.5% and an 83.9% RE of cadmium and copper in one day's worth of contact time. There was no removal but in fact an increase in chromium and zinc was found for the mid-scale experiment.

There was a positive relationship between initial concentration (IC) and removal efficiency for copper and zinc, but a negative relationship for chromium, while no relationship was found for cadmium. Up to 80% of copper can be removed at IC of 2.4ppm compared to 60% with IC of 0.65ppm with same amount of shells (by surface area). RE of 70%, 75% and 83% was observed for IC of 0.3ppm, 0.58ppm and 1.07ppm for zinc, respectively, with 154 cm^2 SA. When IC of chromium is reduced from 1 ppm to 0.2ppm, RE tends to drop from 60% to 26%. There was also a positive relationship between SA and RE, and ET and RE. However, after a certain exposure time, increase in RE was negligible and sometimes, desorption would occur. Additionally, when the difference in surface area is small, the influence of this factor on RE was also small. When treating certain ranges of solution concentration, the effect of surface area on RE is difficult to distinguish. Moreover, the role of HRT in stormwater systems was not clearly found.

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SYMBOLS AND NOTATION

Au	Aurum
Ag	Argentum
As	Arsenic
BOD	Biochemical oxygen demand
BOD5	5-day biochemical oxygen demand
COD	chemical oxygen demand
Ca	Calcium
Cd	Cadmium
Cr	Chromium
Ct	Concentration at certain time t
C_0	Initial concentration
Cu	Copper
CT	Contact time
CW	Constructed wetland
CMFR	Completely mixed flow reactor
DO	Dissolved oxygen
DW	Distilled water
EC	Electric conductivity
ED	Electrodialysis
EPA	Environmental protection agency
ET	Exposure time
E. coli	Escherichia coli
Fe	Ferric
FC	Fecal coliform
H_2S	Hydrogen sulfide
HRT	Hydraulic retention time
IAMBR	Intermittently aerated membrane bioreactor
IC	Initial concentration
IDF	Intensity duration frequency
K	Coefficient
L	Liter
LID	low impacted development
LCD	Liquid crystal display
M	Mass
MBR	Membrane bioreactor
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
Mmol	Millimoles
Mg	Magnesium
Mn	Manganese
N	Nitrate

Na	Sodium
NF	Nanofiltration
NP	Nacreous
Ni	Nickel
NO_3	Nitric acid
NH_4	Ammonium
OLR	Organic soluble solids
P	Phosphate
Pb	lead
PFR	Plug flow reactor
PP	Prismatic powder
PPM	Parts per million
Q	Flow rate
RC	Residual concentration
RE	Removal efficiency
RP	Raw shells powder
RO	Reverse osmosis
SA	Surface area
SBR	Sequential batch reactor
SC	Somatic coliphage
SOUR	Specific oxygen uptake rate
SS	Soluble solids
Temp	Temperature
TSS	Total soluble solids
UF	Ultrafiltration
V	Volume
WHO	World Health Organization
WWT	Wastewater treatment

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CHAPTER 1 INTRODUCTION

1.1 RESEARCH BACKGROUND

Pollution from stormwater has gained more and more attention in recent years because much of the stormwater runoff ends up in local creeks, rivers, streams or the ocean, untreated. Before entering the receiving body, the stormwater can run over a significant length, flushing out roof surfaces, residential yards, industries and roads, etc. The resulting stormwater quality from urban areas can introduce a wide range of pollutants into receiving waters during rainfall events. Victoria, British Columbia has a temperate climate with a rainy winter and a drier summer. Pollution generated on urban surfaces can be more serious in summer than in winter because more pollutants will accumulate between rainfall events. There are various kinds of contaminants in stormwater from different sources. The most typical contaminants in stormwater are nutrients (e.g. nitrogen, phosphorus), BOD, COD, Total Suspended Solids (TSS), pathogens and microorganisms, and trace metals (Huang, 2016).

Low impact development (LID) technologies are land development strategies applied primarily in urban environments to mitigate stormwater related problems sustainably. LID mimic the natural landscape and are designed to mitigate water quantity problems related to urbanization as well as water quality. Examples include bioretention cells (also known as rain gardens, vegetated biofilters) and permeable pavements, both of which are prevalent types of LIDs. These LIDs will treat stormwater quality in different ways, depending on the pollutant. Some pollutants such as nitrogen, COD, BOD, and coliforms are removed biologically, while others (e.g. phosphorus and metals) are removed chemically or physically. LID performance for urban stormwater water quality mitigation is contentious as results are highly varied. This is due to a variety of factors including a lack of uniformity in design. The ability to design LID and predict performance using these highly variable results are further confounded by the fact that traditional urban design concepts like IDF curves (Intensity-Duration-Frequency curve, a graphical representation of the probability that a given average rainfall intensity will occur and over what duration), and the Rational Method are insufficient for understanding and addressing the type of water quality treatment that is required in an urban areas. The area of research most developed for water quality is sewage treatment but stormwater quality treatment does not have the same research foundation, nor concept development

for the simple reason that stormwater was traditionally left untreated, and as well, represents an intermittent pollutant source with lower concentrations than wastewater.

Stormwater treatments occur through three primary mechanisms: physical (such as infiltration and sedimentation), chemical (ion exchange, adsorption, chemical reactions) and biological (biodegradation or organic matter or denitrification with bacteria in bioretention cells and raingardens). All of these mechanisms each require a particular exposure time between the mechanism and the contaminant being treated. In large scale systems like LIDs meant for stormwater treatment, the exposure time is intimately connected with the Hydraulic Retention Time (HRT, also called hydraulic residence/detention time) – a concept taken from wastewater treatment. In fact, they are often the same time period. HRT is "the average period of time that a particular substance or component resides within a reactor or continuously fed vessel" (A Dictionary of Chemical Engineering, 2014). Generally, we use an equation to present HRT:

$$HRT=V/Q \qquad (1)$$

where V is the effective working volume of the reactor or container (m^3) and Q is the inflow rate (m^3/h). The role of HRT in the stormwater treatment process has largely gone un-researched. The role of HRT should be different depending on the mechanism for removal; whether it is physical, chemical or biological. The role of HRT on physical processes such as sedimentation and infiltration is known (Shih & Chang. 2015) but less so for chemical and biological mechanisms. This thesis is focused on a chemical process for stormwater treatment as it is the less complicated of the two less researched mechanisms. In addition, innovative stormwater treatment methods will be considered as opposed to conventional treatment methods for use in determining the role of HRT in stormwater treatment. This research will test the efficacy of a proposed new method and understand the possible role of HRT in a chemical process at the same time.

The new, chemical method for stormwater treatment is to use oyster shells. In this research, four heavy metals (zinc, copper, cadmium and chromium) in stormwater were targeted and treated with whole, unaltered oyster shells. These four metals were chosen because of their toxicity and carcinogenic potential. Zhang et al. (2018) states that cadmium is considered a human carcinogen, and can damage kidneys, lead to fragile bones and even death when receiving long term exposure

to cadmium compounds. Copper poisoning can cause vomiting, nausea and death (Zhang et al. 2018).

Chromium can be traced from industries of wood processing and metal plating, etc. Normally, chromium has two forms: Cr (III) and Cr (VI). Cr (VI) is the toxic form and much more carcinogenic as compared to Cr (III), which is also less soluble (Xu and Zhao 2007). Hexavalent chromium is dangerous because it can induce birth defects and create reproductive impairment. The US Environmental Protection Agency (EPA) stipulates that the total chromium in drinking water must be less than 0.1 mg/L (Williams et al. 2014; Xu and Zhao 2007). Overdoses of zinc can cause zinc toxicosis and copper deficiencies with chronic ingestion (WHO guidelines for drinking water quality, 2011).

There are several methods for removing heavy metals (Tudor et al. 2006; Liu et al. 2009). The most common method is chemical precipitation: transferring the liquid phase of metal ions into insoluble solids by adding flocculants and coagulants. The problem with this method is metals are highly pH sensitive and many metals prefer to be absorbed in alkaline environments (high pH) in this method. Chemical precipitation is also very expensive and creates sludge, thus, leading to secondary pollution. Other frequently used methods having similar problems to chemical precipitation are activated carbon adsorption, membrane technologies and ion exchange. Among these conventional methods, chemical precipitation is only effective in high concentration metal ion solutions. Biosorption is another method with the benefit of low cost and environmentally friendly alternatives such as fungi and poplar trees etc. Chitin and its deacetylated form chitosan, are new applications for water purification. This is basically a polysaccharide and can be extracted from the shells of shrimps, lobsters and crabs, supporting mineral and organic deposits. However, this component only occupies a small percentage of the mollusk's shell (Tudor et al. 2006).

Among the methods noted above, biosorption is considered to be the more sustainable method and may have the most potential for removal of heavy metals in stormwater. In biosorption research, different kinds of absorbents are investigated. Normally, there are two categories of absorbents: natural and modified. However, Lim and Aris (2014) reviewed all the economical absorbents available in recent years based on their source which are more detailed. One type is nano, zerovalent particles and minerals, such as New Zealand iron-sand, magnetite, laterite and cement

kiln dust etc. These showed great efficiency in removing arsenic. Other types are calcium carbonate from seafood waste, such as oyster shells, clam shells, and crab shells, etc. Egg, hen and duck shells from food industries are also popular absorbents. Chitosan is also found to have a good removal efficiency of heavy metals, but higher efficiency can be reached when modified with other absorbents. Agricultural waste is another big category based on the source, for example, coconut husks, which are easy to get in tropical countries. Rice husks are also abundant, and effective when modified with polyaniline. Additionally, palm fruit, nut shells and fruit bagasse are also being developed and are worthwhile exploring as agricultural waste absorbents. Moreover, bone charcoal is a new category of absorbents and needs further study.

Oyster shells are a kind of mollusk shell which has more than 90% of the shell's mass as carbonate calcium with organic matrices only occupying less than 5% (Suzuki and Nagasawa 2013). The process of mollusks building their shells is divided into four steps: assembly of matrix; the first-formed mineral phase; nucleation of individual aragonite tablets; and growth of the tablets to form the mature tissue (Addadi ei al. 2006). Carbonate calcium has three crystal forms: calcite, aragonite, and vaterite; calcite is the most stable form, followed by aragonite, then vaterite. Basically, aragonite is the most common mineral in a mollusk shell, followed by calcite, which are crystal forms of calcium carbonate. Sometimes aragonite and calcite can coexist in shells. The mechanism by which the oyster shell ($CaCO_3$ micro-particles) absorbs metal ions is basically ion exchange in three steps: i) absorption of metal ions on the porous surface area (involving dissolution of partial calcium carbonate because of higher solubility compared to most of the metal carbonates, releasing Ca^{2+} and CO_3^{2-}); ii) precipitation of other metal ions on the surface; iii) the formation of heavy metal complex nucleation and crystals on the surface (Zhang et al. 2018).

1.2 General Thesis Objectives

The objective of this research is to determine the potential for the application of whole, unprocessed oyster shells in the treatment of heavy metals in stormwater within the Capital Regional District. Waste oyster shells are abundant in coastal cities such as Victoria and using this waste for treating pollutants is gaining widespread attention for use in stormwater treatment. The literature shows the efficacy of the shells when reduced to a fine powder for removing heavy metals in water. But the case for unaltered shells and whether they can be used whole (to reduce energy costs in reducing

them to powder form) has not been investigated. In this research, the use of whole oyster shells for treating four metals: zinc, copper, cadmium and chromium is investigated. Parameters involving contact time (also called exposure time), and shell surface area, SA, is used to determine the efficacy of this waste product. The first phase of the research involves lab experiments investigating the effect of different ETs (exposure time) (from one hour to 7 days) and single shells (with varying characteristics of mass, SA and volume) for a range of initial concentrations of a single metal. A mid-scale device is then used with a layer of shells to test the impact of elapsed time, calculated HRT based on the formula in Equation (1), and total SA in the control volume. The test is conducted using the Stormwater Modelling Standards of the District of Saanich. The mid-scale device will allow the information on a single shell to be scaled up to a group of shells that might be used in a catch basin or other stormwater infrastructure.

1.3 THESIS LAYOUT

This thesis is composed of six chapters; Chapter 2 provides a detailed literature review on the role of HRT in wastewater treatment from the lab scale to the field scale, and the application of mollusk shells in water treatment. Following this is Chapter 3, which summarizes the gaps in knowledge and specific research objectives. Chapter 4 describes the experimental design and methodology, and the analysis is contained in Chapter 5. Chapter 6 ends with conclusions and recommendations for future research.

CHAPTER 2 LITERATURE REVIEW

2.1 HISTORICAL USE OF HRT AND RELATIONSHIP WITH REMOVAL EFFICIENCIES FROM LAB SCALE STUDIES RELATED TO WASTEWATER TREATMENT

A tremendous amount of research has been done at the lab scale (bench scale) for wastewater treatment often involving beaker setups. Investigations into HRT are also numerous. For example, Choi et al. (2016) focused on exploring the influence of physical factors (i.e. aeration on/off time and hydraulic residence time) on the efficiency of removing organic matter and nutrients in IAMBR (an intermittently aerated membrane bioreactor). IAMBR is an advanced process of MBR, with a submerged membrane inside of a tank for filtering wastewater, with an effective volume of 6L. When the aeration is off, the wastewater was pumped into the IAMBR from the feed tank, and the permeate flowed out into the permeate tank when aeration is on. Specifically, for HRT (hydraulic retention times) that are of concern in this work, the experiment compared removal under three HRTs: 6, 9, 12 hours. The reason these three HRTs were chosen is because a 9 HRT is a common operating HRT in real conditions. A timer was used to control aeration on and off time and flow in and out. The results showed that removal efficiency of COD didn't demonstrate a significant correlation with HRTs. However, removal of nitrogen and phosphorus increased with shorter times. Total nitrogen and phosphorus removal reached the highest percentage when the HRT was 6 hours. (Choi et al., 2016).

Similarly, Meng et al., (2007) studied different HRTs and three MBRs (membrane bioreactors): 10-12h for MBR-A, 6-8h for MBR-B and 4-5h for MBR-C. The results showed that although HRT proved to have a positive correlation with COD, HRT didn't have a significant effect on COD removal but dissolved oxygen (DO) and specific oxygen uptake rate (SOUR) had a decreasing tendency as HRT decreased. Rosman et al. (2014) found that 6 hours is the most suitable HRT for biogranulation in 2, 6, 12, 24 tested HRTs in a lab scale study of wastewater treatment. Negative correlation was observed between HRT and removal efficiency of COD, ammonia and total nitrogen. The reason is that a shorter HRT will cause higher OLR (organic loading rate), which promotes the microbial activity so that microbes can digest more COD, ammonia and total nitrogen, leading to higher removal efficiency. Muda et al., (2011) conducted a series of experiments to analyze the influence of HRT on removal efficiency of COD, color, and physical and microbial

features of granular sludge. The targeted wastewater was an artificial textile wastewater and the system was a sequential batch reactor (SBR) including both aerobic and anaerobic processes with a working volume of 4L. A negative relationship was observed between HRT and OLR, HRT and MLSS (mixed liquor suspended solids), HRT and MLVSS (mixed liquor volatile suspended solids), HRT and concentration of granular biomass, while there is a positive correlation between HRT and color removal. However, a direct relationship between HRT and COD removal was not observed in this research. Jones et al. (2015) tested the effect of two HRTs (18min and 60min) on phosphorus removal, and the results showed that a green sorption media can absorb more P with higher HRT and influent concentration.

2.2 Investigating the Role of HRT at the Field Scale

There are field scale investigations of wastewater treatment (WWT) with wetlands. HRTs are generally chosen arbitrarily and are often a function of field investigation logistics like sampling ability, or capacity. Toet et al. (2005) focused on the effect of HRT on treatment performance of a surface-flow wetland system (total surface of 1.3 ha) under different HRT: 0.3, 0.8, 2.3 and 9.3 days (i.e. 7.2, 19.2, 55.2, 223.2 hours). Removal performances of pollutants under two different periods: spring to summer, and autumn to winter were detected separately as well. The results demonstrated that with HRT increasing gradually from 0.3 day to 9.3 days, there was a significant increase of some nitrogen related chemicals (i.e. Total N, NH_4^+-N, NO_3^--N) and fecal coliforms. Moreover, nitrogenous pollutants were observed more in autumn-winter than that in spring-summer, while the removal efficiency of the two periods had no significant difference. However, the removal efficiency of Total P (TP) and PO_4^{2-}-P in two periods showed totally opposite results: the RE of TP and PO_4^{2-}-P was positively related to HRT from spring to summer but negatively related from autumn to winter. RE reached the highest level at 9.3 days from spring to summer, but the lowest level from autumn to winter. Additionally, a dramatic positive correlation was observed between removal efficiency of fecal coliform and HRT. Similarly, Garcia et al. (2003) evaluated the influence of HRT and granular medium on *somatic coliphage* (SC) and fecal coliform (FC) in secondary effluent from a pilot plant. HRTs of 0.5, 1 and 3 days were chosen for testing the influence on FC; 1, 3, and 5 days were chosen to explore the effect of HRT on SC. It was found that there was a positive correlation between SC inactivation and HRT, and FC inactivation and HRT.

Tanner et al. (1995) conducted a 20-month experiment to study the effect of plants and loading rate on P and N removal of dairy farm wastewater. A constructed wetland system in Hamilton, New Zealand was used to treat wastewater, which had a dimension of 9.5 x 2 x 0.6 m (depth) with eight channels separated into two groups with four with planted *Schoenoplectus validus* under retention times of 2, 3, 5.5 and 7 days, respectively, and another group without plants under the same four HRTs. Generally, planted wetlands showed a much higher efficiency than unplanted wetlands, especially under high mass flow. The planted wetland had a removal rate of TN from 48% to 75%, and that of TP from 37% to 74%, when HRT ranged from 2 to 7 days.

Avelar et al. (2014) worked on the performance of constructed wetlands with *Mentha Aquatica* to remove coliform bacteria (specifically, total coliform and *E. coli*) from sewage that discharged from primary treatment. There were four beds adopted in this experiment, and two of them were planted with *Mentha Aquatica* (CW 1, 4), the other two were uncultivated (CW 2, 3). Four nominal HRTs were chosen for study: 1.5, 3, 4.5, and 6 days (i.e. 36h, 72h, 108h, 144h). A 4 X 2 factorial experiment was conducted to test the effect of plants and HRT on the performance of the constructed wetland. An obvious increasing removal efficiency of coliforms were observed in the wetland with *Mentha Aquatica*. Moreover, whatever is planted in the wetland, there is a significant positive relationship between HRT and average removal of total coliforms and E. coli. Table 1 provides a summary of the relationship between HRT and physical dimensions for various parameters in wastewater treatment found in the literature.

Table 1 The relationship between HRT and physical dimensions for various parameters in wastewater treatment

Literature review	**HRT(h)**	**Physical dimensions**	**treatment system**	**DO**	**MLSS**	**MLVSS**	**Ammonia**	**Nitrogen**
Choi et al. (2016).	6,9,12	6L	IAMBR					negative
Meng et al. (2007).	4-5,6-8, 10-12	12L	MBR	positive	negative			
Rosman et al. (2014).	6,12,24	1.8L(H:36cm; D:8cm)	SBR		negative	negative	negative	negative
Muda et al. (2011).	6,12,24	4L	SBR		negative	negative		
Toet et al. (2005).	7.2, 19.2, 55.2,223.2	1.3 ha	surface-flow wetland					positive
Garcia wt al. (2003).	12, 24, 72 for FC	6834L(6.7m L×1.7m W×0.6m H)	tertiary reed beds					
Tanner et al. (1995).	48, 72, 132, 168	1140L (9.5m L x 2m W x 0.6m H)	constructed wetland					positive
Avelar et al. (2014).	36, 72, 108, 144	8400L (24m L × 1m W × 0.35 m H)	constructed wetland					
Jones et al. (2015).	0.3, 1	0.62L (H:30.48cm; D:5.08cm)						

Phosphorus	Color removal	E. coli	Total coliform	Fecal coliform	filamentous bacteria	Organic matters (COD)
negative						No obvious relationship
					negative	slight positive relationship, but not obviously
						negative, but mainly because of high OLR
	positive					No obvious relationship
various in different				positive		No obvious relationship
				positive		
positive						
		positive	positive			
positive						

2.3 Conventional Methods Removing Heavy Metals

General methods on this topic were introduced in Chapter 1. This section details more specific methods of interest in this work. Zhao et al. (2016) reviewed all the methods available for removing heavy metals along with their advantages and limitations.

The first to consider is chemical precipitation, including sulfide and hydroxide precipitation, grouped according to insoluble solids created from chemical reactions. Hydroxide precipitation is highly related to the pH of the solution because the solubility of hydroxide participation can only occur in a small pH range; so that they can be removed afterwards by controlling pH. This method is always used for bivalent metal ions (e.g. Cd^{2+}, Zn^{2+} Cu^{2+} etc.). However, this method only works for high concentration wastewater with simple composition because of pH sensitivity. Sulfide precipitation mainly uses sulfuretted hydrogen and is easier to be removed after treatment compared to hydroxide - but with the risk of toxic H_2S fume and later problem of separation. Membrane filtration is also a big category, which involves filtering metal ions based on their particle size under pressure. Therefore, there are four normal technologies: ED, RO, UF, NF, corresponding electrodialysis, reverse osmosis, ultrafiltration and nanofiltration. ED allows ionized species passing through, and it was found effective in removing copper and ferric. This technology behaves well in wastewater treatment, but it requires great maintenance and high cost. RO normally has a pore size less than 2nm and has high removal efficiency of Zn^{2+}, Ni^{2+} and Cu^{2+} as reported but less used considering the high-energy requirements. UF targets metal sizes larger than 50nm and NF targets sizes bigger than 0.5 to 2nm. UF has similar drawbacks as RO and ED, but NF is the most often used one since it has many benefits like liability and reported high RE, and it is suitable for large-scale usage. Ion exchange is another category that use ion exchange resin (natural or synthetic) to uptake metals in wastewater. New application of natural zeolites and minerals such as montmorillonites for resin to remove metals shows a good uptake ability but under the lab scale. The disadvantage of resin is that periodic rejuvenation is needed. Moreover, novel technologies like adsorption on biological absorbents such as industrial by-products exist and although they are demonstrating some great results, further exploration is needed. Additionally, biosorption is more environmentally friendly and less expensive, and used more frequently in in low concentration bioremediation. Investigated effective biosorption absorbents include bacteria,

fungi, poplar (phytoremediation), etc. Others like chitin and photocatalysis are both novel methods but no further details are provided here (Tudor et al. 2005).

2.4 Application of Oyster Shells Removing Heavy Metals in Water Treatment

Mollusk shells can be an important source of calcium carbonate, attracting many scientists to explore the application of this waste product. To date, mollusk shells have been used in wastewater treatment for many purposes, such as purifying wastewater by trapping suspending solids and particulates by forming a filter bed with shell powder; reducing phosphate, BOD_5, SS, NH_4^+-N, NO_3^--N etc. (Shih and Chang. 2015); adjusting pH to provide an alkaline environment for some specific reactions; and ion substitution for removing heavy metal ions. The mechanism of using mollusk shells for water treatment is mainly using calcium carbonate for heavy metal sedimentation, while releasing calcium into the water at the same time. The original hypothesis dates from early studies on the strong adsorption ability of metal ions on calcite, a calcareous geologic counterpart (Tudor et al. 2006).

Most research to date uses shells in the form of certain size particles, and most studies have proven that shell powder works well in high concentration solutions. For example, Tudor et al (2006) studied the application of minimally processed shells on heavy metals in high concentration industrial wastewater and compared the differences in removal efficiency among three molluscan species: clam, oyster and lobster. All materials were crushed into the same size particles. Moreover, one group of limestone rock, aragonite and calcite - materials of geologic origin were also chosen for parallel experiments. In each test tube, one-gram particles were set to treat 50 ml metal salts from 5 minutes to 14 days. Two initial concentrations were set-up for metal solutions in order to compare the effect of initial concentration, 48.3mM (10000mg/L = 10g/L) and 145mM (30044mg/L≈30g/L). The results showed that for a lead (Pb^{2+}) solution of 10g/L, shells have a much higher and quicker removal efficiency than calcites, etc. Among the three geologic materials, calcite worked the best, but can only reduce lead to around 3000mg/L in one hour and keep this concentration stable afterwards. But the all shells performed well with the clam shell performing the best, reducing lead to less than 1mg/L (>99.99% RE) in five minutes, followed by lobster (73.9%) and oyster (15.3%). All the shells can reach over 99.99% in one hour, and the treated water's pH for the three types of shells increased to a neutral value of 7-7.5 from initial pH of 4.57.

For higher IC lead solutions, more time is needed for shells to reach a high efficiency. For example, 99.99% could be reached in one hour for the oyster shell when initial lead concentration was 10g/L but needed one day when initial concentration was 30g/L. An interesting phenomenon was observed in this work: in high concentration solution, lobster worked the best in one hour, 67% RE, followed by clam: 64.9% and then oyster: 25%, while in five hours, oyster had an RE of 92.2%, followed by lobster: 87.1% and then clam: 77.3%. In one day, the oyster was still the first one to reach over 99.99% RE, while lobster was 90.7% and clam was 81.1%.

For cadmium (Cd^{2+}), when IC is 10g/L, the lobster shell showed the best RE in one hour - 99.5%, followed by clam of 71%. They both reached over 99.99% in one day. The oyster shell did not seem to absorb very much cadmium with only 41.5% being reached after 14 days. For 145Mm (30g/L) cadmium solution, the removal rates decreased with 93% RE reached by clam shells, followed by lobster with 63.7%; while oyster showed RE below 20% even after 14 days. Other metals were also tested in this research: for zinc, clam shells showed the best removal ability in both low and high concentrations, 92% and 87.6% in one hour, followed by oyster shells, 80% and 52.3% respectively. For copper, oyster and clam shells can remove all of copper (100%) in water in one day. For 10g/L trivalent chromium, oyster and lobster shells can remove all pollutant in one hour. For 0.1g/L (100mg/L) hexavalent chromium solution, 100% can be reached in one hour by lobster shells, followed by clam and oyster shells (both 91.7%) with a stable RE afterwards. For 100mg/L Hg solution, over 99% Hg can be removed by lobster shells in five hours. Lobster shell also showed the best removal ability in 10g/L Ag, 5.3g/L Au and 10g/L Ni solution, reaching 93.8%, 87.4% and 73.6%, respectively, while at the same time, oyster shells can only reach 82.6%, 28.3% and 9.5%, comparatively. Overall, this research showed that all seashells work better than materials of geologic origin, which also matched the viewpoint in Zhang et al. (2018) that natural calcium carbonate such as calcite, aragonite and vaterite etc. have limited removal efficiency for heavy metals. Contact time was proven to have a positive relationship with RE and no release of these treated metal ions was observed in 14 days. When contact time is up 1h, the lobster shell showed the best absorbing ability.

Similarly, Liu et al. (2009) also worked on the removal ability of bivalve mollusk shells (raw vs pretreated) on single and mixed metals solution at the lab scale. However, this project did not specify species of shells, just collected bivalve mollusk shells for general use. In this project, the

shells were also smashed into a powder form and pretreated with washing, centrifugation, etc. Lab experiments primarily studied the relationship between copper efficiency and effective factors (i.e. contact time, initial concentration, temperature) with raw and acid treated shell powders, but a mixed metal solution including copper, zinc, cadmium and ferric (each 100mg/L) was also tested. After this, a real electroplated sample was also tested for better overview of heavy metals removal. The experiment was conducted in 250ml Erlenmeyer flasks with 100ml sample solutions. The flask was shaken during the treatment time after adding the shell powder. For the copper solution (100mg/L) made with $CuSO_4 \cdot 5H_2O$, the removal efficiency increased with the amount of shell powder added, regardless of whether the shell material was pretreated or not. But pretreated shells have a higher sorption capacity, which could be because more Ca ions are eliminated by acid, thus exposing more functional groups on the surface area that could bind metal ions. A capacity experiment was run with 1g of raw shell powder and 1g acid treated shell powder, with initial concentrations varying from 100mg/L to 1400mg/L. The results showed that when the initial concentration is less than 400mg/L, the removal efficiency of raw shell powder reached over 97%, but declined a lot with increasing initial concentration (IC) over 400 mg/L to a sorption capacity of 38.93 mg/g when IC is 400mg/L. However, the acid-treated shell showed a high-level removal efficiency over 99% whatever the initial concentration. Moreover, with regard to contact time, the removal efficiency (RE) of raw and acid treated powders both increased greatly in 90 minutes when IC was 100mg/L (100ml total, 1g shell powder, pH 5), over 99% at 90 minutes, and RE also increased with longer time periods. pH is also important for metal ion absorption but varies for different systems. For this system, the authors only tested a pH range of 1 to 5, and the result showed that efficiency of copper removal increased with higher pH with raw powder; but there was not a large difference for acid treated shells, which always kept the RE to over 99% with pH from 1 to 5. Additionally, both raw and acid treated shell powders showed a high removal efficiency (over 99%) when the temperature is between 15 - 40℃. Copper removal can stay over 98% after 12 cycles of sorption/desorption for raw shell powder. For a mixed metal solution (100mg/L each metal) with 90-minute contact time, 32℃, pH of 5, and 1g shell powder, the order of removal efficiencies for raw shells was as follows: Fe (99.99%) > Cu (98.62%) > Zn (26.81%) > Cd (14.5%). The acid-treated shells showed 99.99%, 99.45%, 69.53% and 30.21% for Fe, Cu, Zn and Cd, respectively. The adsorption difference is considered the result of competition absorption. Analysis on the mechanism of shell absorption was also conducted in this paper: it is believed that metal ion

exchange happens between metal ions in solution and the Ca^{2+} from the shells. The acid treatment adds more active groups such as –OH, –NH, C=O and S=O, thus, increasing capacity.

Other studies using a more general approach include the use of porous $CaCO_3$ microparticles, including shell powder etc. (Zhang et al. 2018). In this paper, three divalent metal ions were targeted: lead, cadmium and copper. Different effective factors were also investigated. Single metal adsorption and mixed metal adsorption were compared as well. Firstly, the effect of contact time was studied with 5mg microparticles to treat 10ml to 50mg/L initial concentration single metal solutions for various contact times (i.e. 10min, 20min, 30min, 60min, 90min, 120min, 180min, 360min). The result showed that Pb^{2+} solution reached equilibrium state at just 10 minutes; the equilibrium state means the concentration does not change very much after that state is achieved, while cadmium and copper solutions reached equilibrium at 3 hours. The maximum removal efficiency of lead was the highest: 99.9% followed by cadmium 99.4% and copper 82.6%. The initial concentration of metal ions was also tested: 3mg microparticles were mixed with 6 ml metal ion solution with different initial concentrations from 50mg/L to 3200mg/L. The results showed that all three metals reflected a positive relationship between removal capacity and initial concentration but with individual areas of strength – for some metals there was a great increase in capacity at certain ranges of initial concentrations. For example, copper prefers to be absorbed in relatively low concentration solutions (< 100mg/L), with the highest removal efficiency 85.3% when IC is 50mg/L and dropped continuously until 500mg/L. For single metal and mixed metals solution tests, the multiple metal solutions showed much less removal efficiency compared to single metal solutions, and $CaCO_3$ prefer to absorb copper and lead to cadmium. Also, the authors mentioned that the amount of heavy metals per gram of microparticles absorbed are higher than previous research studying the capacity of calcium carbonate mainly because of increasing surface area.

Du et al. (2011) also studied three metal ions: Cd^{2+}, Zn^{2+} and Pb^{2+}, and compared the absorption ability of oyster shells and razor clam shells when considering their different phases of development: calcium carbonate, calcite and aragonite. The influence of shell powder particle size, material dosage and pH (2-6) were studied as well. Cadmium and lead are quicker to get to equilibrium than zinc at 48h vs 96h, respectively. When pH is below 2, the removal was hard to

observe for all three metals, while it increased greatly as pH rose. Lead RE reached 100% when the pH was 6. It worth mentioning that pH doesn't affect cadmium removal very much, showing low removal when pH is between 2 and 5. Additionally, three grain sizes were compared: 38-75 μm, 150-250 μm and 500-850 μm. The results showed that in the following conditions: IC of 200mg/L, pH 5, 150ml and 20mg dosage, capacity increased dramatically with smaller size. Among three metals, oyster shell powder had the highest capacity for lead removal per gram and could absorb 820mg of lead for the smallest size, followed by zinc (670mg/g) and cadmium (42mg/g). However, per gram of mass, clam shells can absorb more cadmium as compared to oyster shells (470 mg/g vs 42mg/g), but with limited RE for the other two metals. The interesting thing in this case was that a positive relationship between dosage amount and capacity had not been observed. For example, for a range of 0.1 to 0.5g/L dosage, oyster shell powder reached the best capacity at 0.2g/L dosage for zinc; while for lead, the capacity even decreased with greater dosage. The same project also published a paper one year later (Du et al. 2012) studying the comparison of mollusk shells and geological calcite both at the nano size. The results showed that mollusk shell nanoparticles had a higher absorption of Cd^{2+} (8.91 mmol/g) and when adsorption occurred in mixed metal ion solutions, the shell material preferred to absorb metals ions as follows: $Cu^{2+} > Cr^{3+} > Pb^{2+} > Zn^{2+} > Ca^{2+}$. The authors also raised several explanations for this competition phenomenon: the first is hydration energy of all metals; ionic potential effect; and if the ionic radium of metal ions is similar to the calcium ion.

Moreover, another paper (Wu et al. 2014) focused on the treatment of oyster shells on copper in wastewater but with lower IC values. They were interested in how various parameters could affect removal efficiency, such as individual layers of the shell (i.e. prismatic (PP) and nacreous (NP) shell layers), initial concentrations, metal affinity and pH. As defined, there are three clear and well-defined layers of oyster shells: a cuticle (covering the surface of the whole shell, less than 20%), a prismatic (PP) layer and a nacreous (NP) layer (mainly composed of calcium carbonate, occupying most of the oyster shell). Firstly, oyster shells were treated physically to remove unwanted impurities and air-dried. Considering the study on individual contribution of raw shells, PP and NP layers for copper absorption, a 5% NaClO solution was used to rinse the raw shell (RP) to remove the cuticle, and PP and NP layers were separated by a knife. All RP, PP, and NP layers were ground into powders with particle size less than 177μm. Copper nitrate dihydrate (Cu

$(NO_3)_2 \cdot 2H_2O$) was used to prepare the copper solution. For the pH test, pH from 4 to 8 increased by 0.5 every time with other parameters fixed and controlled (i.e. 0.3g PP layer powder in 10mg/l copper solution for 24 hours), NaOH and HCl solutions were used to adjust the pH value. A pH electrode was used to measure the pH value, and 5.5 was proven to be the best pH for copper absorption. To study the effect of initial concentration, eleven concentrations (starting from 5 mg/L to 50mg/L, and 100 mg/L incrementally by 5 ml) were chosen for comparing with a contact time of 24h and pH of 5.5 with 0.5g raw powder. Atomic adsorption spectroscopy was selected to test the value of copper concentration left in the water. The results showed that when initial concentrations were 10mg/L, the efficiency climaxed to 99.9%, but after that, the efficiency decreased with increase initial concentrations my only 29% (IC was 100 mg/L). However, the efficiency can be maintained to over 90% when initial concentrations were under 25mg/L. Comparatively, the equilibrium adsorption capacity (i.e. the mass of absorbed copper divided by the mass of shell powder) curve showed a different tendency: a strong positive correlation was found between initial concentration and equilibrium adsorption capacity. When C_0 = 5mg/L, per gram raw shell can absorb 1 mg copper but it can absorb 3.23mg of copper when C_0 increased to 45mg/L. Additionally, two equilibrium equations (Langmuir and Freundlich model) were used to fit the copper absorption for NP and PP. The results showed that when the initial copper concentrations were between 5 and 30 mg/L, both RP and PP layer can be fitted to a strong homogeneous Langmuir model. However, when initial copper concentrations were between 30 and 200 mg/L, heterogeneous Freundlich model produced the better fit.

Seco-Reigosa et al. (2012) tried to use shell ash from shell calcination to treat hexavalent chromium, arsenic (As^{5+}) and mercury (Hg^{2+}), which has characteristics of high EC and pH (over 12). Another absorbent material - a mix of shell, wood ash and wastewater sludge - was used to compare absorption ability. Firstly, X-ray fluorescence was used to analyze the characteristics and existing elements of shell and shell ash. The result showed that the shells had a much lower concentration of all elements (i.e. Mg, Al, S, Mn, Fe, Ni, Cu, Zn, As) than ash except calcium, which is expected. For Cu and Zn, these metals existed in shells lower than 1mg/kg and 20mg/kg, respectively. This project also compared absorption and desorption efficiency. For adsorption experiments, 3g of ash or mixture was added to treat different IC solutions (30ml) of As and Cr from 0 to 100 mg/L (0, 0.5, 5, 10, 25, 50, 100), and 10ml Hg solution with known concentration. Both solutions were

shaken for 24h and centrifuged afterwards. The results showed that ash and the mixture both work well for Hg and As, reaching 94% and 96% RE for ash, respectively, and 98% and 88% for the mixture, respectively. However, hexavalent chromium removal efficiency varied between 11% and 30% for shell ash and 30% to 80% for the mixture, with increased initial concentration. The desorption of three metals from two materials was also tested. After absorption, the materials were collected and added to the same volume solution but metal free and repeating the adopted process (shaking etc.). The result showed that desorption of Hg and As in different materials were both less than 5%, but that of Cr (VI) was in the range of 45-92% for ash and 0-19% for mixtures. The reason why shell ash performed poorly in chromium removal was also mentioned: hexavalent chromium removal prefers pH of 1 to 2.5, and it will be low when pH > 4 because of the competition between hydroxyl ions and chromium oxyanions (Wang et al. 2009).

Moon et al. (2013) also used calcined oyster shells to treat metal ions of copper and lead. They observed a 95% reduction for copper while a mixture of calcined oyster shell and cow bones showed a 99% and 95% reduction for lead and copper. Moon et al. (2013) also compared the difference in calcined oyster shells and natural oyster shells on removing arsenic from contaminated soil. Both of them were sieved with a 0.83mm mesh size and treatment time lasted 28 days. The results showed that natural oyster shell could not satisfy the Korean standard (1.2 mg/L) even after 28 days.

CHAPTER 3 THESIS OBJECTIVES

3.1 GAPS IN KNOWLEDGE

Several questions need to be answered in this research to realize the application of whole oyster shells in stormwater treatment for Victoria, BC. These are detailed below.

3.1.1 STORMWATER CHARACTERISTICS

Most of the literature describes the performance of mollusk shells for quality mitigation in the area of wastewater/sewage treatment, which has a much higher concentration of heavy metals than stormwater and is supplied virtually continuously. However, stormwater is totally different from wastewater in that the former is intermittent and has much lower concentrations. Also, since most of the reports proved that there is a positive relationship between initial concentration and the absorption ability of shells, the author cannot be certain if shells can still provide acceptable treatment levels in low concentration solutions. Therefore, it is necessary to explore the performance of oyster shells under low concentration conditions.

3.1.2 WHOLE OYSTER SHELLS INSTEAD OF POWDER

All of the literature reviewed used a powder form or ash form of the shells to ensure complete contact between the shell and the solution. To the author's knowledge, no one has checked for the feasibility of using whole oyster shells in this capacity, to date. The energy cost of crushing shells into nano-sized particles may be significant when attempting to scale-up this material for practical use. Therefore, this project will adopt whole oyster shells instead of powders to remove metal ions in stormwater. It is expected that the whole oyster shell will be less effective than powder form, but considering cost, we want to test the performance of whole oyster shells with the potential of exploring if relevant parameters can improve the removal efficiency and make it a useable method.

3.1.3 THE ROLE OF HYDRAULIC RETENTION TIME

In wastewater treatment, hydraulic retention time is an important parameter related to *inflow rate* and reactor volume. Hydraulic retention time in the field of environmental hydraulics (Mihelcic & Zimmerman, 2014) is a parameter in CMFR (completely mixed flow reactor) design or in PFR (plug flow reactor) design and is related to volume and *outflow rate*. In this formula, if steady state is assumed, outflow does not change appreciably over long-time scales, which is applicable to large

bodies of water likes lakes. However, for the case of oyster shells for metal removal in stormwater, only contact time or exposure time is considered. At the lab scale, it's difficult to mimic hydraulic retention time, so the author will use contact time in the laboratory experiments in order to provide an understanding of the relationship between RE and time. However, in real world, the shells are not likely to be bathing in static water for the long periods of time required to reach high RE levels simply because stormwater is intermittent and continuously flowing (depending on the application). Thus, an HRT concept from the two fields that describes the time that the shells are in contact with water and its influence on the removal will be explored in this project. In the mid-scale experiment, inflow will be varying and based on a design storm. In addition, certain quantities of outflow will be extracted for testing. The HRT will be calculated based on two definitions for different systems in order to explore its meaning in stormwater treatment.

3.2 Specific Research Objectives

The specific research objectives are:

1. To investigate the role of Exposure time (ET), also known as contact time, on the efficacy of a single oyster shell, or several oyster shells defined by their combined mass, volume and surface area, for removing zinc, copper, chromium and cadmium.

2. To determine the relationships between removal efficiency RE and the oyster shell's characteristics (defined above) for removing the four heavy metals noted in 1.

3. To determine if these relationships are scalable to the small field scale and the meaning of HRT in stormwater treatment.

These objectives will be achieved with the methods described in the next Chapter.

CHAPTER 4 METHODOLOGY

4.1 OYSTER SHELL PREPARATION

A large quantity of whole and unprocessed oyster shells was obtained from a storage site in Victoria. These shells were originally collected from coastal areas of Victoria, mainly Fanny Bay oysters in Baynes Sound. Over one hundred shells were chosen for the experiments. Each shell was cleaned carefully with a brush and then air dried. The mass, volume and surface area of each shell was tested and documented before treatment. All shells were weighed by using a 500g (0.01g resolution) digital LCD scale. The volume of each shell was measured using a beaker of water and observing the amount the displaced volume of the shell. Different volumes of beakers (100ml, 200ml, 600ml and 1000ml) were chosen to test various sizes of shells as smaller shell volumes required more sensitive analog scale graduations. A pipette was used to transfer water to a 25ml graduated cylinder at 0.5 increment, until the water level reached the waterline observed before the shell was placed in the beaker. The volume of shell then can be read from the cylinder.

The literature shows that surface area (SA) is an important parameter as the higher the surface area (the finer the particles in shell powders), the higher the removal efficiency. Thus, SA was measured for each shell as precisely as possible. Because of the shells' irregular shape, several methods were attempted to measure SA including using a 3D scanner, but this was not successful. The method adopted involved measuring the SA by molding aluminum foil to the surface and measuring the flattened aluminum foil. This process is described below.

1. The top surface of each shell was covered with aluminum foil by hand carefully to get into the grooves of the shell (See figure.1a);
2. The foil was cut along the rim of the shell with fine scissors and then carefully removed and flattened overtop of graph paper with 0.25 in^2 squares (see Figure 1b);
3. A fine-tip marker was used to outline the foil and a rectangle very close to the foil edge (rectangle area is known based on the number of squares) – see Figure 1b and 1c;
4. A regular marker was used to blacken the void area between the foil rim and the rectangle (see Figure 1d);
5. A photo was taken of the graph paper and then cropped to the rectangular area with photo editor tools.

6. The picture was imported into MATLAB and a code (see Appendix 2) was used to calculate the proportion of black and white area, so that the foil area can be calculated precisely.
7. Steps 1 to 6 were repeated for the underside of the shell so that areas of both sides were obtained.

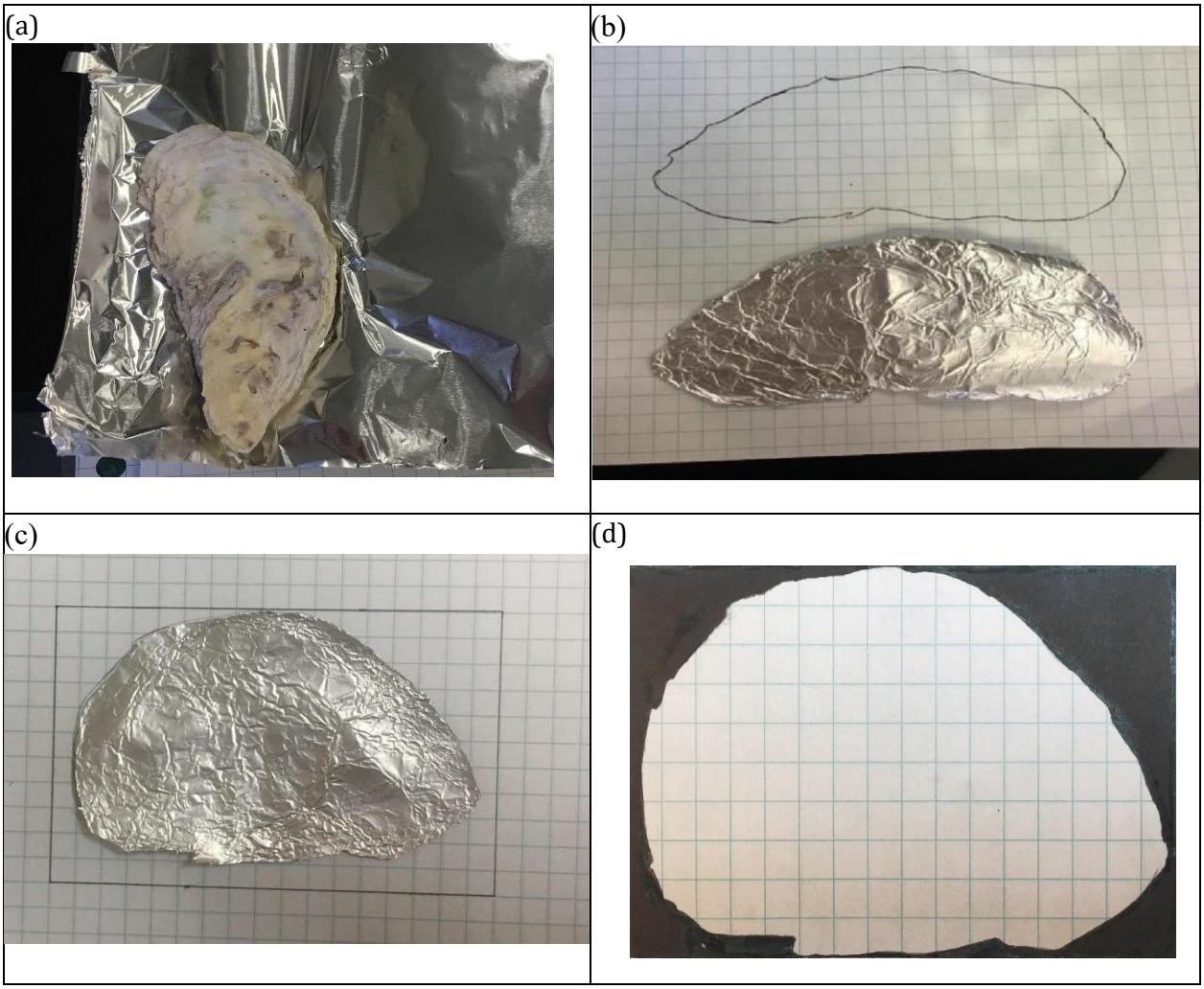


Figure 1 Photographs (a)(b)(c)(d) show the main steps to calculate SA of a shell:(a) wrapping (b) depicting the rim of a shell (c) depict the rectangle (d)paint the void area.

In total, 132 shells were measured in this manner and all labeled. The top side was measured separately from the bottom side (which would be the inside of a closed shell when the oyster was alive in the shell). Figure 2 shows a histogram of the number of shells with ranges of surface area. The shells ranged from 26.7 cm^2 to 194.6 cm^2 in surface area, with respective masses of 5.76g and 79.12g, and volumes of 3.5ml, and 34ml, respectively.

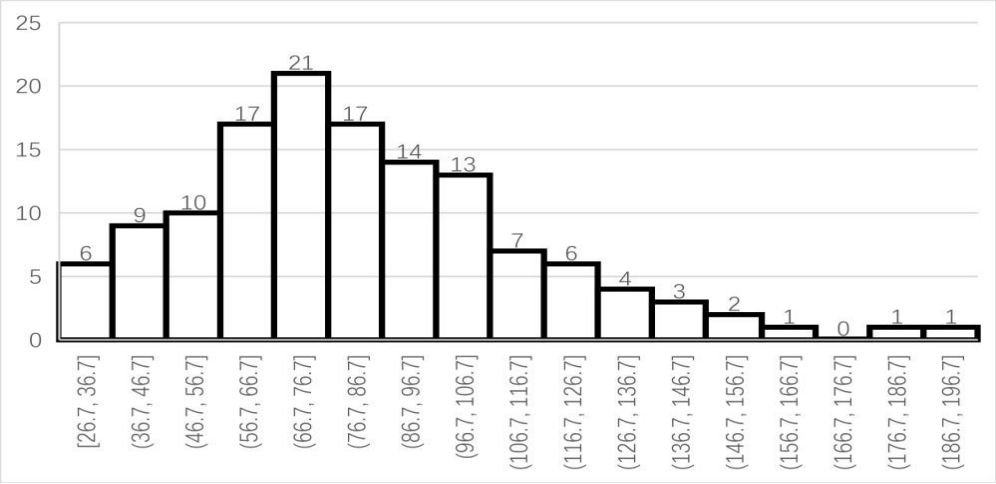


Figure 2 Distribution of surface area

The scatter function in MATLAB was used to plot all sample shells and then a surface was fitted to model the relationship between volume, mass and surface area for the 132 shells used in this study. The scatter plots are shown in Figure 3.

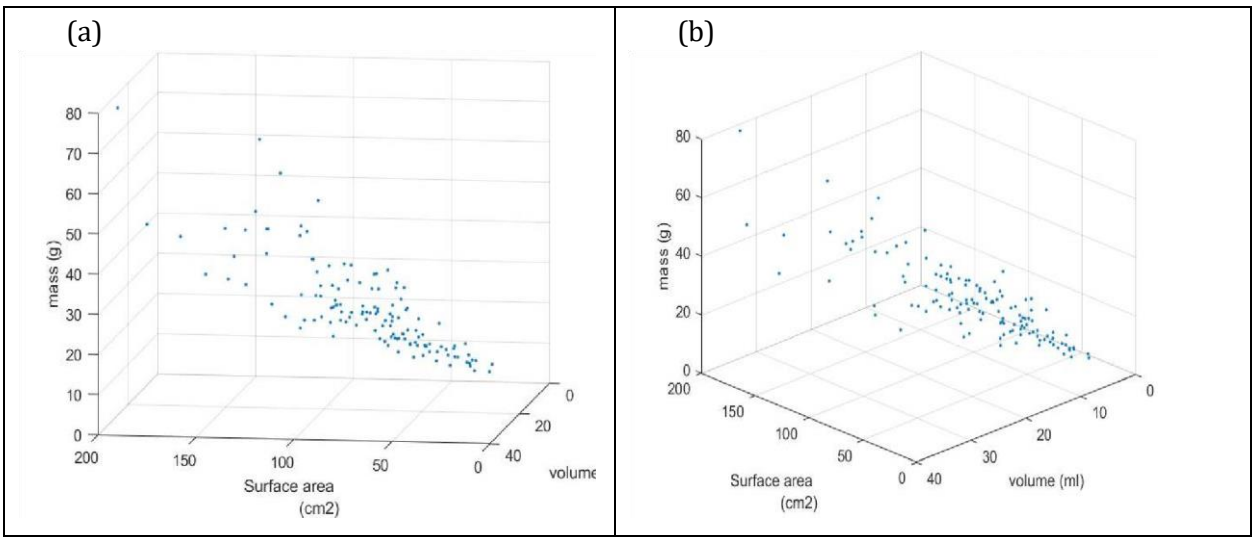


Figure 3 3D figure of mass, SA and volume of 132 sample shells

These points were fitted with a custom function with variables of M (mass), V (volume) and SA (surface area). The modelling form is based on the units they of each variable: g for M, cm^3 for V and cm^2 for SA. Also, density has the formula of $\rho = M/V$, and the equation should be dimensionally consistent and the density of the shells should be fairly consistent. Here, ρ has a unit of g/cm^3. In MATLAB modelling, the general equation can be written as followed:

$$M = cV + dSA^{3/2} + e \qquad (2)$$

where *c* and *d* are constants having units of g/cm^3 (same as density) and *e* has units of g. The modelling figure shown in Figure 4, has an adjusted R^2 of 0.77 with the upper and lower curves being the 95% confidence interval. The parameterized equation is:

$$M = 0.62V + 0.97SA^{3/2} + 0.01 \qquad (3)$$

In Equation 2 the value of *c* should be some portion of the average density of the oyster shells. The average shell density was obtained using the average mass of all the shells (22.956g) divided by the average volume (13.75 ml/cm^3) and was calculated as 1.67 g/cm^2. Interestingly, the sum of *d* and *e* is 1.59 g/cm^3, which is very close to the calculated average density.

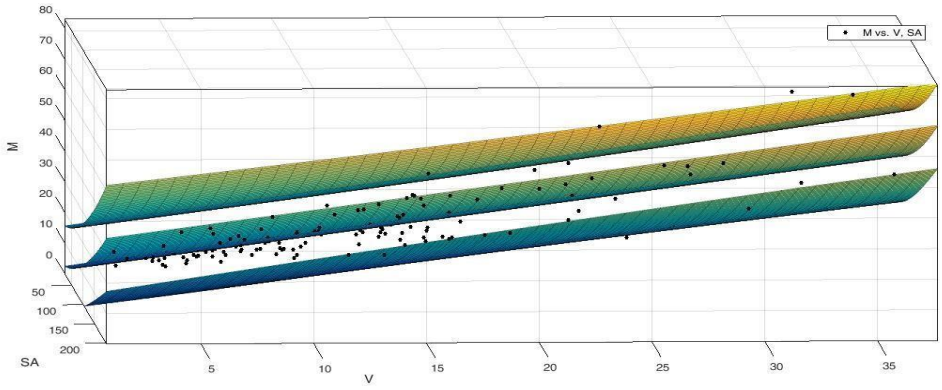


Figure 4 Surface modelling between mass, SA and volume

4.2 PRELIMINARY EXPERIMENTS WITH A COCKTAIL SAMPLE TO FACILITATE DESIGN

Since most of the literature only describes the ability of crushed oyster shells, the removal ability of whole oyster shells is unclear. Thus, a preliminary experiment was conducted to judge whether further study is even warranted for the use of whole oyster shells for metal removal.

One oyster shell (volume: 25ml, weight: 24.67g, contact surface: 115.7 cm^2) was chosen to sit in a 1000ml beaker to treat 1000ml cocktail sample mixed with different metals. All the chemicals were bought directly from Science Store at the University of Victoria. Concentrations were measured following colorimetric methods with easy conducting strips from HACH and test kits from LaMotte. Solutions were prepared as followed:

$CuCl_2.2H_2O$: based on standard atomic weights, a standard copper solution of 930mg/L was made. HACH test kit with code number 2745125 was used for testing concentration. The expected chemical reaction is shown below:

$$Cu^{2+} + CaCO_3 \longleftrightarrow CuCO_3 + Ca^{2+}$$

$NH_4.N0_3$: a standard ammonium solution of 1000mg/L was made. HACH test kit with code number 2755325 was used for testing concentration. The chemical equation is:

$$2NH_4.N0_3 + CaCO_3 \longleftrightarrow Ca\ (NO_3)_2 + (NH4)_2CO_3$$

Nitrite and nitrate were tested with HACH test kit (#2745425).

Ferric Nitrate: a standard iron solution of 1000mg/L was made. HACH test kit with code number 2745325 was used for testing concentration. This is the reaction:

$$Fe^{3+} + CaCO_3 \longleftrightarrow Fe_2(CO_3)_3 + Ca^{2+}$$

Zinc Chloride: a standard zinc solution of 1000mg/L was made. LaMotte test kit with code number 7417-02 was used for testing concentration. The chemical reaction is shown below:

$$Zn^{2+} + CaCO_3 \longleftrightarrow ZnCO_3 + Ca^{2+}$$

Potassium Phosphate, monobasic: a standard phosphate solution of 1000mg/L was made. HACH test kit with code number 2757150 was used for testing concentration. The corresponding reaction is:

$$2KH_2PO_4 + 3CaCO_3 \longleftrightarrow Ca_3(PO_4)_2 + H_2O + 3CO_2 + 2KOH$$

The sample water was mixed with chemicals with high concentrations at the maximum testing levels for our test kits. Samples of 10ml zinc solution (10mg zinc), 5ml $NH_4.N0_3$ solution (5mg ammonium and 7.5mg nitrate), 5ml ferric nitrate solution (5mg iron and 16.6mg nitrate), 2.5ml $CuCl_2.2H_2O$ (2.325mg copper), and 50ml KH_2PO_4 solution (50mg phosphate) were extracted and then diluted to 1000ml. The sample water includes 10mg/L zinc, 5mg/L ammonium, 24.1mg/L nitrate, 5mg/L iron, 2.325mg/L copper and 50mg/L phosphate. Contact time of 1, 6, 18, 24, 48, 96 and 216 hours were chosen for this experiment and the sample of 0h was also tested with strips or kits depending on the chemical.

4.3 INDIVIDUAL EXPERIMENTS

The preliminary results were poor for the cocktail sample as many pollutants showed little to no reduction. Among those metals, we selected up two metals of interest to stormwater modelers: zinc and copper and added chromium and cadmium as our target metals. To study the effect of oyster shells on these metals, four, factorial design 4x4 individual experiments were planned with one blank. But instead of a cocktail, for every individual experiment, only one metal was put in solution with the shell. Although HRT is an important parameter, other parameters (i.e. surface area and initial concentration) are also considered. In a lab scale portion of the study, contact time (CT) was used instead of HRT from 1h to 7 days.

Starting with the Cu^{2+} individual metal experiment, 16 one-liter beakers were prepared with four initial concentrations (including one blank, which only contained distilled water inside) with four different shell sizes. The SA of first 108 shells measured were grouped based on surface area such that a SA difference of less than 3 cm^2 constituted a member of a group size with the same surface area. Among these groups, four different sized groups were chosen to determine the impacts of surface area.

During the whole experiment, all of the glassware instruments are washed with laboratory detergent. All beakers were covered with a piece of plastic wrap to prevent the water evaporation. Four parameters were monitored for each HRT, they are PH, temperature, Electric conductivity (EC) and concentration. pH, temperature and EC were tested with an EXO multiparameter Sonde, and concentrations were determined using a spectrophotometer following the colorimetric method from LaMotte with different metal reagent systems following the LaMotte manual (LaMotte, 2005). Although initial concentrations were prepared to specified values (as detailed above), when measured with the spectrophotometer, deviations from the expected values existed. Thus, the concentration recorded for IC was the one produced by the spectrophotometer and not that determined from molar calculations. Moreover, for the beaker-based experiment, since no inflow and outflow were determined, a batch reactor system of first order decay reaction was used to model the absorption kinetics (Mihelcic & Zimmerman, 2014):

$$\frac{C(t)}{C_o} = e^{-kt} \qquad (4)$$

where k is the decay constant and $C(t)$ is the concentration at any time t, and C_0 is the initial concentration.

4.3.1 COPPER EXPERIMENT

The chemical used to prepare the 930mg/L copper solution is Copper (Ⅱ) chloride dihydrate, $CuCl_2.2H_2O$. According to relative atomic mass, Cu is 63.5, Cl is 35.5, H is 1, and O is 16. Therefore, the total mass of $CuCl_2.2H_2O$ is 170.5, and Cu 63.5 occupies about 37.24% of total mass, for 930mg/L copper solution; thus, we need 930/37.24%, which is about 2500mg (i.e. 2.5g) copper chloride dihydrate. This 2.5g of chemical was dissolved in a small amount of DW (distilled water) and then diluted to 1000ml, so the concentration of copper in the new solution is 930mg/L. Based on the standard solution, we prepared three low initial concentrations:

1. 2.79mg/L, extracting 3ml standard solution and diluted to 1000ml;
2. 0.93mg/L, extracting 1 ml standard solution and diluted to 1000ml;
3. 0.23mg/L, extracting 1ml standard solution first diluted to 1L and then extracting 250ml from the diluted 1 L diluted again to 1L.

In this experiment, there are eight HRTs: 0h, 1h, 6h, 18h, 36h, 72h(3d), 120(5d), 168h (7d). The four different surface areas that were initially chosen: 69 cm^2, 85 cm^2, 99.5 cm^2 and 108 cm^2, proved to have too small a difference in SA to see the effect of SA on RE. Therefore, we added one more experiment, which used 0.2 ppm initial concentration and six 2-liter beakers with much bigger SA shells from 38 cm^2 to 550 cm^2 (i.e. 38 cm^2, 121.6 cm^2, 223 cm^2, 320.8 cm^2, 433 cm^2 and 550 cm^2). The contact time was from 1h to 28d to explore the possibility of desorption. According to the result, we proved that with certain SA differences, the effect of SA is negligible. Also, the blank experiment indicates that for Cu, shells do not release the metals previously absorbed (in their own environment before the experiment) to distilled water. However, their pH does increase. Therefore, we suspect few to no ions are released to water. Also considering the chemical limits and cost, for the other three metal individual experiments, only a factorial design 3 X 3 experimental setup (3 initial concentrations X 3 SA with larger differences) was used (Figure 5). The blank experiment will be cancelled.

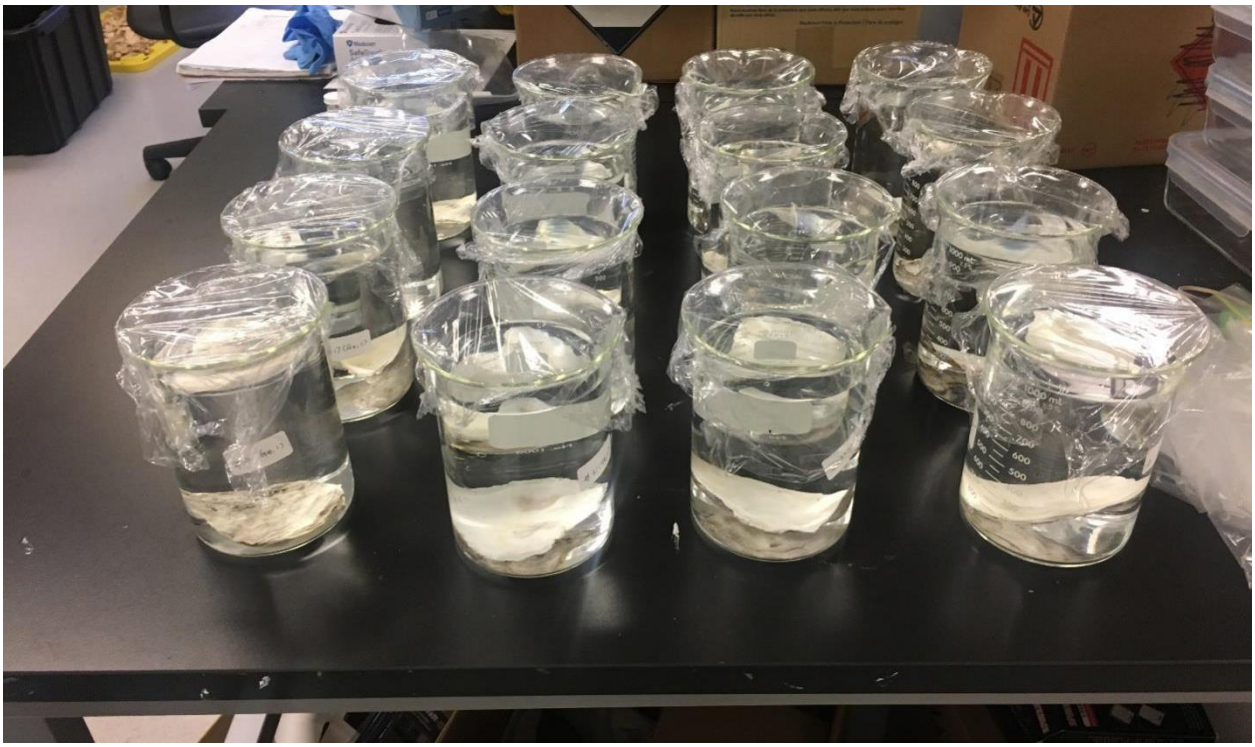


Figure 5 the photo of copper experiment

4.3.2 ZINC EXPERIMENT

Eight contact times were chosen: 0h, 1h, 6h,12h,24h(1d), 72h(3d), 120h (5d), and 168h (7d). 1ml, 0.5ml and 0.2 ml were extracted separately from prepared standard 1000mg/L solution and diluted to 1 liter, to make three initial concentrations: 1mg/L, 0.5mg/L and 0.2mg/L. Three average surface areas chosen were: 35 cm^2, 154 cm^2 and 303 cm^2. All parameters were tested and recorded in Excel.

4.3.3 CHROMIUM EXPERIMENT

The chemical used to prepare the chromium sample solution was the chromium standard, hexavalent, 50mg/L from HACH. Three initial concentrations (IC): 0.2, 0.5 and 1mg/L. 20 mL were extracted from a standard chromium solution and diluted to 1000ml, which is 1mg/L. Similarly, 10ml and 4ml was extracted for preparing 0.5 and 0.2 mg/L IC. The contact time was the same as zinc and the average surface areas were 37.8 cm^2, 151 cm^2 and 300.5 cm^2. The expected reaction between hexavalent and shell would be: $Cr^{6+} + CaCO_3 \longleftrightarrow Cr(CO_3)_3 + Ca^{2+}$.

4.3.4 CADMIUM EXPERIMENT

The chemical used to prepare a cadmium standard solution (1000mg/L) was Cadmium Chloride $CdCl_2$. The atomic weight for Cd is 112.4, and Cl is 35.5, so the total atomic weight is 183.4, and Cd occupies 0.6129. The chemical weight should be 1000/0.6129, which is 1.63g. Then, 1.63g was dissolved into 1000 DW. Also, three initial concentrations were prepared: 0.2, 0.5, and 1mg/L. Eight contact times were chosen as it was for zinc and 43 cm^2, 152.8 cm^2 and 300 cm^2 surface area groups were used. The expected reaction is followed: $Cd^{2+} + CaCO_3 \longleftrightarrow CdCO_3 + Ca^{2+}$.

4.4 MID-SCALE EXPERIMENT

From the individual experiment, some reduction of heavy metals by whole oyster shells is expected. But better comprehension of the potential of whole oyster shells at the field scale is required. To explore a larger scale application above the lab scale beaker size that could facilitate more relevant HRTS, a mid-scale device was designed and fabricated to mimic real conditions. This device was composed of five plexiglass pieces and one more piece that is movable within the tank to change the tank volume. The whole tank has a dimension of 3ft length X 2ft height X 1ft width. A schematic is shown in Figure 6.

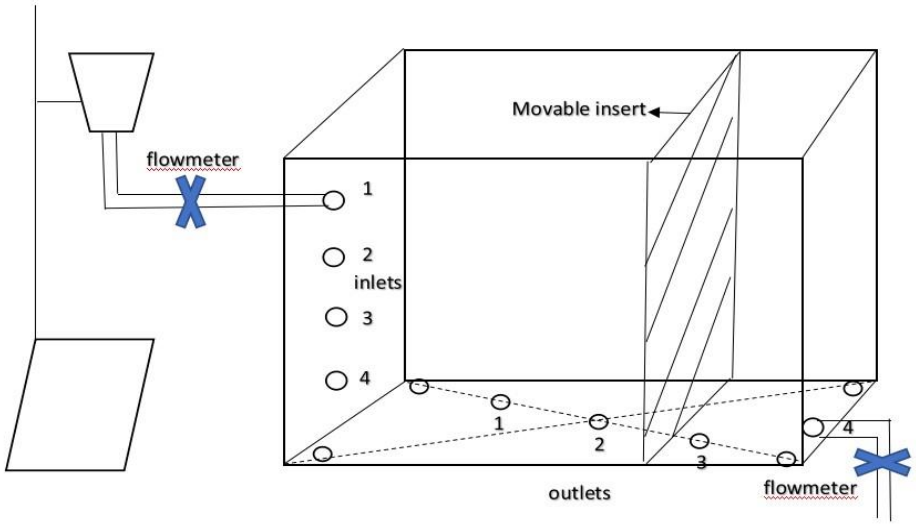


Figure 6 The script of design concept

Five plexiglass plates were glued tightly to create a tank and one plywood sheet was added to the bottom and a metal brace added around the tank for enforcement. There are seven holes on the

bottom panel, four of them were drilled in the corners for monitoring the water level, while the other three were used for outlets, dividing the diagonal equally. The left panel has four inlet holes onside, 1/8", 4", 10" and 16" away from the bottom to provide a vertical and horizontal runoff just like a real condition. There is an outlet hole in the very bottom corner of the right panel, which can create a line with the other three outlets on the bottom panel. There is also a hole closer to the bottom on the movable panel which can connect to the hole on the right panel, to allow water out when controlling the tank volume. All holes are half inch in diameter and connected to connectors and tubing. Inlet and outlet holes were also connected to flowmeters, which can monitor cumulative volume of inflow passing into the tank. When connecting connector and tubing, clamps were used to inhibit leaking. However, leaking was still observed so waterproof orange tape and electrical tape were used to attach to the connection part of the connector to add thickness. The reason why two kinds of tape were used is because the orange waterproof tape doesn't have viscidity. It is hard for waterproof tape to stick and wrap around the slippery mental connector. Therefore, the non-waterproof but sticky electrical tape was used first to wrap around the connector and then that was covered by waterproof tape, so that the water will not corrode the electric tape. Moreover, some of the tubing will bend because it is flexible, so an "L" shape connector was used at every turn of tubing to make sure the tubing was not experiencing any significant bends.

Additionally, geotextiles were used to cover the holes to prevent particles passing through. Four screws were fixed to the bottom plywood for adjusting the height of each bottom corner in order to provide a slope that will allow water to pass through to the corner outlet. A 16-liter water jar was put on a top of high wood stool to provide a supply. Four holes were drilled near the bottom of water jar and connected to tubing, a valve, a flowmeter and then inlets on the left panel of the tank. A glue gun was used to glue the connection part between holes and tubing to ensure no leaking. Because of the height difference, the water from the jar can flow into the tank naturally. The valve can be used to control flow rate. Before the mid-scale experiment, several trial experiments with only tap water were conducted to ensure the tank was leak proof and operable. Four baskets were used to collect outflow. The residual water leaving the water jar was also measured. Because the four holes on the water jar is not on the bottom, some water will be left inside when flowing out. Therefore, a 500 ml graduated cylinder was used to pour water into the water jar until one of the

holes has outflow. The amount of water was recorded as 1820ml. The final mid-scale tank is shown in Figure 7.

Figure 7 The final look of mid-scale device

The mid-scale experiment was conducted according to 6-hour Duration Design Storm from the District of Saanich Stormwater Modeling Standards (Jeff, 2013). Twenty minute increments were used instead of 10 minute increments for the actual experiment. The inflow volume of every twenty minutes was calculated based on rain depth and the bottom surface area of tank (2787 cm^2). For example, the first inflow is 0.36 mm, when multiplied by 2787 is 0.1L, so the first flush would be 100ml. The specific data is shown in Table 2. According to cumulative inflow and residual water that would be left in the water jar, a total volume of 8.645L (cumulative volume) and 1.82L, which is 10.465L sample solution, was prepared mixed with 0.3mg/L zinc and 0.5mg/L of cadmium, chromium and copper. A layer of shells was put on the bottom of the tank with a total surface area of 9437 cm^2, total volume of 1599ml and total mass of 2660g. The concentration of zinc, copper and chromium was tested with the spectrophotometer, but that of cadmium must be tested under the absence of zinc and copper ions. Therefore, a cadmium test kit from LaMotte was used to test cadmium with 0.1ppm accuracy. When the experiment begins, every corresponding volume of water is poured into the water jar and flows into the tank from the inlet continuously for twenty

minutes. At every twenty minutes, 60ml from the furthest outlet is extracted and tested for various parameters.

Considering the formula of HRT from wastewater treatment and CMFR/PFR system, controlled volume V is divided by either inflow rate or outflow rate (Q). For HRT calculations in wastewater treatment, Q is the inflow rate which varies and thus, V also changes based on different Q. Therefore, HRT was calculated every twenty minutes, and the volume of water at that time would be considered as V and Q is the inflow rate at that twenty minutes. For CMFR/PFR system, Q is the outflow rate which is 60ml/20 mins, equal to 3ml/min constantly in this case. V is also cumulative volume minus cumulative outflow. CMFR is a completely mixed flow reactor, while PFR represents plug flow reactor. The tank experiment was considered as a non-steady state CMFR, with a hypothesized model of first order decay of

$$\frac{C(t)}{C_o} = e^{-(\frac{Q}{V}+k)t} \qquad (5)$$

where Q is flow rate and V is volume of reactor. Since we know that HRT is defined as V/Q, the model reaction can be replaced as:

$$\frac{C(t)}{C_o} = e^{-(\frac{1}{HRT}+k)t} \qquad (6)$$

where t is still the elapsed time, and HRT would be the result of HRT(CMFR) - elapsed time. The detailed data is shown in Figure 8.

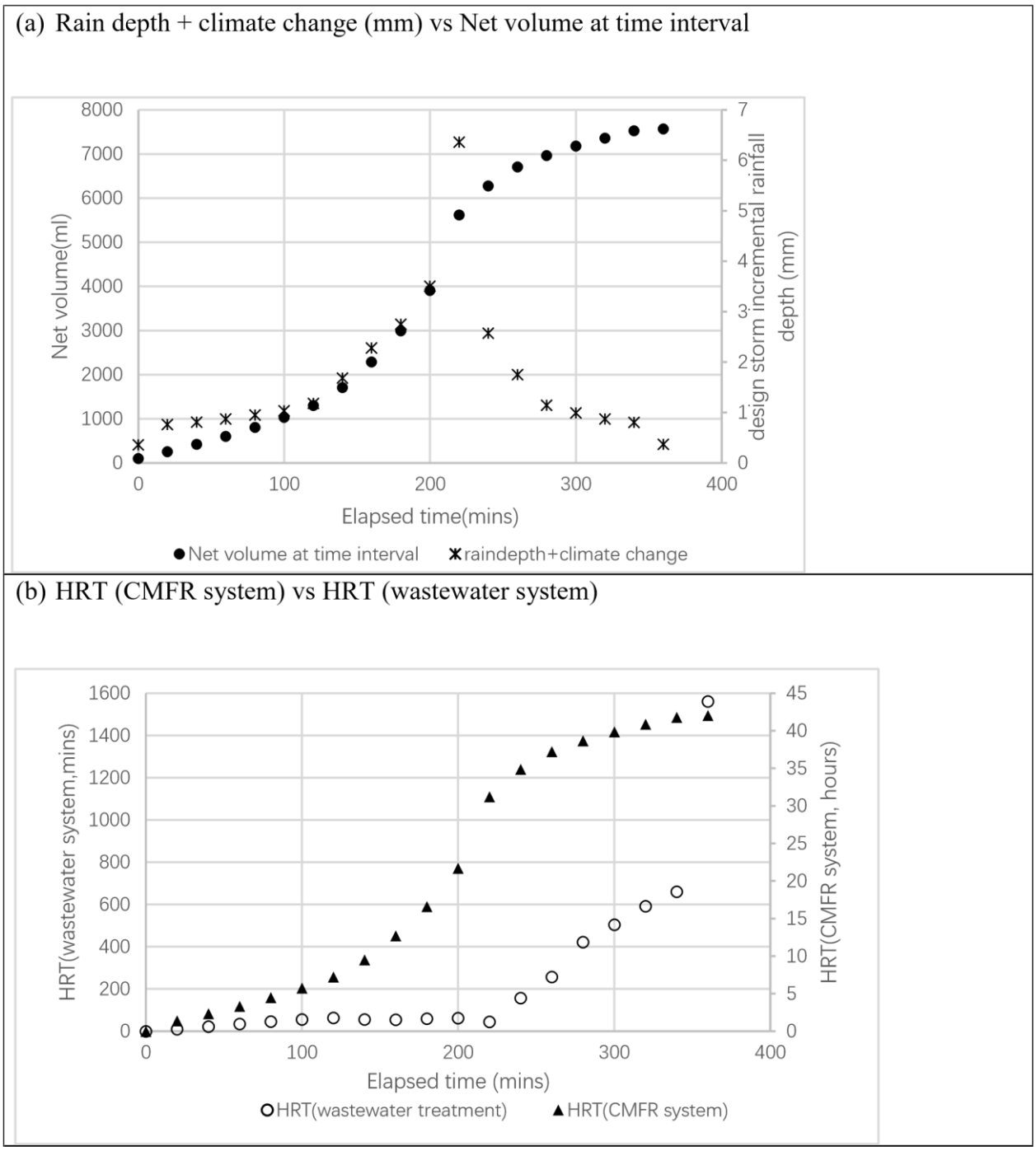


Figure 8 Design storm (inflow) and resulting HRT from mid-scale experiment

Table 2 Design storm (inflow) and resulting HRT data from mid-scale experiment

time	Elapsed Time (min)	inflow V(ml)	HRT wastewater treatment (hrs)	HRT in CMFR model (h)
0	0	100	0	0
20	20	212	0.156666667	1.40
40	40	226	0.371666667	2.32
60	60	242	0.575	3.33
1:20	80	265	0.755	4.47
1:40	100	287	0.935	5.73
2:00	120	329	1.045	7.23
2:20	140	468	0.926666667	9.49
2:40	160	635.5	0.896666667	12.69
3:00	180	766.5	0.993333333	16.62
3:20	200	975.5	1.021666667	21.70
3:40	220	1772.6	0.735	31.22
4:00	240	716	2.616666667	34.86
4:20	260	487.7	4.288333333	37.24
4:40	280	317.7	7.033333333	38.67
5:00	300	275.9	8.41	39.87
5:20	320	242.5	9.865	40.88
5:40	340	223	11	41.79
6:00	360	103	26.01	42.03

CHAPTER 5 ANALYSIS AND RESULTS

5.1 RESULT OF THE PRELIMINARY EXPERIMENT OF THE COCKTAIL SAMPLE

5.1.1 TOTAL IRON CONCENTRATION TENDENCY

There is a great reduction shown for total iron, with initial concentration of 5mg/L, but reducing to 0.15 - 0.3mg/L when exposure time is 24h, which is about 94% removal efficiency. However, an increase can be found obviously with a longer exposure time (ET showed in the figure later) after 24 hours, to over 1 mg/L when ET is 9 days. This could be the desorption of iron occurring over long time periods. The results are shown in the Figure 9, and Appendix 1 contains the colorimeter results through photographs of each test:

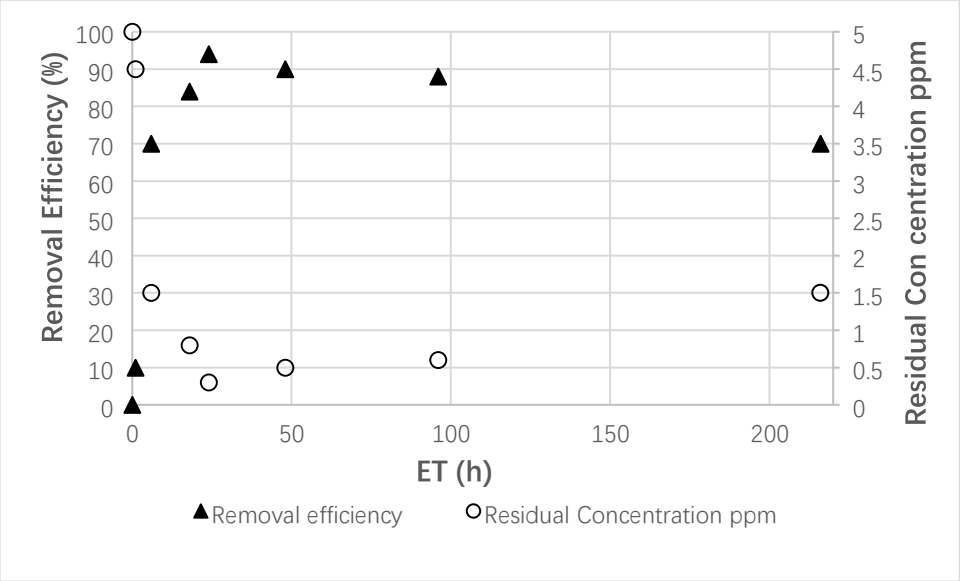


Figure 9 Removal of Iron (IC is 5mg/L) vs ET shown as a level of removal based on the colorimeter test

5.1.2 TOTAL AMMONIA CONCENTRATION TENDENCY

The initial concentration of ammonium is 5mg/L, but the strip showed that the concentration is between 0.5-1mg/L (Figure 10). Two possibilities are explained here for this condition: one is an operational mistake where the test strip didn't show the color clearly, and the other is that the ammonium reacted with the metals or H_2O in the sample water, thus reducing the concentration in the first place. Then an increase was found for ammonia concentration, reaching around 5mg/L

(should be the initial concentration) when ET is 6 hours; after that, a slight reduction was discovered when ET is between 18h and 96 h, while the concentration was reduced to almost 0 (0-0.25mg/L) when ET is 9 days.

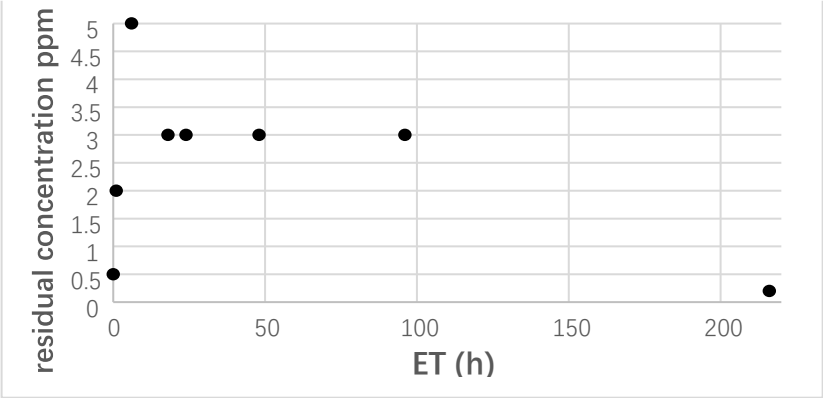


Figure 10 *Removal of total ammonia (IC of 5mg/L) vs ET shown as a level of removal based on the colorimeter test*

5.1.3 PHOSPHATE CONCENTRATION TENDENCY

There is no observed difference in concentration no matter the ET. Oyster shells do not seem to be effective in removing phosphate, or this result could also possible to be due to competition.

5.1.4 COPPER CONCENTRATION TENDENCY

The concentration of copper was 2.325 mg/L firstly. The reduction was slight but can be observed: when ET is between 0 and 24 hours, the concentration was almost the same, but when ET is longer than 48 hours, the color was slightly red, thus indicating a measure close to 1 mg/L (Figure 11).

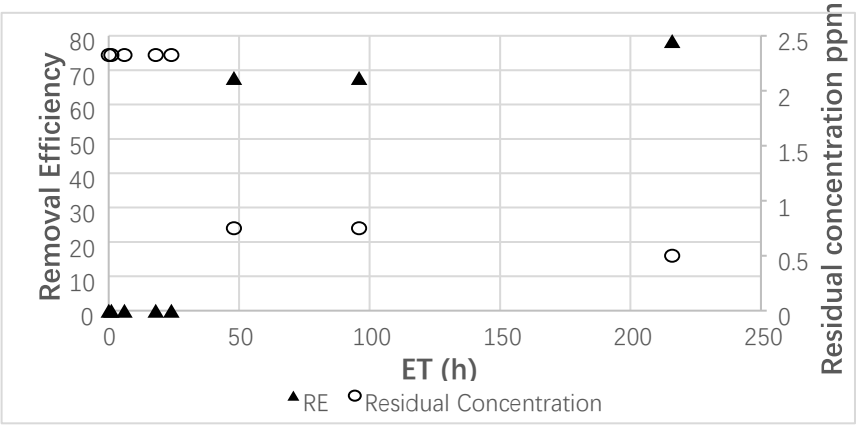


Figure 11 Removal of total ammonia (IC is 5mg/L) vs ET shown as a level of removal based on the colorimeter test

5.1.5 NITRATE CONCENTRATION TENDENCY

The sample water only has nitrate nitrogen, which was 24.1 mg/L initially and the strip showed a lower initial concentration. There is no large difference for nitrate nitrogen no matter the ET; however, it is worth mentioning that for ET between 0h and 48h, there is no nitrite in the water but after 96 hours, there was an appearance of nitrite in the water, which increased when ET increased (to almost 1mg/L when ET was 9 days).

5.1.6 ZINC CONCENTRATION TENDENCY

The sample solution should have 10 mg/L initial concentration of zinc. A color change from dark to light can be observed for zinc, which means the concentration was reduced, but it is hard to identify the range (see Appendix 1).

5.2 RESULT OF INDIVIDUAL EXPERIMENT

5.2.1 THE FIRST COPPER EXPERIMENT

In the first copper experiment, 16 beakers were used for the test. The temperature was monitored and varied between 15℃ and 20℃. Figure 12 depicts the average temperature over 7 days to show the tendency in temperature.

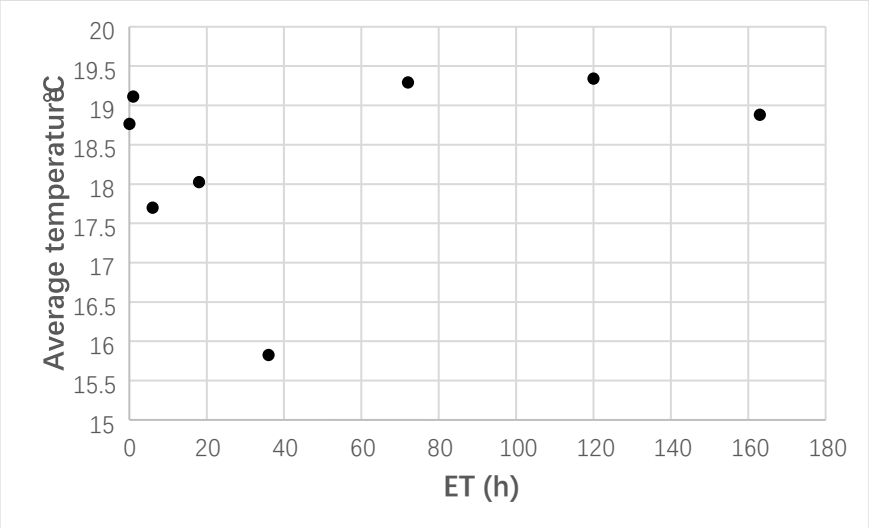


Figure 12 Average temperature tendency during 7 days for all beakers for copper

Two different methods were used to test the concentration of copper: test strips bought from HACH and the spectrophotometer. The strip results are shown in Appendix 3, and it was found that, when the initial concentration was between 0 and 1 mg/L, no clear color difference can be seen from the

strips, suggesting that the strip method is likely insufficient for low concentrations less than 1mg/L. However, when IC increased to 2.4 mg/L, the color difference is easy to differentiate, and a great reduction can be seen from the darkest color to less than 0.5 mg/L.

At the same time, concentration was also tested with the spectrophotometer. The initial concentration tested with machine showed 0.65mg/L, 0.71mg/L and 2.4 mg/L. The blank group with distilled water (DW) did not show any absorption or desorption. In this experiment, an obvious relationship was not observed between SA and RE at different initial concentrations (Figure 13). RE was calculated as:

$$RE = \frac{C(t)-C_o}{C_o} \times 100\% \qquad (7)$$

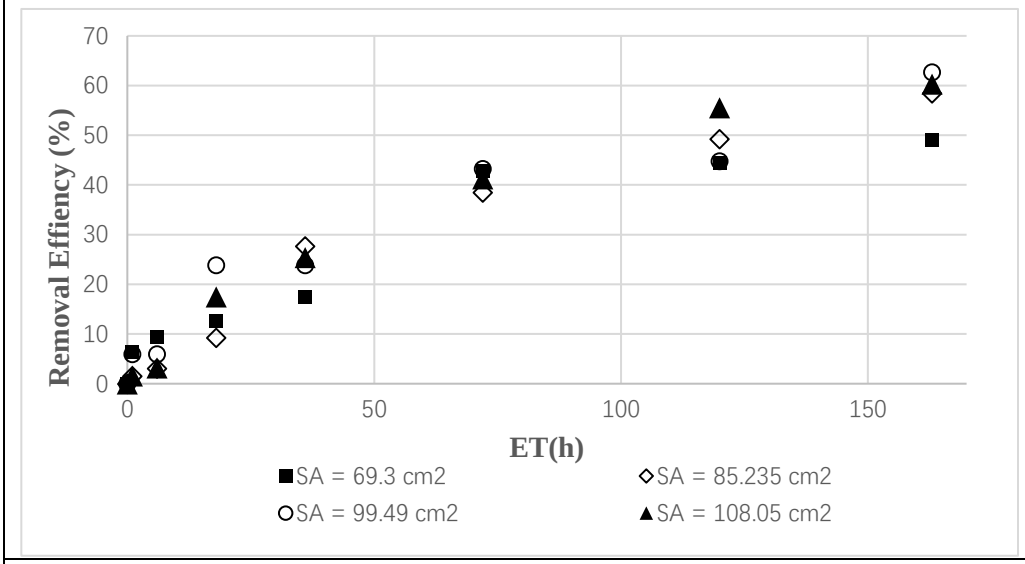
Residual concentration was reduced with increasing exposure time while RE increased for all surface area shells. When IC is 0.65 mg/L, RE is 49% with the smallest SA (69.3 cm^2) and 58% with 85.2 cm^2 and increased to 63% when SA increased to 99.5 cm^2. Until now, a positive relationship can be seen, but when SA is a maximum 108 cm^2, the RE reduced to 60.3%. Similar trends occurred for IC of 0.71 ppm, while RE peaked at SA of 99.5 cm^2 (59%). Additionally, when IC is up to 2.4mg/L, a rise of RE was seen over 80% at 7 days, while the relationship between RE and initial concentration of 0.63 ppm and 0.71 ppm was not clear, and this is probably due to small difference in IC.

pH has showed some interesting phenomenon (Figure 14). pH increased dramatically after placing the shell inside the beaker due to the alkalinity of calcium carbonate, peaking at 8.5 for IC of 0.65 and 0.71ppm at three days, and then reducing slowly to 8.3 when ET is 7days. For highest concentration solution, the point of a pH drop was delayed from occurring until after five days. The reason for the initial increase is the release of carbonate which is alkaline; also absorbing acidic metal ions can take up pH. The final slow reduction is probably due to the re-binding of Ca^{2+} and CO_3^{2-}, and the binding of H^+ and CO_3^{2-} to create HCO^{3-}. All the solutions with shells tended to neutral pH finally.

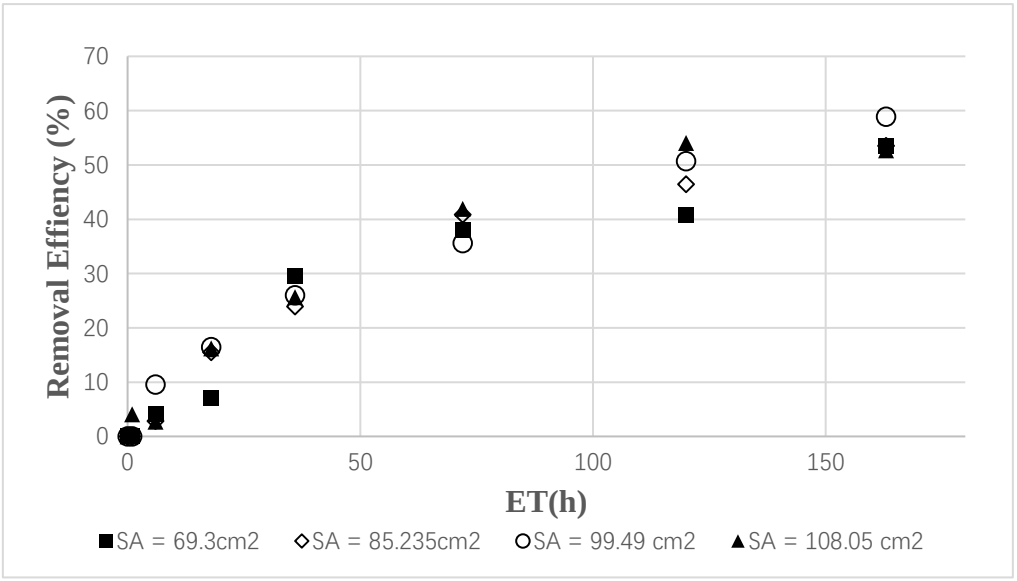
Electric conductivity is the measurement of a material's ability to transport electric charge, so it reflects the number of total ions in solution. For all beakers (Figure 15), EC showed an increasing

tendency with longer times. Although not a strong relationship between EC and SA was observed, the smallest shell always has the lowest EC whatever the IC is.

(a) Co = 0.65 ppm



(b) Co = 0.71 ppm



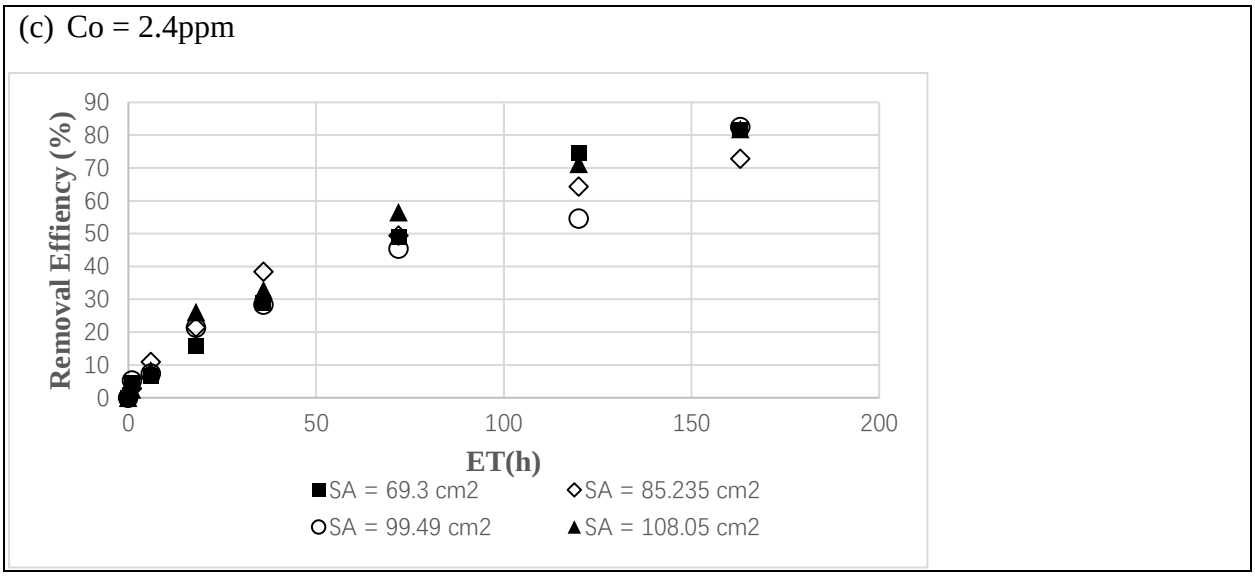
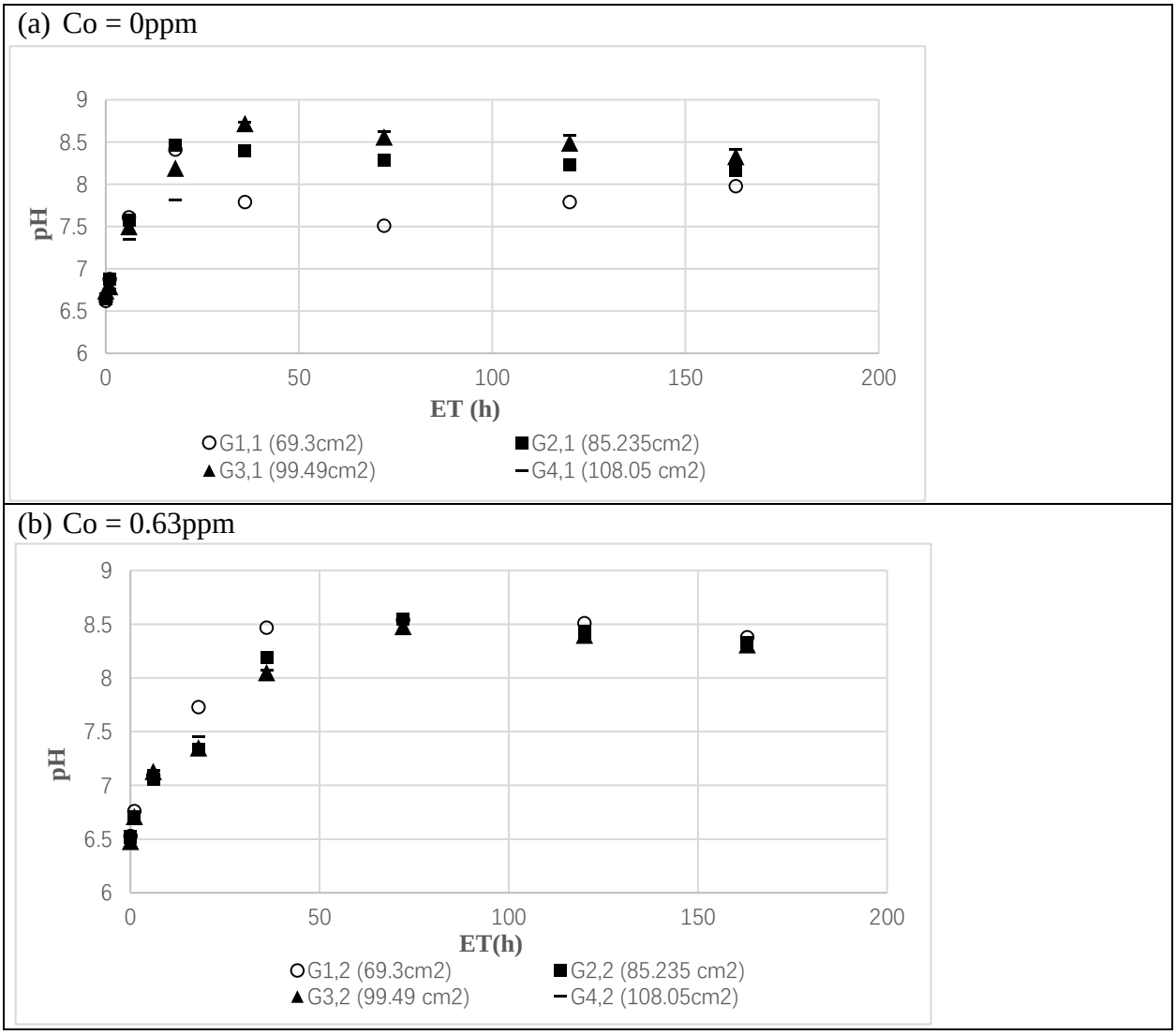


Figure 13 the relationship between RE and SA at different initial concentrations for copper



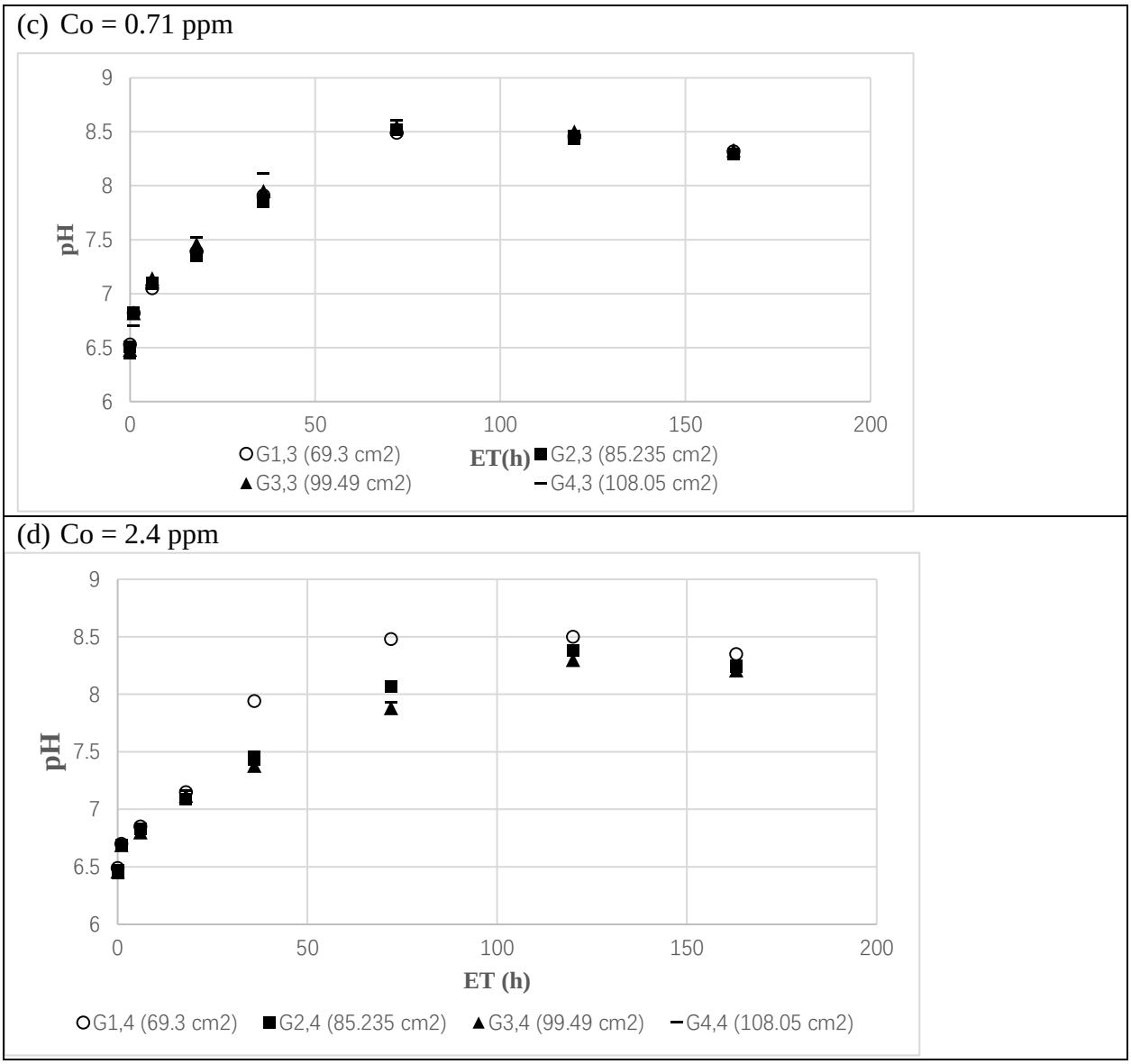
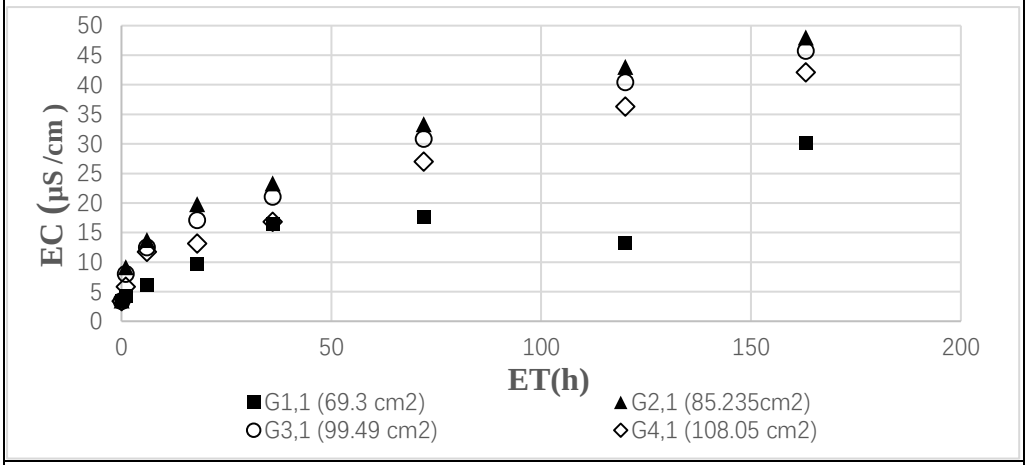
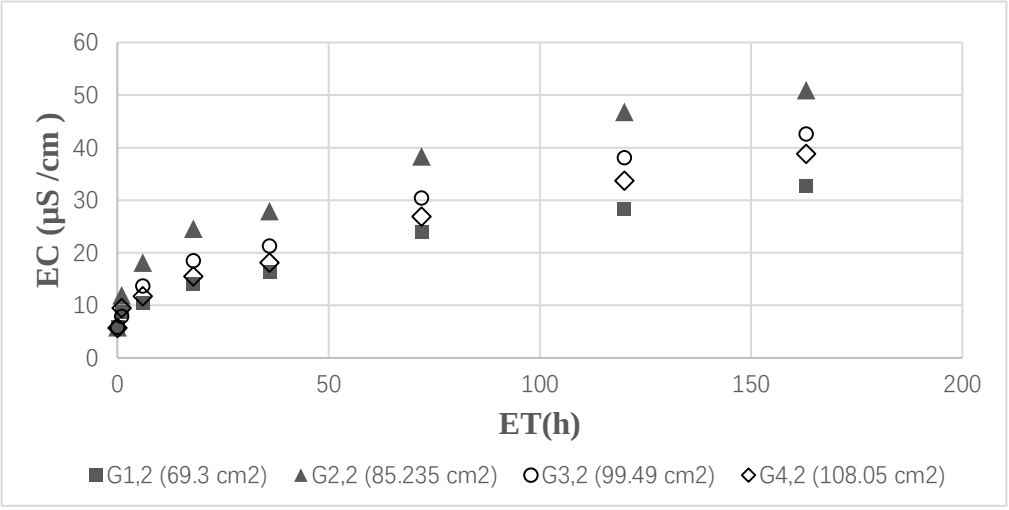


Figure 14 The relationship between PH and ET for different initial concentrations for copper

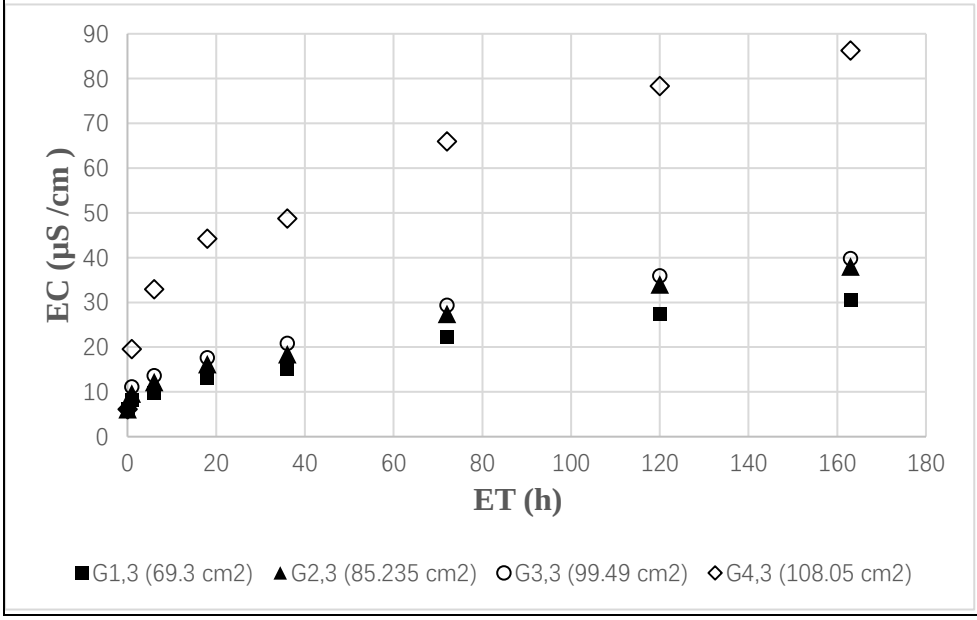
(a) Co = 0ppm



(b) Co = 0.63 ppm



(c) Co = 0.71ppm



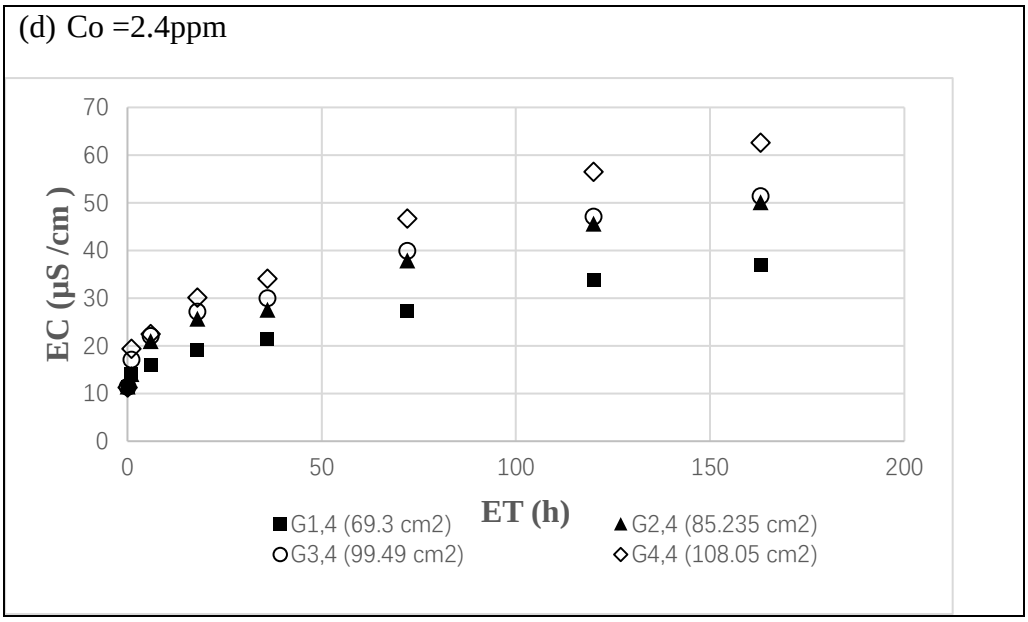


Figure 15 *The relationship between EC and ET for different initial concentration for copper*

5.2.2 THE SECOND SIX BEAKERS COPPER EXPERIMENT

This experiment only used 0.2 mg/L as initial concentration because it is the one closest to real stormwater concentrations. The temperature was monitored and ranged from 18℃ to 21℃ (see Figure 16).

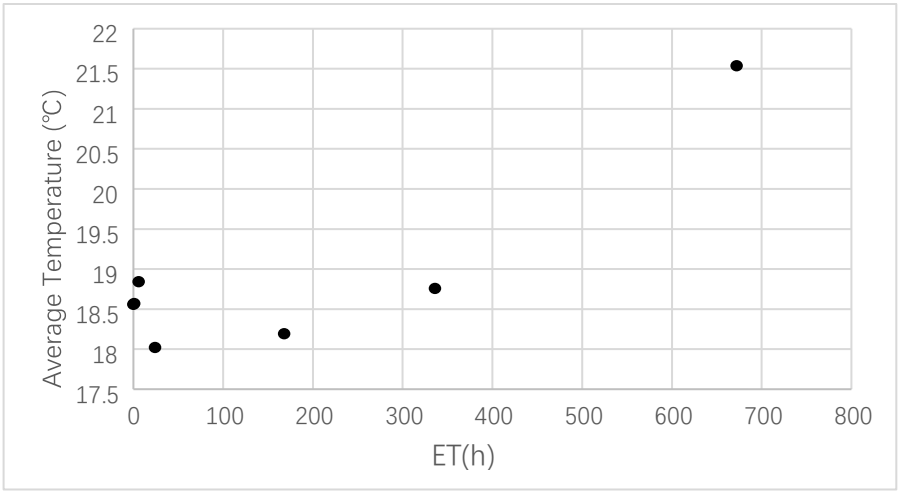


Figure 16 Temperature tendency for copper

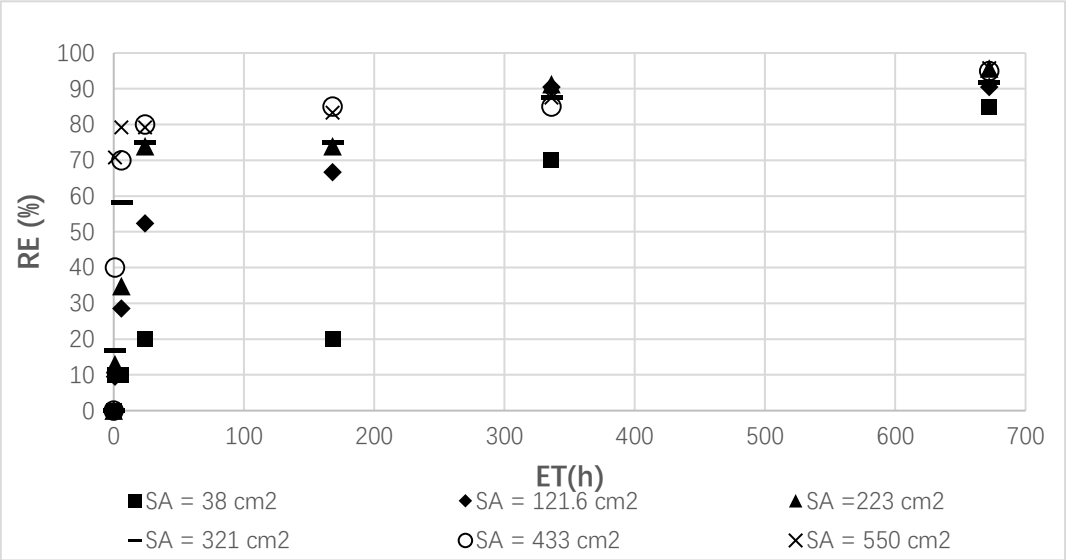
The relationship between RE and ET is clear to see from Figure 17 such that the beaker with the larger surface area reaches the same RE quicker than that with smaller SA values. As can be seen from Figure 17, shells with different surface areas can reach over 85% after 28d, however, when ET is 1 hour, the beaker with maximum SA 550 cm^2 already showed a removal efficiency of 70.8%,

but the shell with minimum SA 38 cm^2 only reduced 10% of metal ions in solution. However, overall, the first 24 hours for treating copper with shells is the rapid reaction period. Also, the removal rate of the smallest three surface areas show large differences, but when SA is between 223cm^2 and 550 cm^2, the difference in removal efficiency after 24 hours (1d) is quite small. It is suspected that for certain amounts of sample water, the effect of surface area is quite important when using certain surface areas of shells. However, when surface area is over a certain value, the difference in removal efficiency caused by SA is not very large and can be minimized by working on other parameters such as longer exposure time. The most reactive reaction time is in one day, and after that, SA over 223cm^2 showed a similar RE tendency.

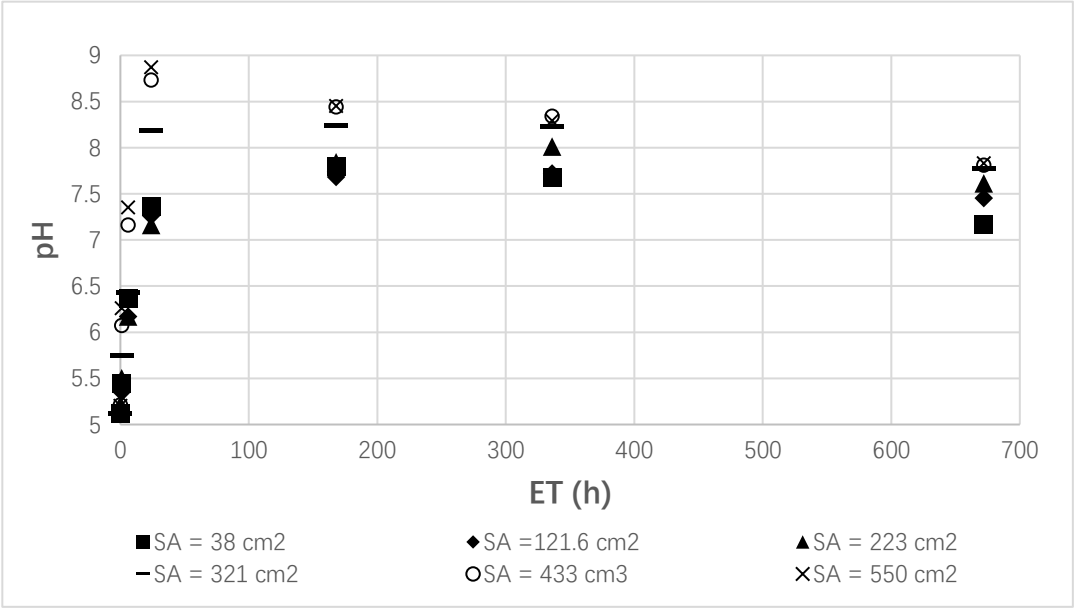
The increase of pH related to the surface area was also observed. The initial pH was all the same for the six solutions, but after putting shells into the beakers, pH increased significantly; the solution with more SA increased higher compared to lower SA at same ET. This phenomenon matches the concentration tendency; the pH fluctuation during the rapid reaction period was also dramatic. The bigger shell tended to release more carbonate which could take up pH. A reduction was observed as in the first copper experiment, such that after 24 hours, the reaction tended to be stable, so pH and RE showed a gentle curve. It was found that the solution with larger SA reached the peak pH quickly and dropped afterwards, while a longer time was taken for small shells to reach the high pH level. For solution treated with 550cm^2, pH peaked at 24 hours to almost 9 and then reduced to 7.8 after 28 days; while solutions with 38cm^2 shells had the highest pH at 7 days - 7.8 and dropping to 7.16 after 28d.

Electrical conductivity also rises with longer times, and they all show a strong positive relationship between EC and SA (Figure 17): larger SA shells have the possibility of greater release of calcium into the water which could raise EC, with the exception of SA of 321cm^2 and 433cm^2. The solution with 321cm^2 showed a higher EC than that with 433cm^2, which is probably because of the degree of abscission. During the experiment, we found that some particles of shells are fragile, and break off easily. For those shells, they will have a relatively higher RE, even compared to those shells with a bigger surface area.

(a) The relationship between RE and ET



(b) The relationship between PH and ET



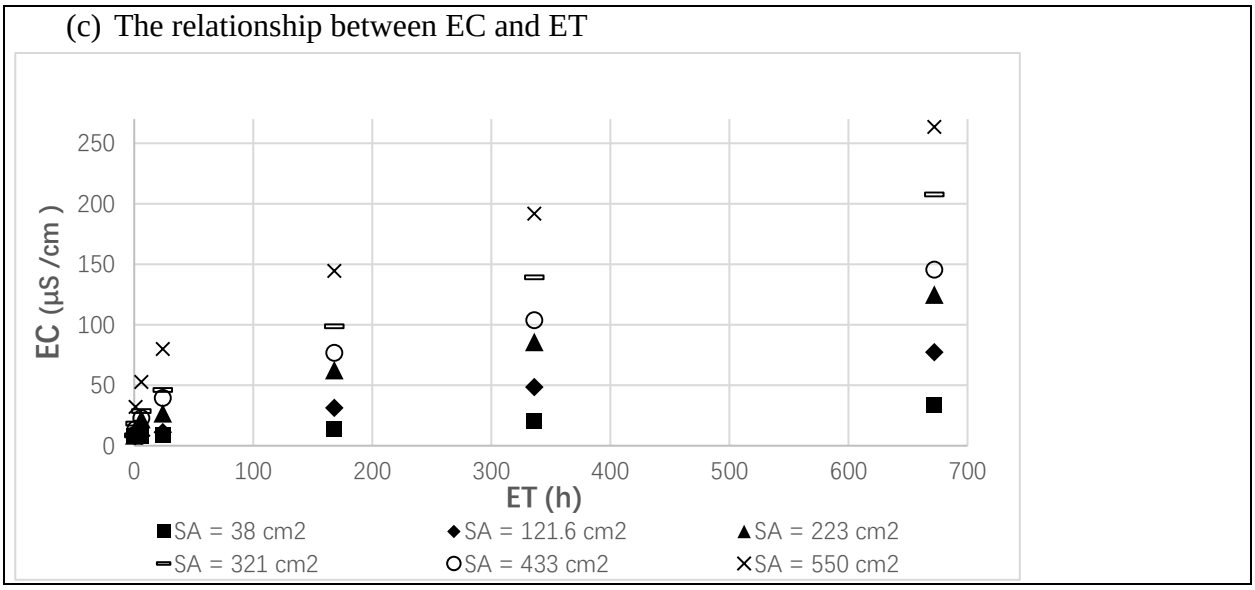


Figure 17 The relationship between RE, PH, EC and ET for copper

For modeling the adsorption kinetics (Figure 18), the data of 550cm^2 was chosen because it showed the best removal efficiency. C_0 is 0.24mg/L, $C(t)$ is the concentration at each tested time in hours. Therefore, the general model is:

$$C(t) = 2.4e^{-kt} \qquad (8)$$

The model was fitted with data in Matlab and the figure shown in Figure 18 has a k of 1.22 hrs^{-1}, and an adjusted R^2 of 0.79.

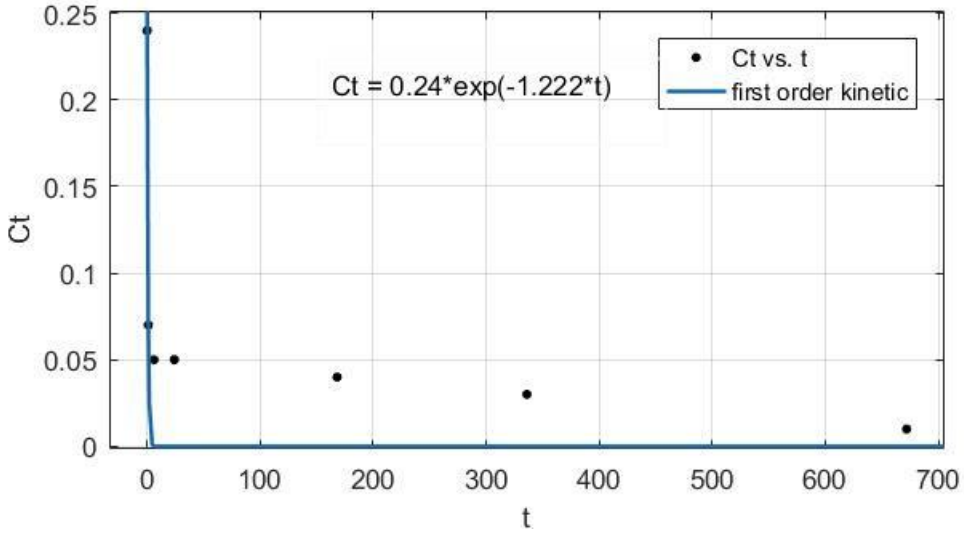


Figure 18 first order model of copper

5.2.3 ZINC EXPERIMENT RESULTS

The temperature varied from 18℃ to 23℃ (Figure 19). The average lowest initial concentration tested with the spectrophotometer for three beakers showed 0.3 ppm, followed with 0.6ppm and 1.07ppm. In Figure 20, the solid marker means removal efficiency, while the same open marker means corresponding residual concentration. The RE showed a positive relationship with SA. For the highest IC, the maximum SA shells reduced metals quicker than others and reach almost 90% after 7days, while 35cm^2 shells reached only 45.7% at the same time for the highest IC.

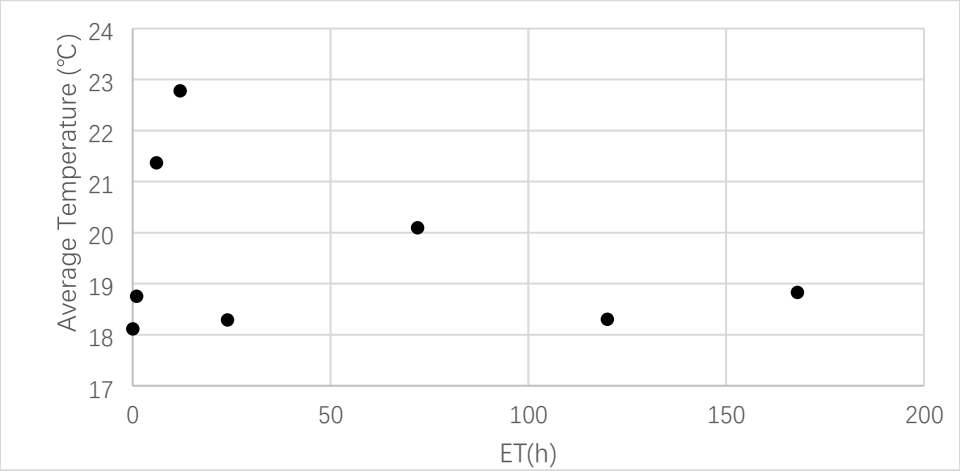
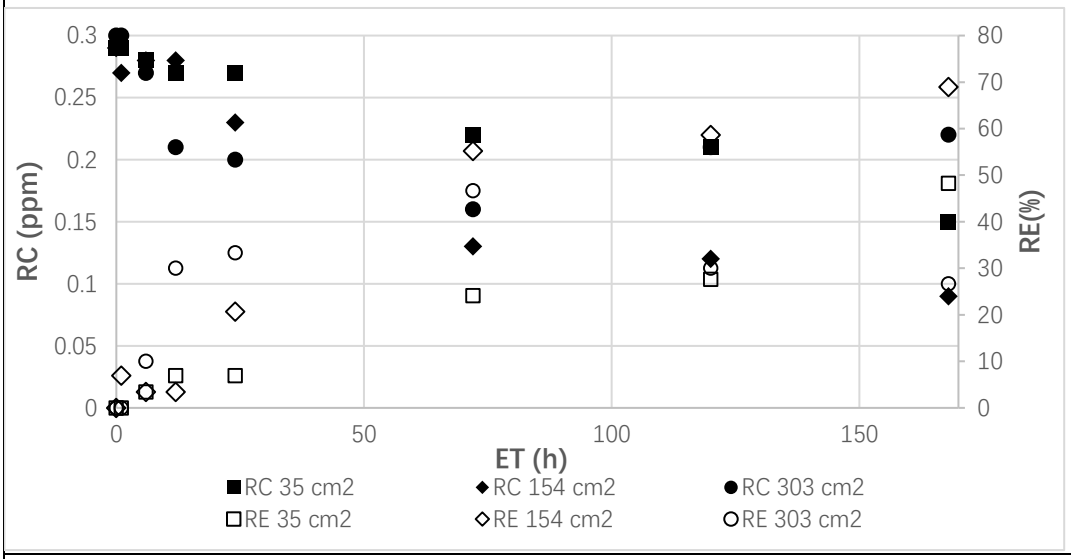


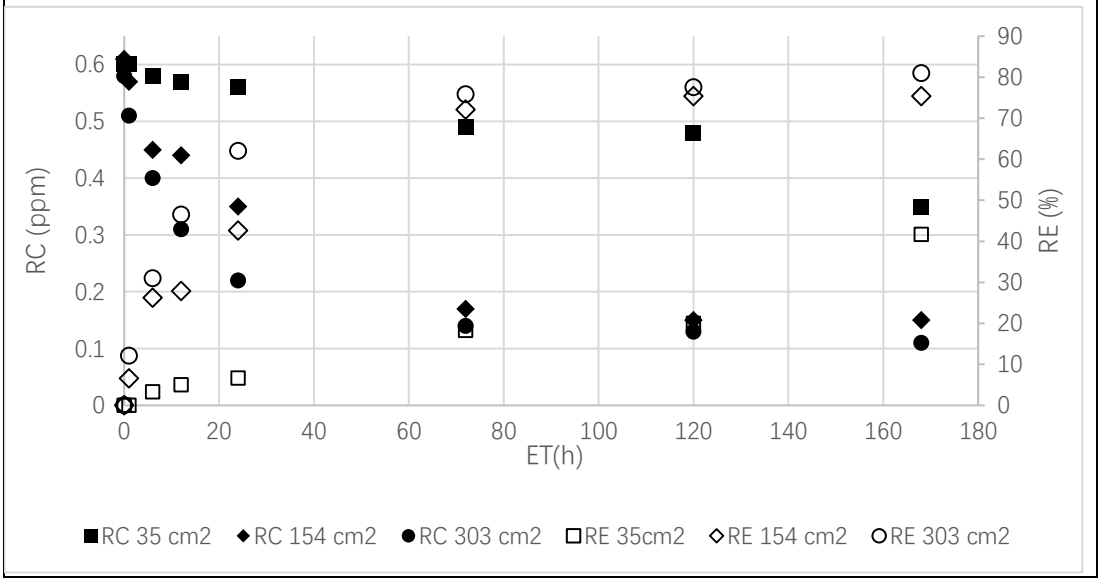
Figure 19 Temperature (℃) change for zinc

The absorption ability of the same amount of shells tended to have a higher removal efficiency with increase of initial concentration. For example, the shells of 154cm^2 showed 69%, 75.4% and 83.2% when IC is 0.3ppm, 0.6 and 1.07ppm, respectively. However, an interesting phenomenon was noticed when IC is 0.3ppm - the residual concentration of solution that was treated with 303cm^2 reduced to 0.16 ppm after three days, and then went back to 0.22 ppm. The relative RE reached 46.7% at three days and reduced to 26.7% finally (Figure 20). The reason is probably: 1) some of shells were used to treat zinc before and desorbed when in the alkaline environment; and 2) the personal difference in shells. Compared to copper, zinc has a much lower reaction rate, but the rapid reaction also occurred in the first 24 hours, especially for high IC solutions. Figure 21 showed how pH changed during the treatment time. Generally, solutions with the maximum size shells shows the biggest variation whatever the IC is, which means higher SA can speed up the reaction rate. This was also verified by the tendency of EC (Figure 22); the maximum amount of shells always had the highest EC. In the first few hours, the tendency of RC is hard to differentiate, which is probably because of product creation in that period.

(a) Co = 0.3ppm



(b) Co = 0.6 ppm



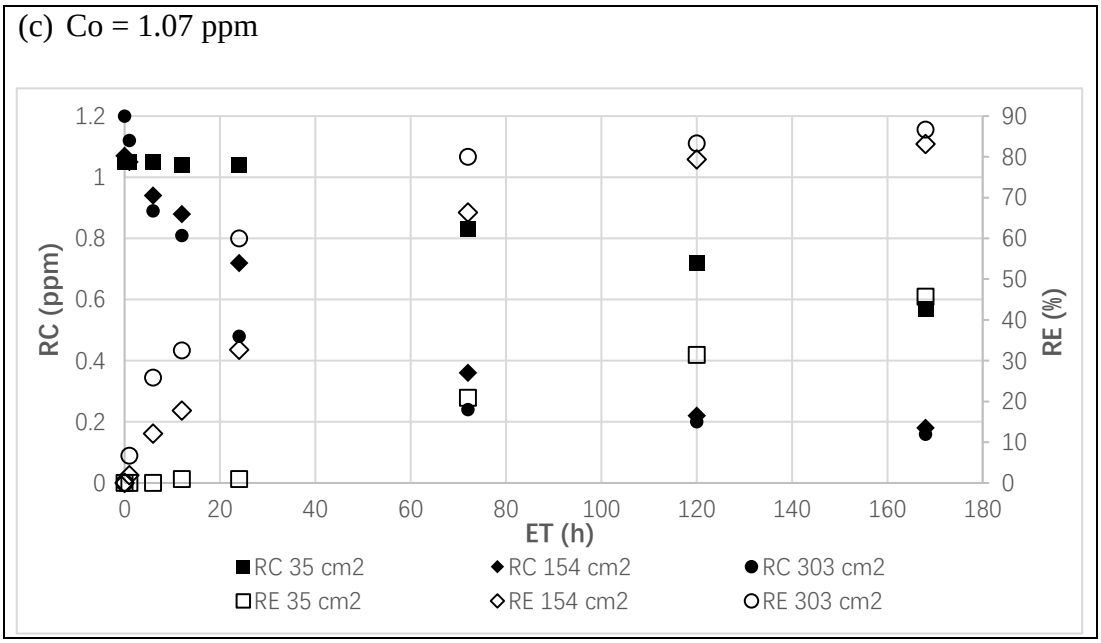
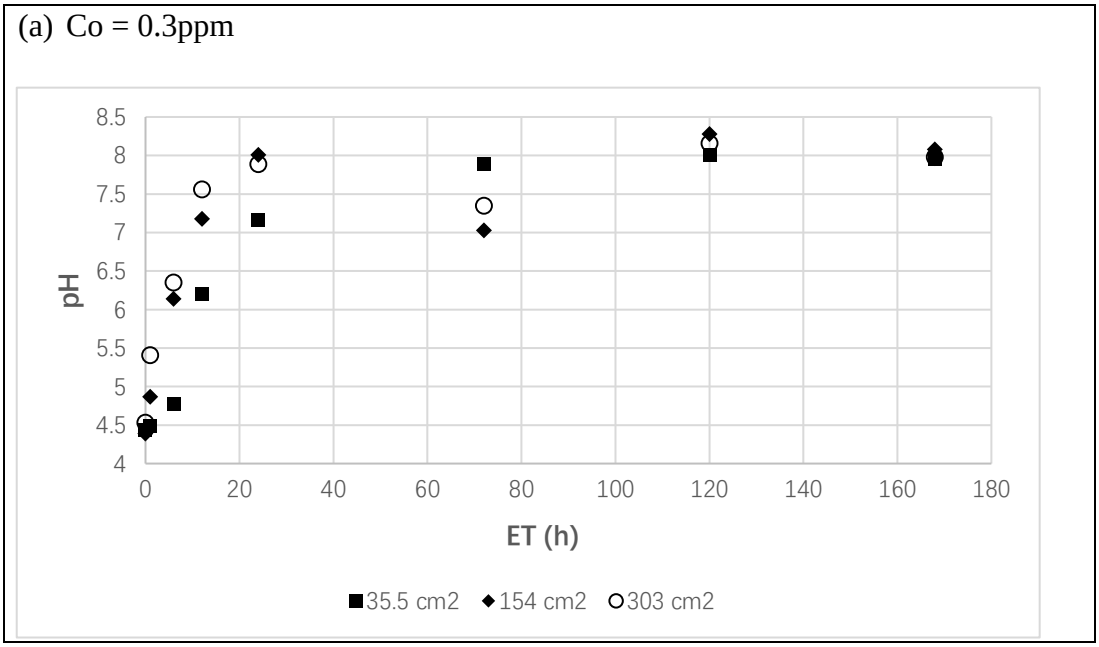
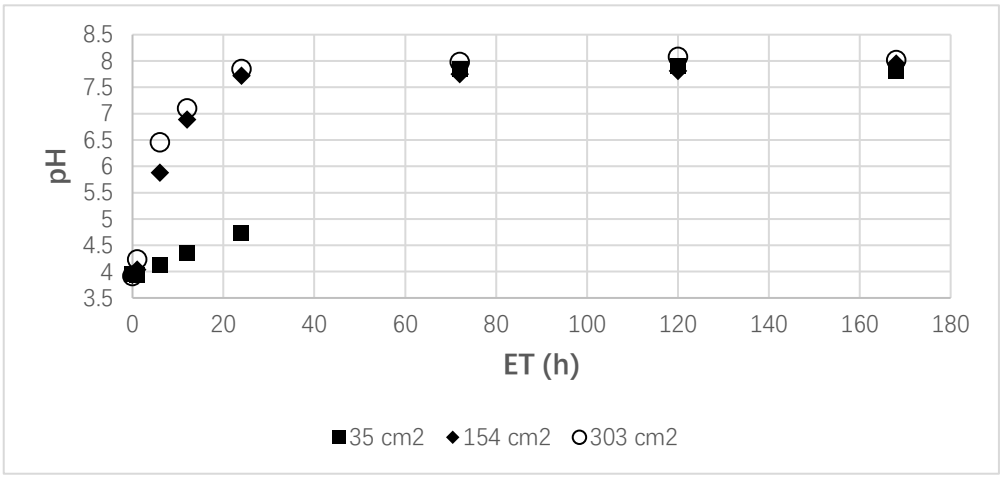


Figure 20 The relationship between RE, RC and ET for different initial concentrations for zinc



(b) Co = 0.6 ppm



(c) Co = 1.07 ppm

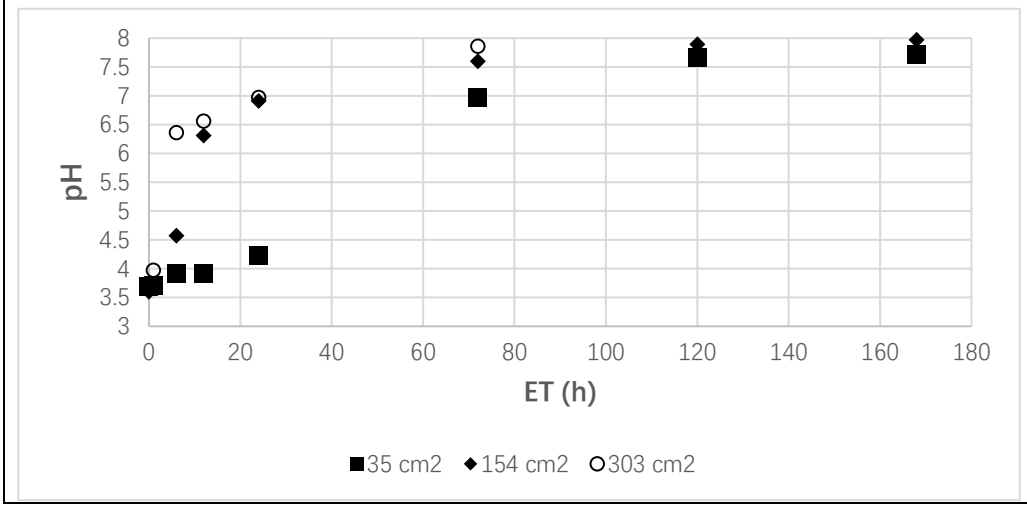


Figure 21 The relationship between pH and ET for different initial concentrations for zinc

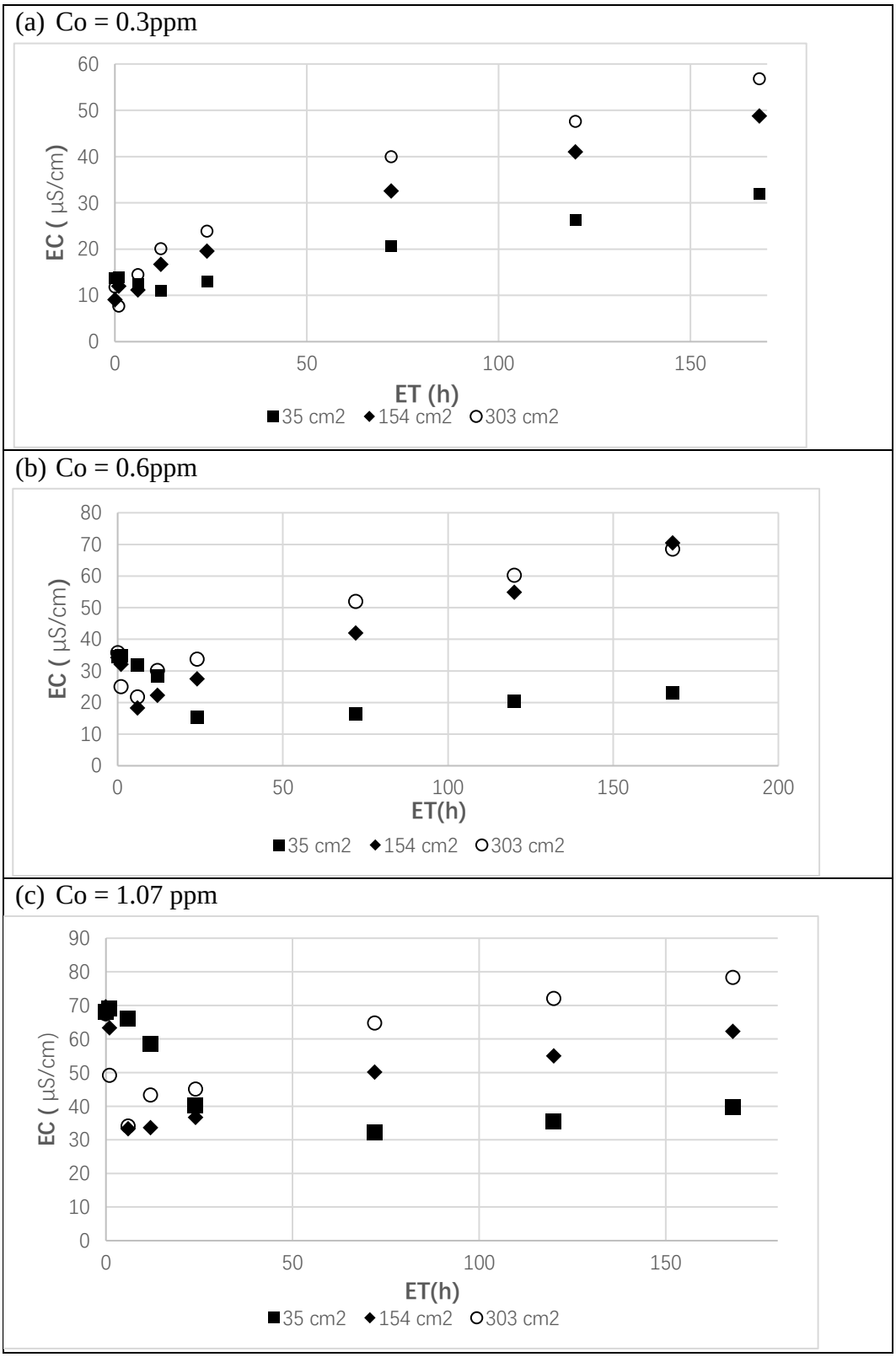
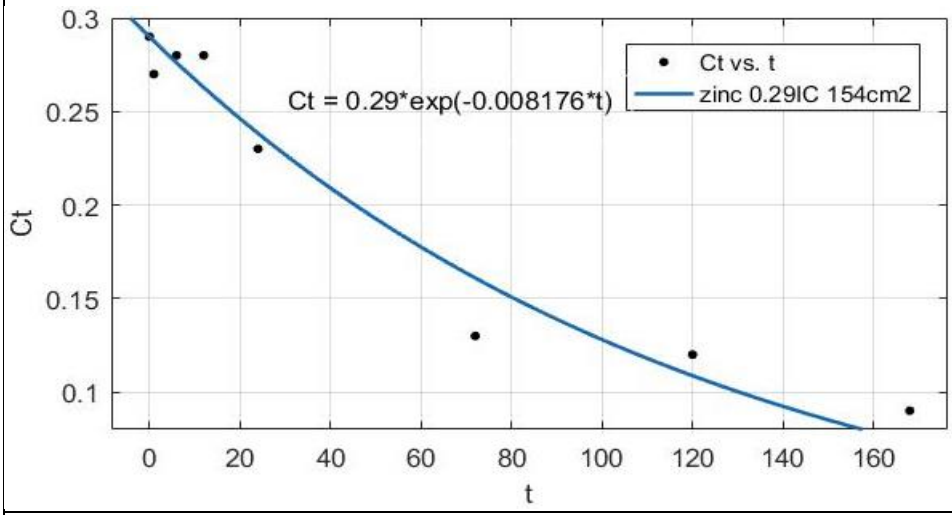


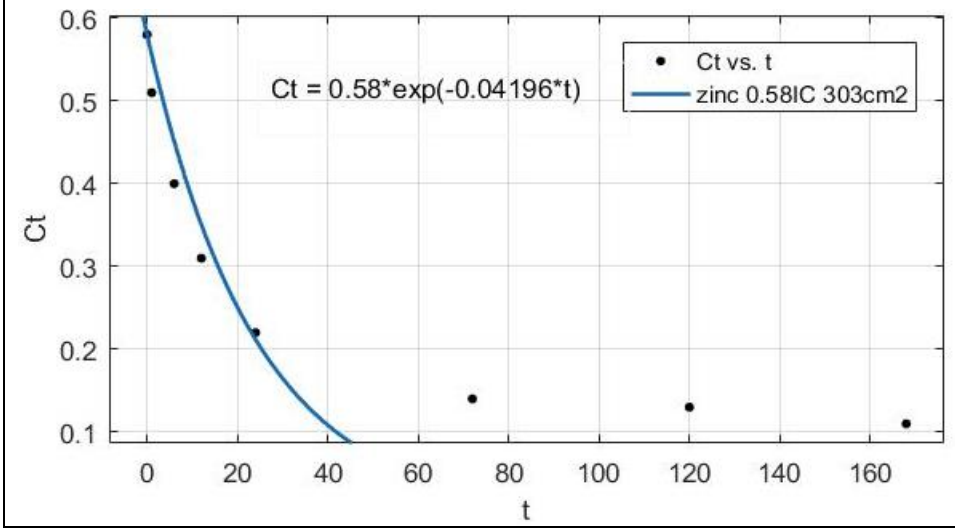
Figure 22 The relationship between EC and ET for different initial concentrations for zinc

The first order kinetics model was used for fitting three different initial concentrations (Figure 23). For every IC, the shells with the best removal efficiency were chosen to fit the model. The SA of 154cm^2 of shells showed the best RE of zinc, and so this treatment data is used to fit the model and had an initial concentration of 0.29 ppm. The data of 0.58 ppm IC and 1.2 ppm IC treated with 303cm^2 shells was used to fit the model. The results are shown in Figure 24. The lowest IC with 154cm^2 fit first order decay well with an adjusted R^2 of 0.96. The value of k is 0.0082hrs^{-1}. The 1.2ppm initial concentration also fitted by this model very well with an adjusted R^2 of 0.93, and the coefficient k is 0.032hrs^{-1}. The middle IC of 0.58 showed relatively worse fitting: adjusted R^2 is 0.8 and k is 0.042hrs^{-1}.

(a) 0.29ppm



(b) 0.58ppm



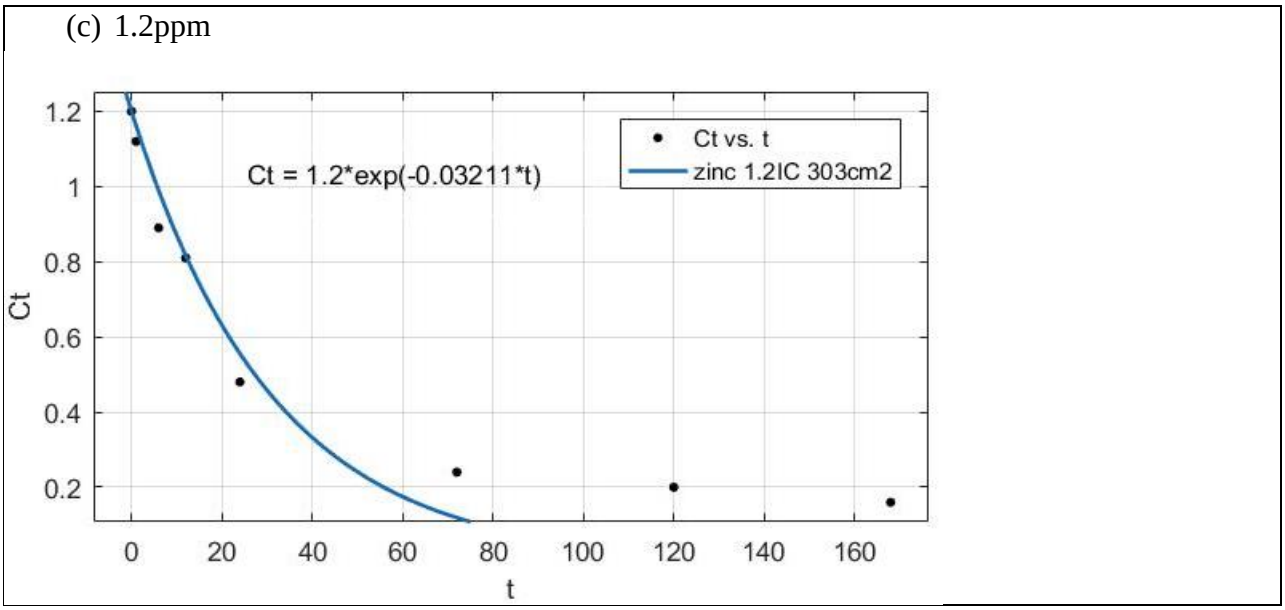


Figure 23 the first order model of zinc for different ICs

5.2.4 CADMIUM EXPERIMENT RESULTS

The temperature varied from 18 ℃ to 24℃ based on the monitoring data (Figure 24).

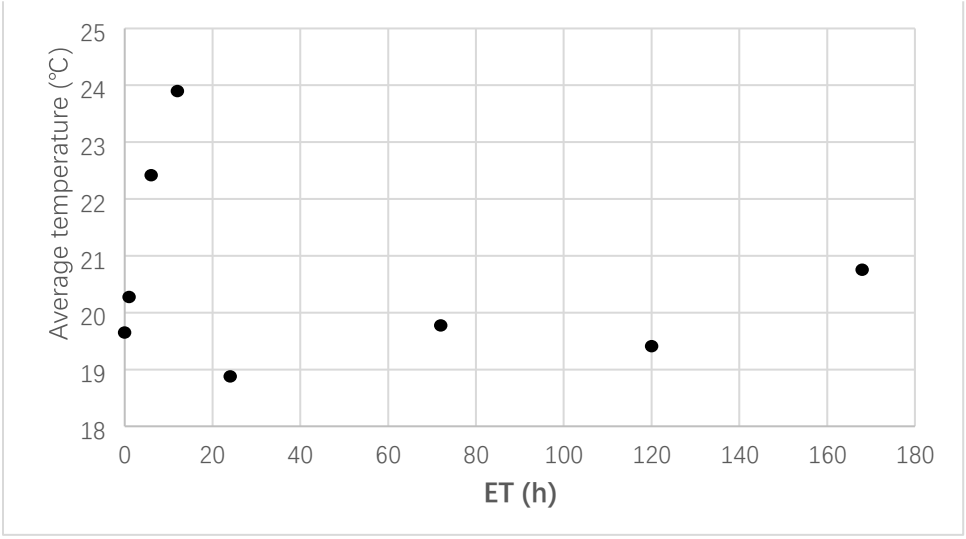
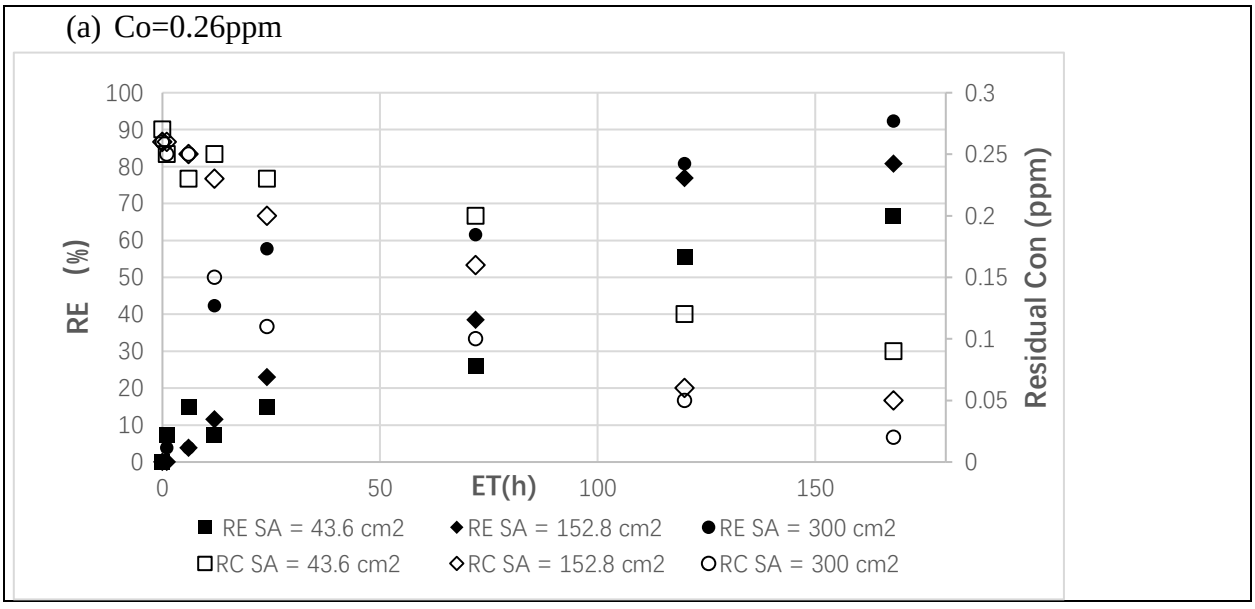


Figure 24 temperature change for cadmium

Figure 25 shows that in this case, the removal efficiency also showed a strong relationship with exposure time. At seven days, RE of shells from smallest SA to maximum SA was 66.7%, 81% and 92.3% for IC of 0.26ppm, 57%, 87.7% and 87.9 for IC of 0.58ppm, and 59.1%, 86.9% and 89.1% for IC of 0.95ppm. For cadmium, the effect of initial concentration did not seem to be important. When IC increased from 0.26ppm to 0.95ppm, removal efficiency of the maximum shells reached 92.3%, 87.9%, and 89%, respectively. There is not a big difference of removal

efficiency for different initial concentrations. Moreover, the difference in the two bigger SAs on removal efficiency is small for longer contact time. For example, when IC is 0.58ppm and 0.95ppm, RE of 152.8 cm^2 and 300 cm^2, respectively was almost the same after seven days. However, considering the effectiveness, the maximum amount of shells will react with metal ions faster over the same time. The removal efficiency of 300cm^2 treating solution with IC of 0.26ppm was over 50% in one day, while that of 152.8 cm^2 only reached 23%. According to pH, the reaction was active in the first day, with a pH ranging from 5.7 to almost 9, with an average removal of around 60% for all initial concentrations. pH for all solutions were fixed around 8 after 7days, compared to 5.7 initially and has the tendency to go lower with longer time, but this needs to be verified in later research (Figure 26). Electric conductivity data were in close proximity for bigger SA of shells, even with a difference of 150cm^2. Compared to the difference between 152cm^2 and 43.6cm^2 (108.4cm^2), the EC was 63.5 µS/cm and 17.4 µS /cm separately for highest IC after 7 days (46.1 difference), while EC of 300 was 74 µS /cm (Figure 27). This implies that although a positive relationship between SA and RE exists, it does not suggest that having more shells is necessarily better. Over a certain amount of shells, the difference in SA may be negligible, which also matches the result of the copper experiment.



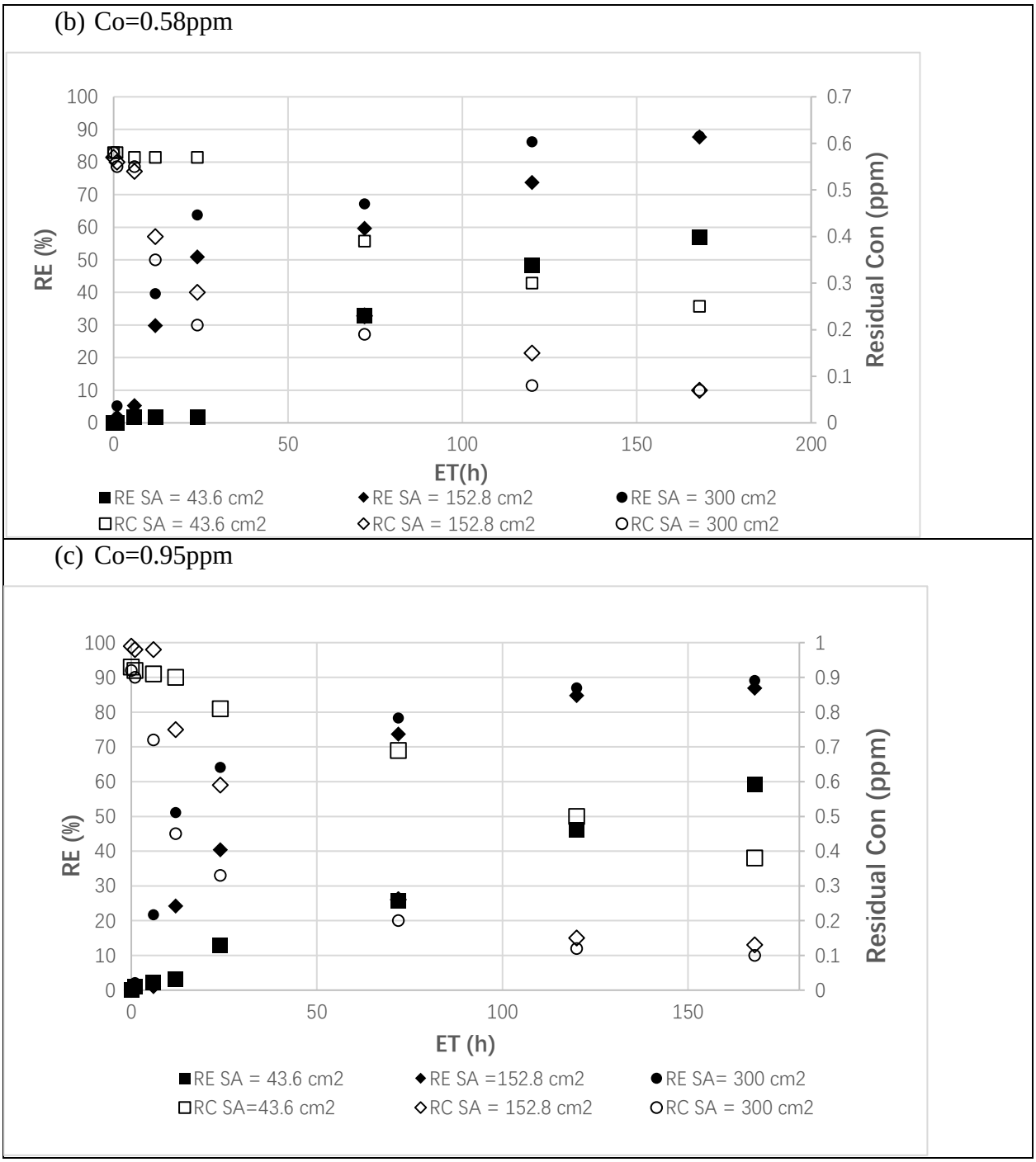


Figure 25 The relationship between RE, RC and ET for different concentrations for cadmium

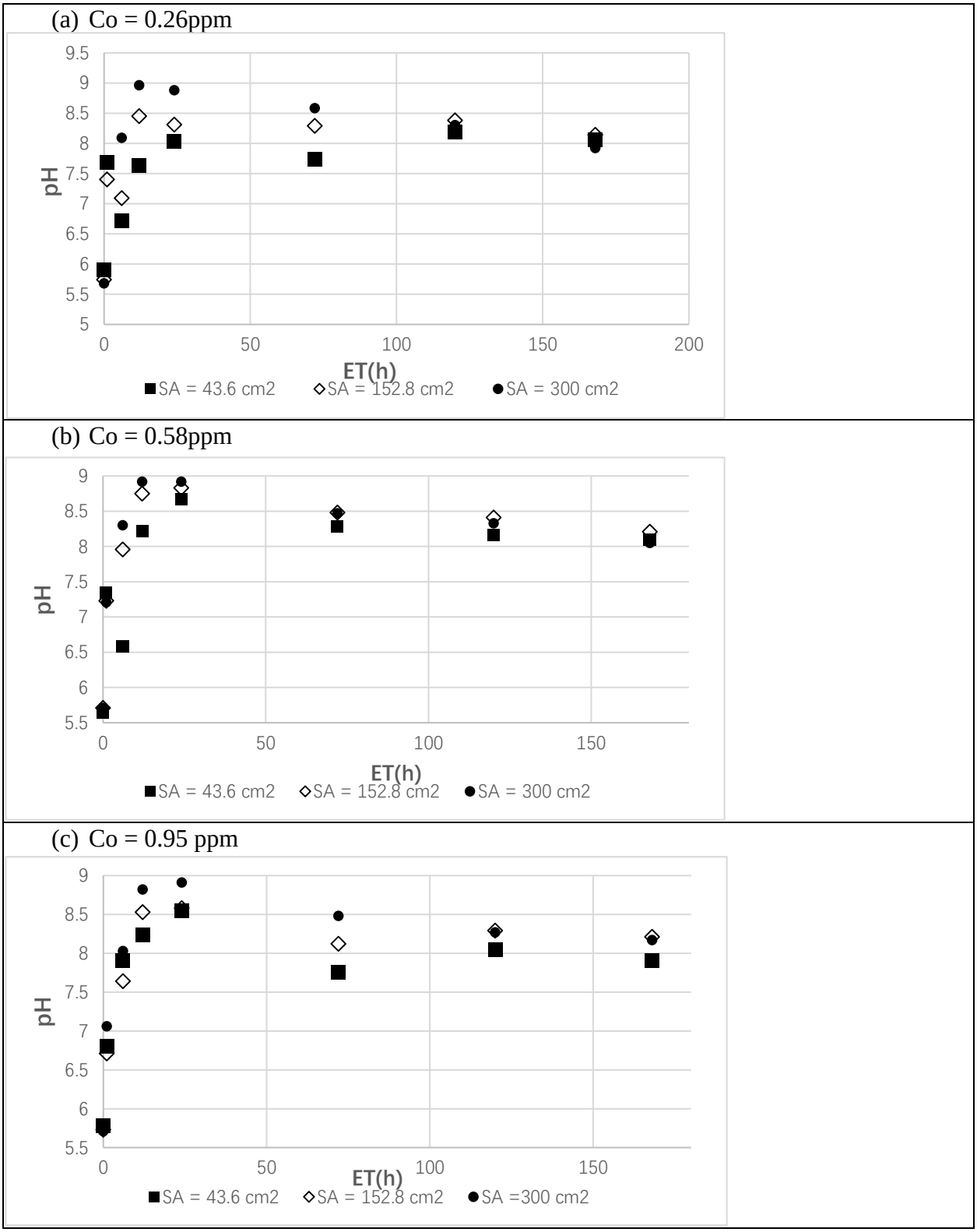
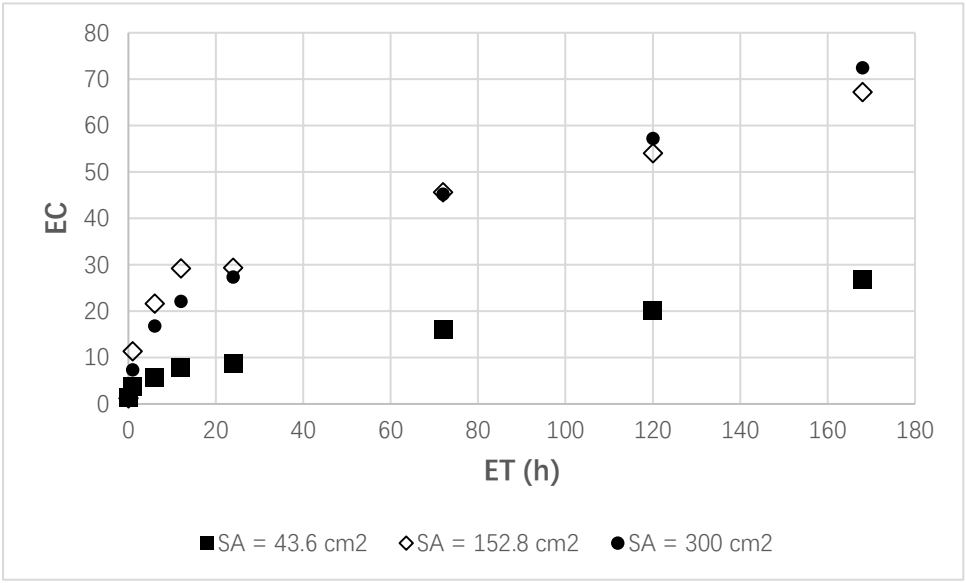
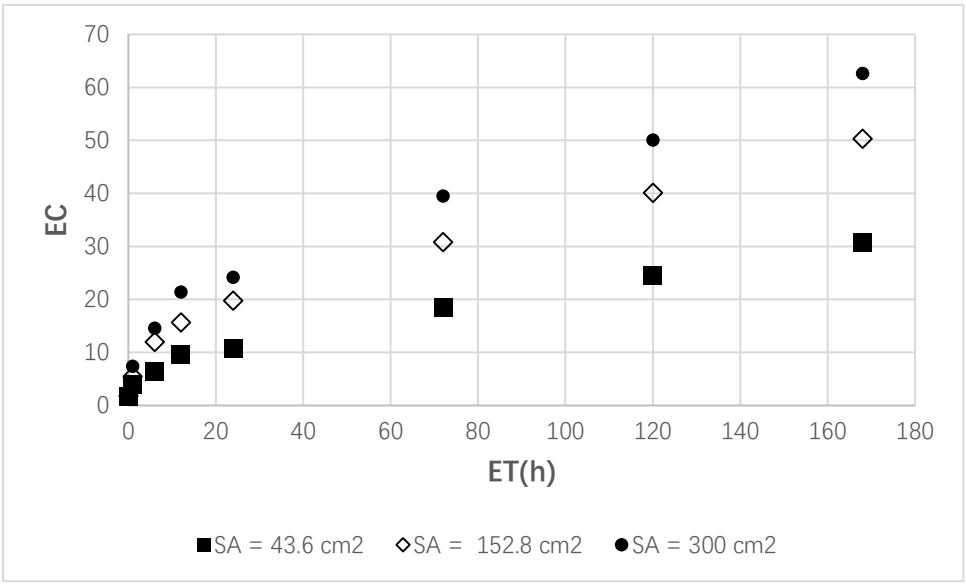


Figure 26 The relationship between PH and ET for different initial concentration for cadmium

(a) Co = 0.26 ppm



(b) Co = 0.58 ppm



(c) Co = 0.95 ppm

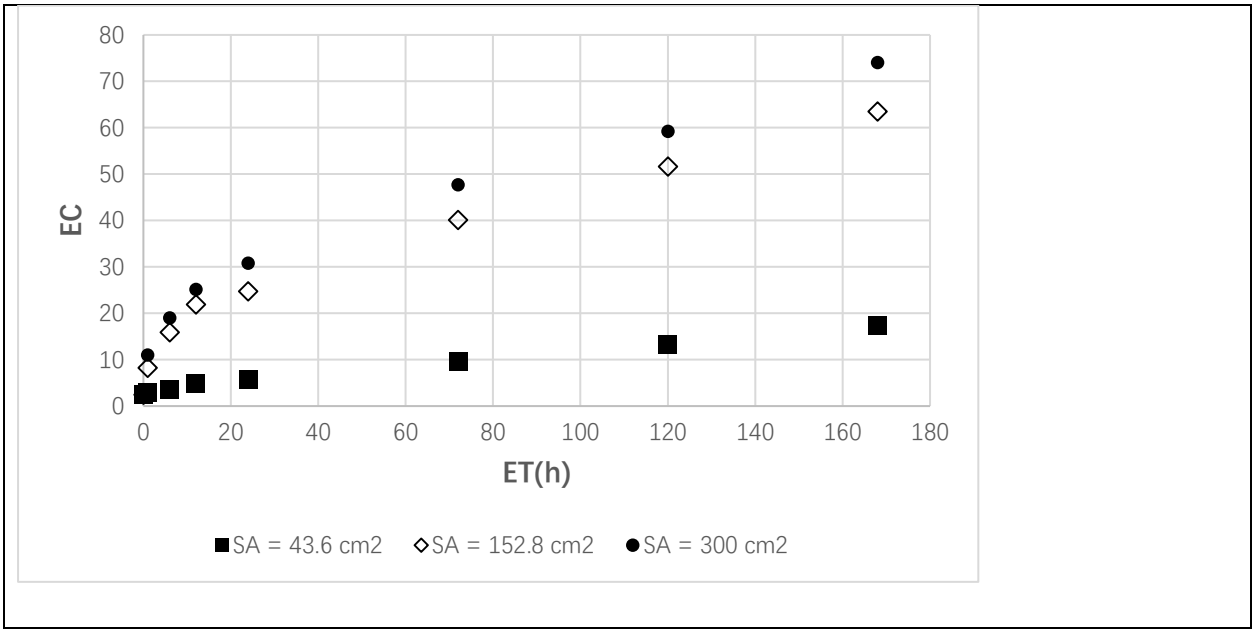
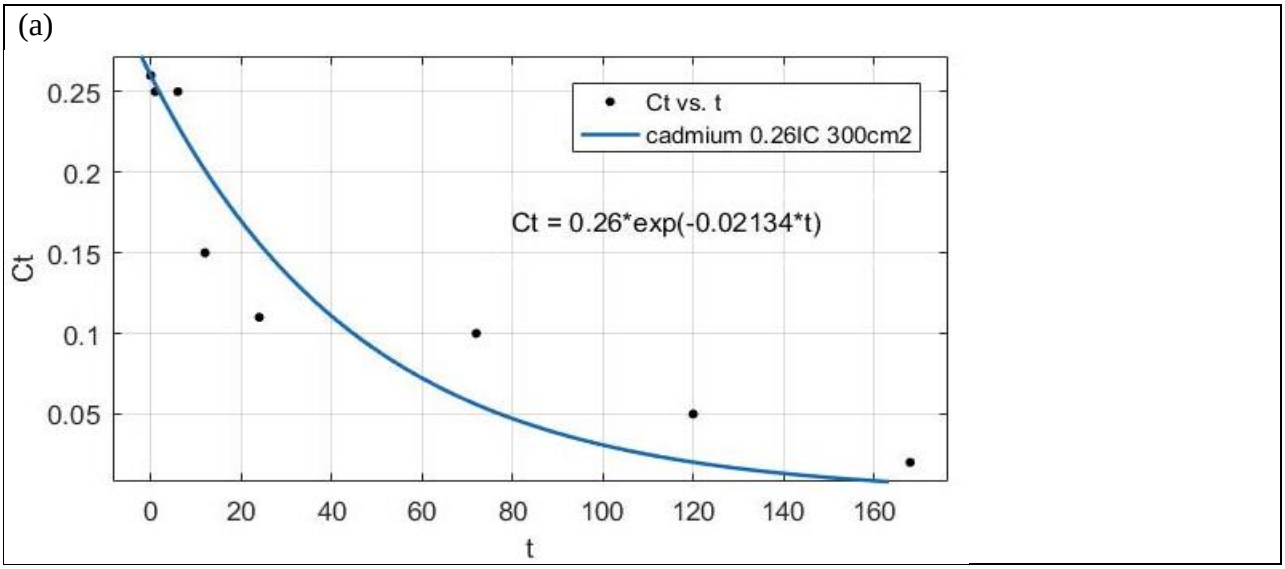


Figure 27 The relationship between EC and ET for different initial concentrations for cadmium

Cadmium data showed the maximum shells of 300 cm^2 had the best removal efficiency considering treated time (Figure 28). Therefore, data of 300 cm^2 shells treating every initial concentration solution was used for fitting. All of them showed a strong fitting with first order kinetics, adjusted R^2 of IC from low to high was 0.87, 0.89, and 0.93, respectively. From this data, it looks like the higher IC had better fitting with first order decay. The results shown below, and the corresponding *k* with 95% confidence bounds are 0.021hrs^{-1} (0.0093, 0.033), 0.027hrs^{-1} (0.012, 0.042) and 0.043hrs^{-1} (0.024, 0.062), respectively.



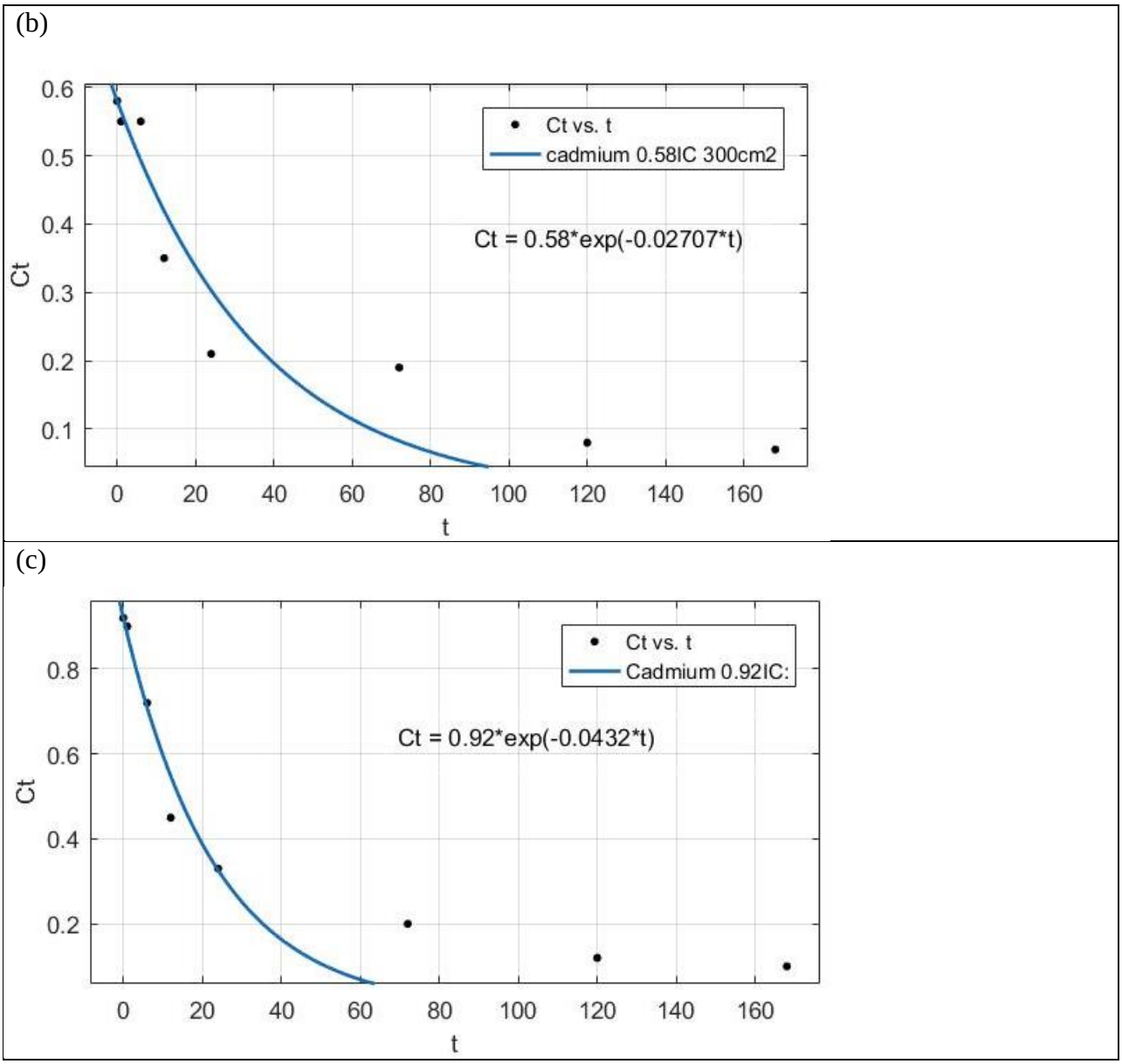


Figure 28 The first order model of cadmium for different ICs

5.2.5 CHROMIUM EXPERIMENT RESULTS

The temperature ranged from 18.5 ℃ to 24.5 ℃ (Figure 29). Hexavalent chromium showed a much lower efficiency compared to other metals which is most likely because of the ion radius difference as seen in Figure 30. While the maximum shells did achieve the highest removal efficiency, for hexavalent chromium, the effect of SA is not that obvious in higher IC solutions. For the solution with IC of 0.5ppm, shells with different SA showed similar absorption ability, reducing chromium to 0.33mg/L, 0.3 mg/L and 0.32mg/L after 7 days; the corresponding removal

efficiency was around 36%. For solution with IC of 1ppm, the shells reduced the concentration to 0.78mg/L, 0.75mg/L and 0.71mg/L, respectively, with SA level.

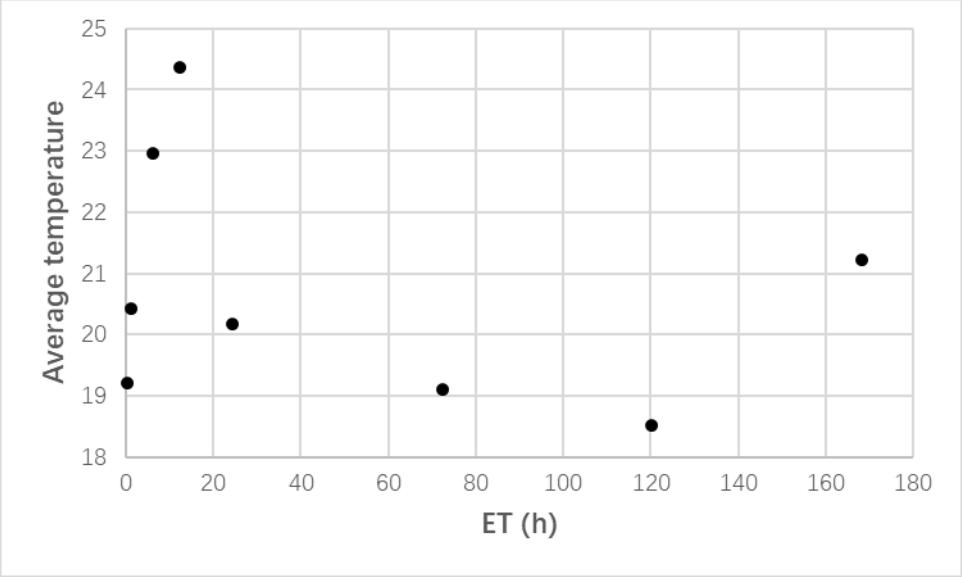
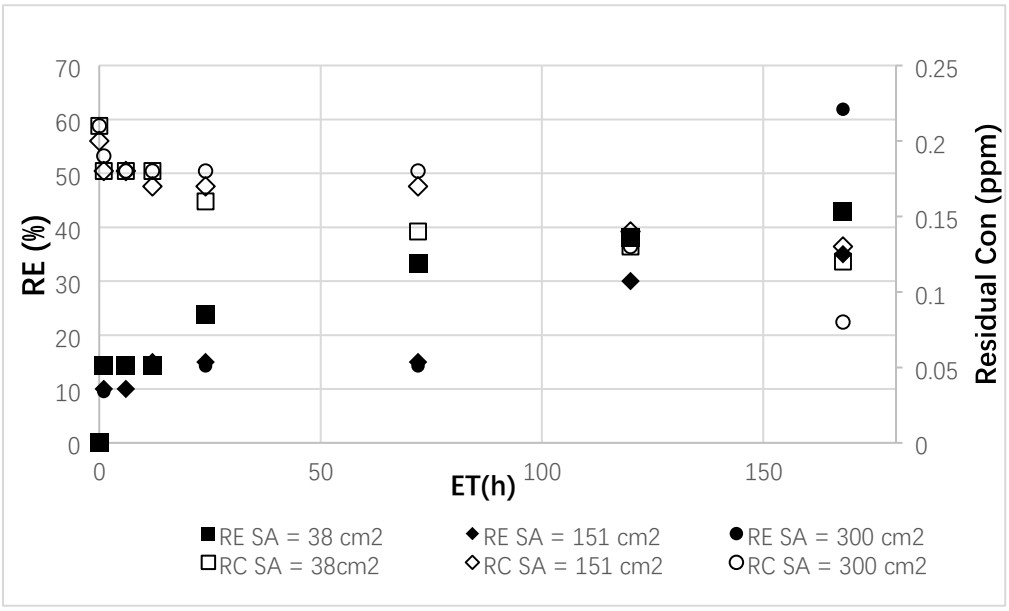


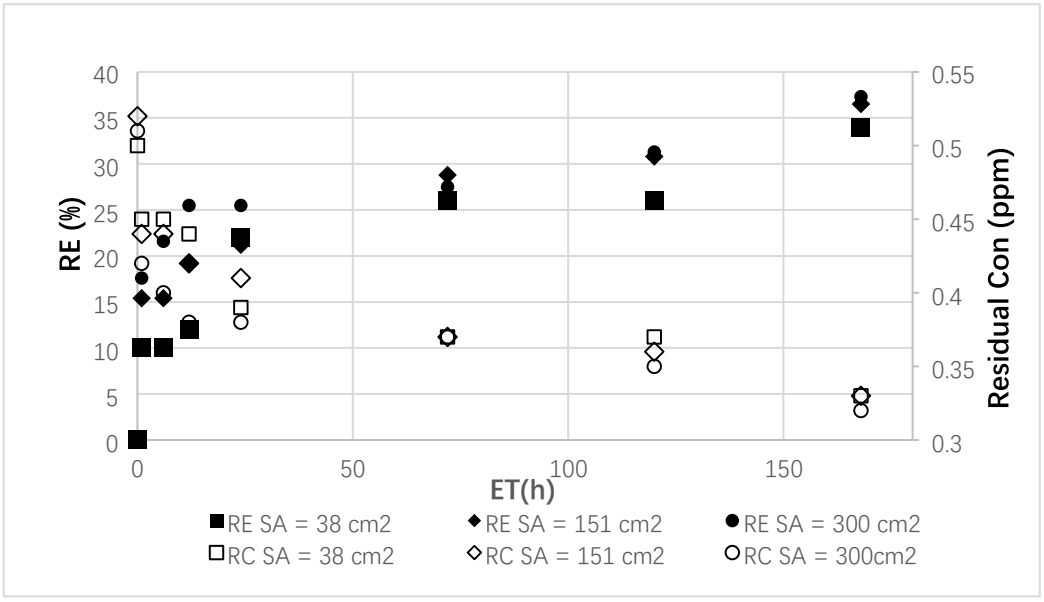
Figure 29 temperature change for chromium

There is one result that caught the author's attention: a negative relationship between RE and IC was found for chromium removal, which is unlike the other metals (RE positively related to IC). It was observed that 300cm^2 of shells can remove over 60% in solution with IC of 0.2ppm, 37.3% in solution with IC of 0.5ppm and 26% in that of 1ppm. Figure 31 shows that pH varied from 5.5 to 9 in 24 hours and went down slowly to around 8 (Figure 31). EC also kept a stable increase, but the EC for 300cm^2 SA in 0.2ppm solution was higher than the other two with the same SA at almost 80 μS/cm (Figure 32). This matches the result that the beaker with 300cm^2 and 0.2 ppm IC showed the highest removal efficiency. More ions exist in the solution, which would increase the possibility for chemical reactions to occur so that removal efficiency can be improved.

(a) Co = 0.2 ppm



(b) Co = 0.5 ppm



(c) Co = 1ppm

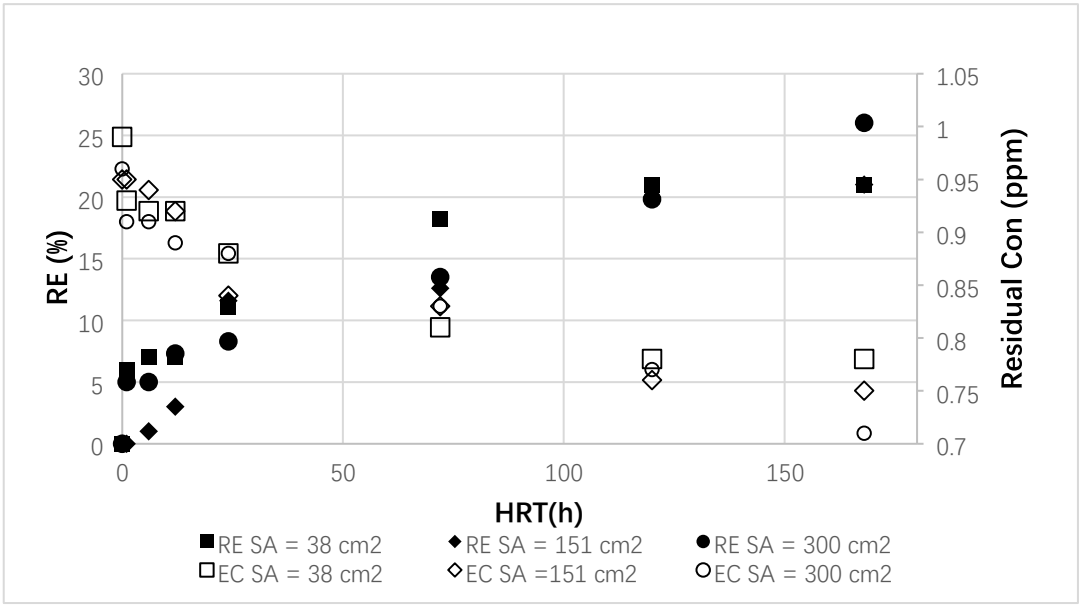
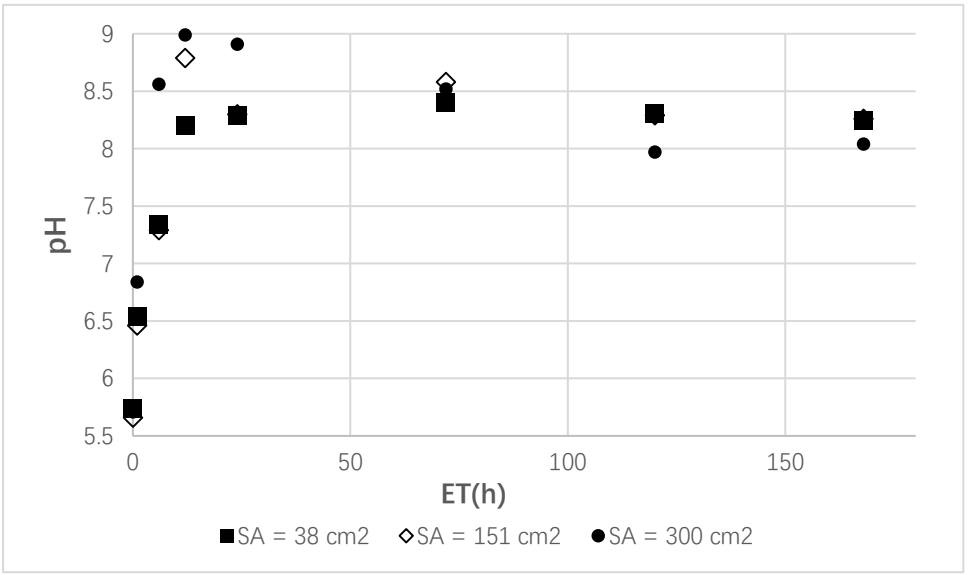
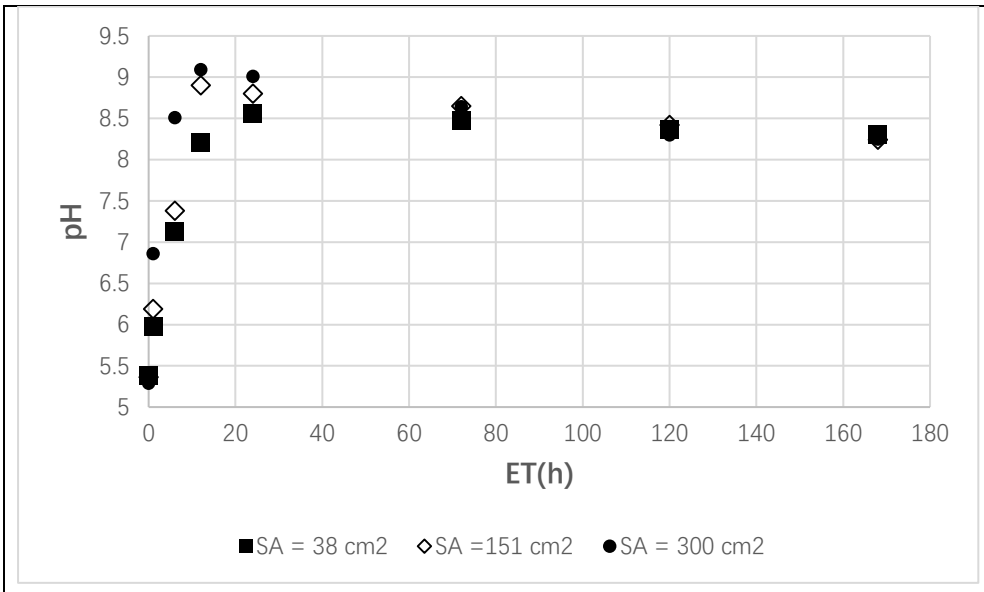


Figure 30 The relationship between RE, RC and ET for different initial concentrations for chromium

(a) Co = 0.2ppm



(b) Co = 0.5ppm



(c) Co = 1.0 ppm

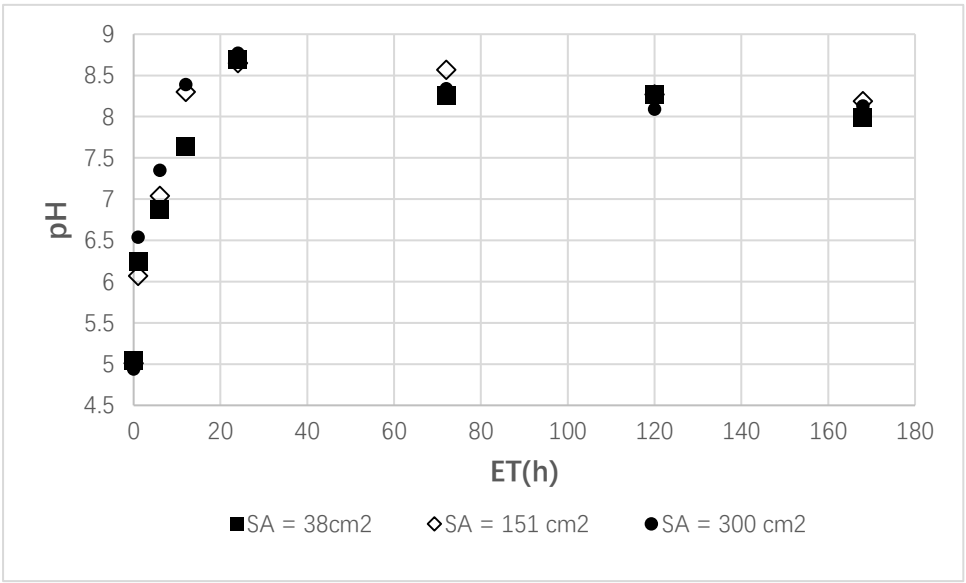
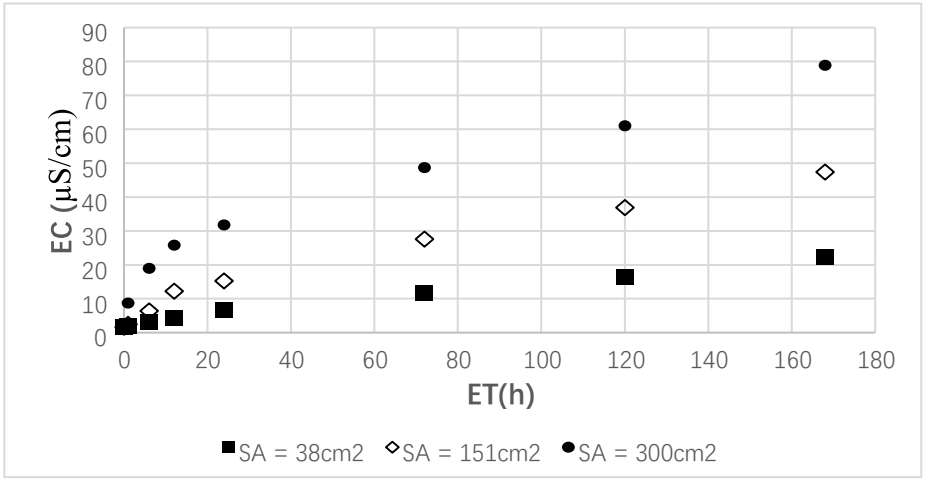
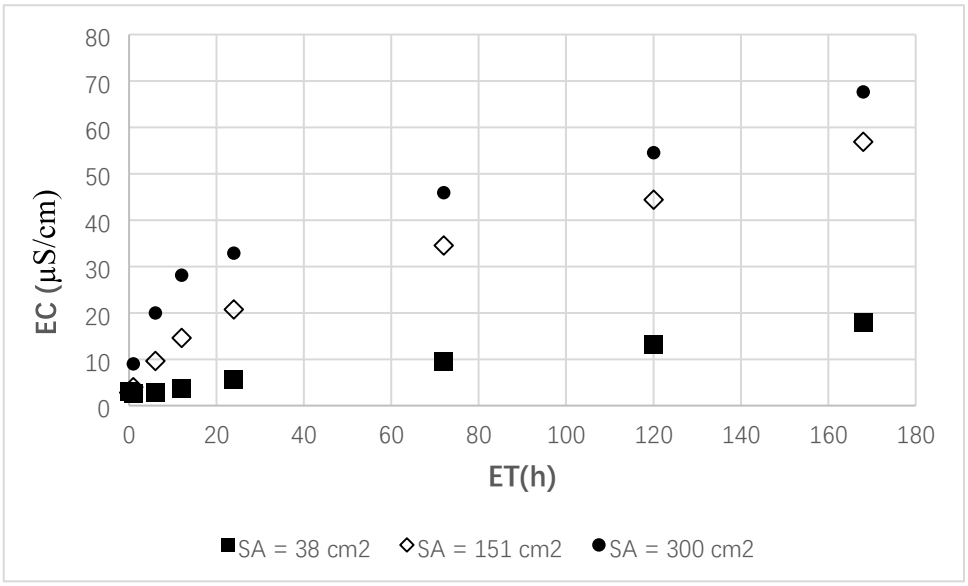


Figure 31 The relationship between pH and ET for different initial concentration for chromium

(a) Co = 0.2ppm



(b) Co = 0.5ppm



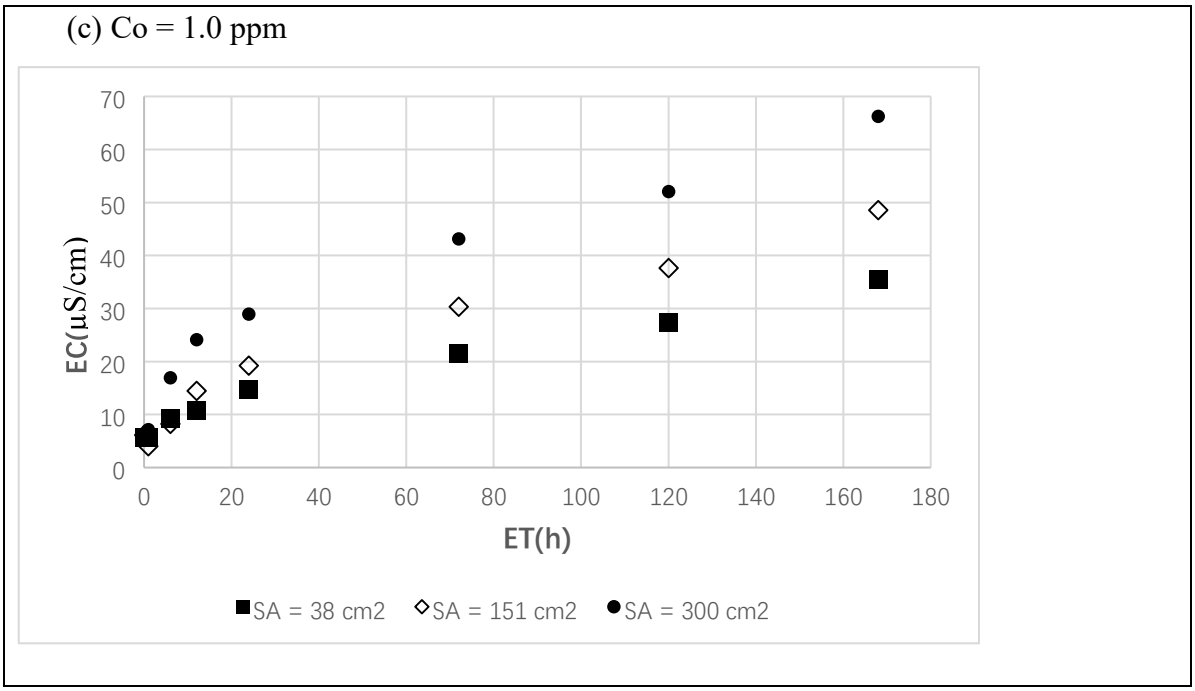
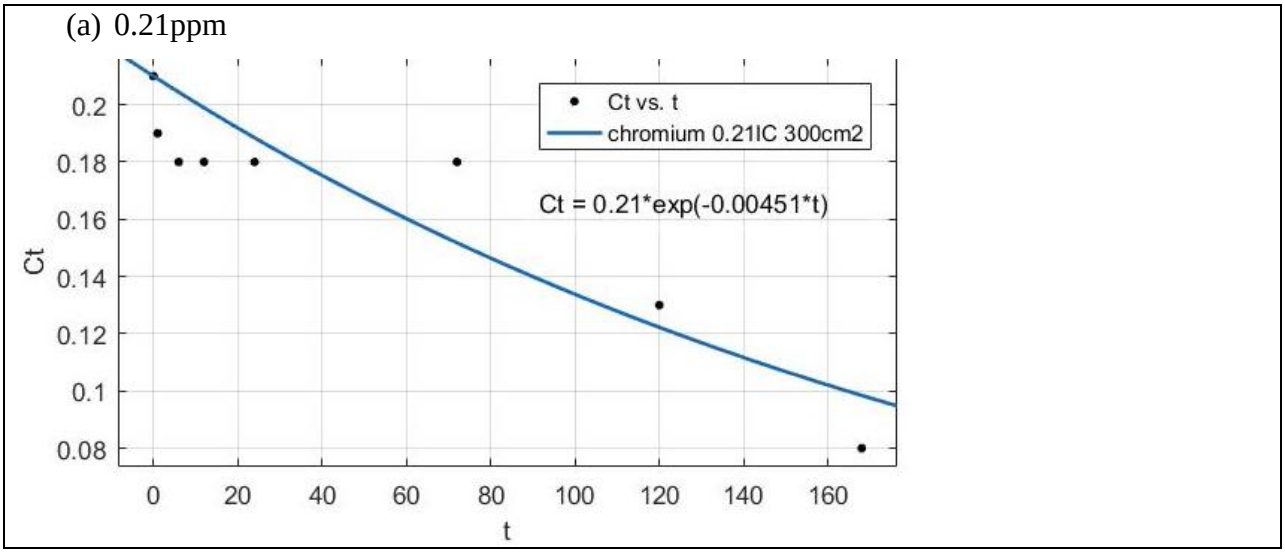
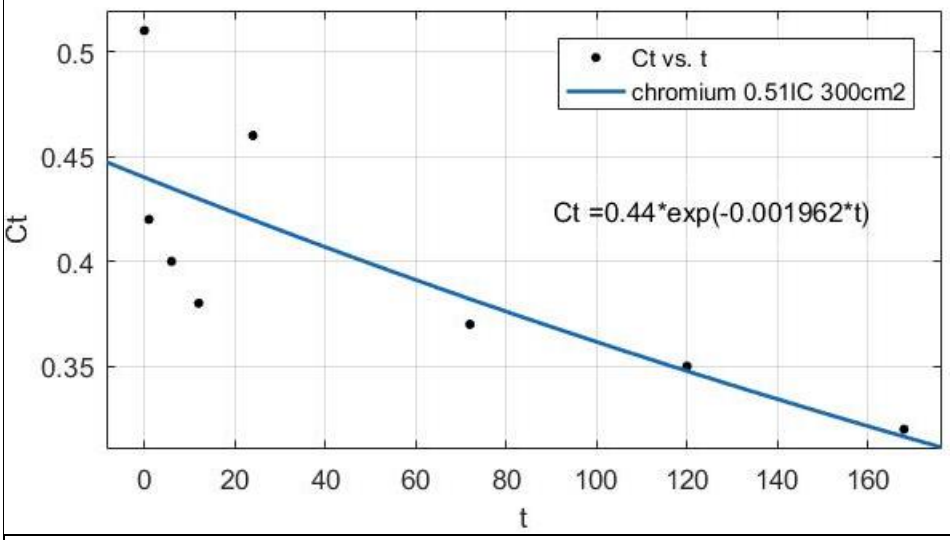


Figure 32 The relationship between EC and ET for all initial concentrations for chromium

Chromium is the one metal in which oyster shells are not effective, and thus, its adsorption kinetics maybe more complicated than others. Although IC of 0.21ppm and 0.96ppm showed a relatively good fit with a first order kinetic (adjusted R^2 of 0.78 and 0.84, respectively; and k of 0.0045hrs^{-1} and 0.0019 hrs^{-1}, respectively). The fitting of IC of 0.51ppm with 300cm^2 shells is poor, with a negative R^2. An exponential model was then used for model IC of 0.51ppm, and had higher adjusted R^2 of 0.52, but still lower than other concentration modeling (see Figure 33).



(b) 0.51 ppm



(c) 0.96ppm

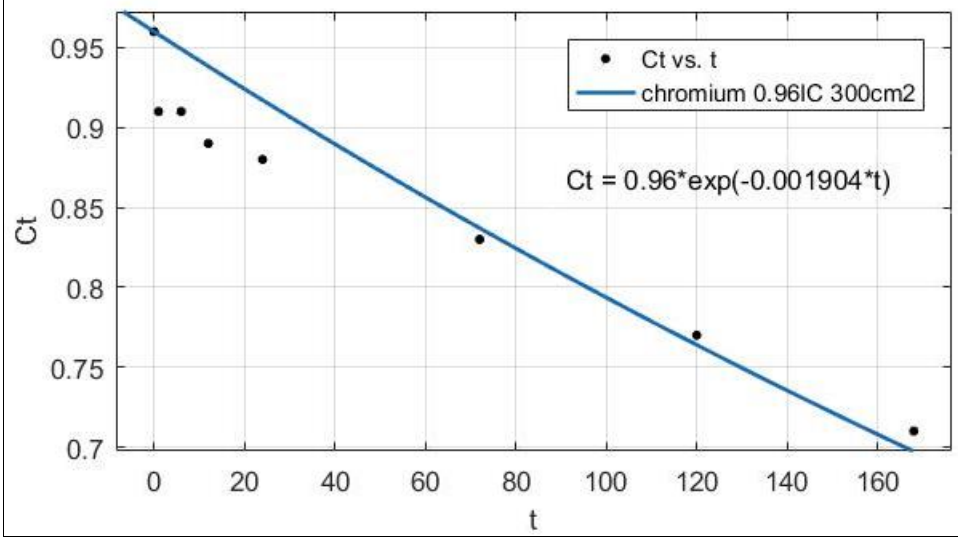


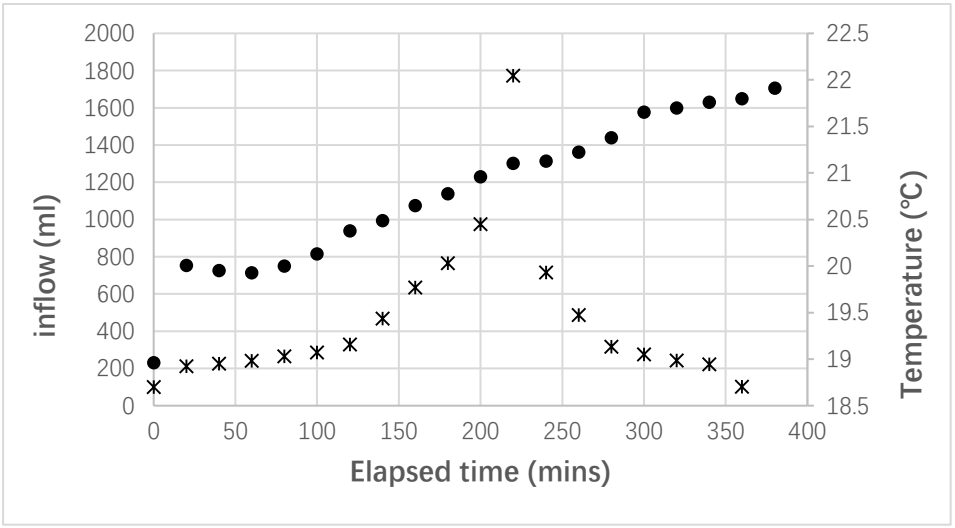
Figure 33 The first order model of chromium for different ICs

5.3 Results of the Mid-scale Experiment

The mid-scale experiment is totally different from the beaker experiment, which only uses static water - the mid-scale mimics the runoff to an urban infrastructure to have an inflow and outflow. The temporal axis would be just elapsed time instead of contact time because for every 20 minutes, new inflow will come into the tank and mixed with treated water, and 60ml extracted every 20 minutes would be a mixture of new and treated inflow. It is hard to see how long this part of the water comes into contact with the shells. After runoff, data was monitored again at 1, 4 and 7 days,

to see if anymore contact time could increase removal. Therefore, in this tank experiment, elapsed time would be used to instead of contact time. Moreover, HRT is based on the formula related to flow rate and volume (Equation 6). The author suspects that HRT is related to elapsed time somehow. A difference between HRT and elapsed time would be used and modeled to explore its relationship with RE in a six-hour design storm. Figure 34 shows the results for the tank experiment.

(a) The variation of temperature, inflow during elapsed time (minutes)



(b) The relationship between EC, PH and elapsed time (minutes)

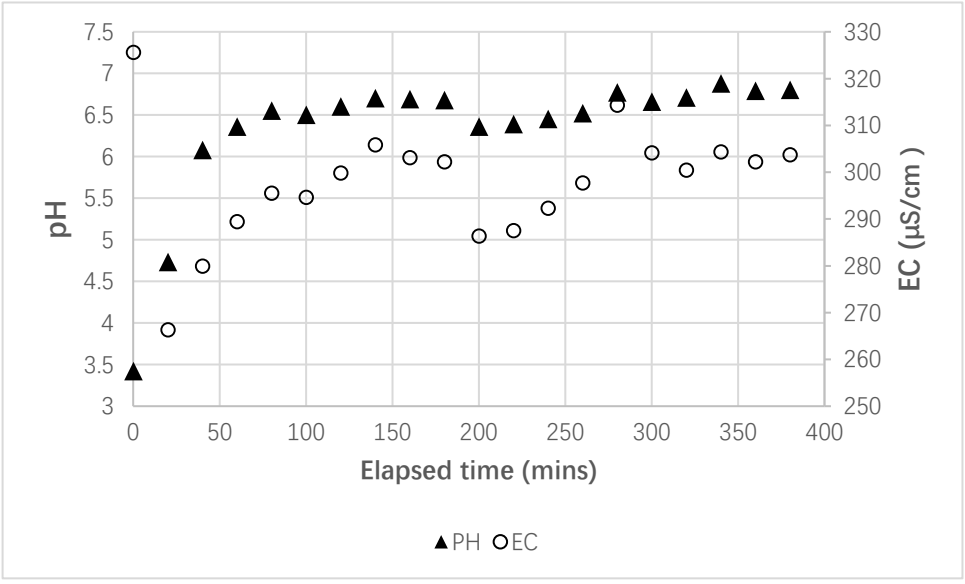


Figure 34 The relationship between temperature, inflow, EC, PH and elapsed time (minutes)

The temperature ranged from 19 ℃ to 22℃ (Figure 34 (a)). The mixture solution has a low pH of 3.5 initially and increased quickly in the first forty minutes to 6, then fluctuated between 6 and 7. The drop of pH and EC in the middle of the graph around 200 minutes was due to the peak inflow. The EC varied from 266μS/cm to 314μS/cm (Figure 34 (b)). In this 6 hour storm design, copper was treated to a relatively high RE compared to other metals, proving that oyster shells are effective in removing copper. At 80 minutes, RE is over 50% even with continuous inflow. However, more contact time between solution and shells can improve the RE of copper, with one day contact, RE can reach over 80%. Although longer times can improve RE slightly, given practical considerations and the issue with pH, 24 hours should be the best reaction time for copper. pH increased gradually after the six hours storm from 6.8 to 7.9 when elapsed time is from 6h20mins to 7 days. We would like to control outflow pH to a neutral range. This also matches the beaker experiment of copper, where RE was around 80% in one day for the maximum and second largest shells (Figure 35(a)).

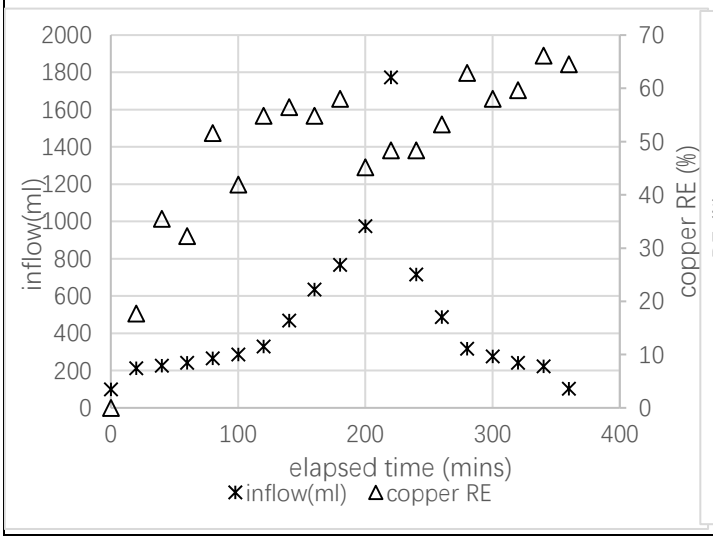
Zinc and chromium (Figure 35 (b) & (c)) didn't show any removal in six hours of inflow; inversely, their concentrations tended to increase. Especially for zinc, the concentration increased from 0.5ppm initially to 0.9ppm at only twenty minutes. This phenomenon is not expected but rational: the mechanism of oyster shells for absorbing metal ions is based on the chemical reaction between ions and calcium. However, the actual mechanism of absorption would be much more complicated and would include physical and chemical adsorption. Although this paper does not focus on exploring these mechanisms individually, the physical adsorption should exist. To explore the reuse of shells, the shells used in the mid-scale experiment were the ones that were used for individual experiments. Therefore, the increasing concentration of chromium and zinc is likely because of inflow flushing over the ions that were physically fixed on the surface area of the shells. We found that after an initial sharp increase in zinc, the shells removed zinc gradually, to same final concentration at six hours. Later contact time was taken to test the concentration of zinc: at one day, zinc ions were reduced to 0.26ppm, which is basically 50% RE. However, a slight increase of concentration of zinc can be seen with longer times than one day which is probably because of physical desorption of zinc ions again. Generally, chemical adsorption is much more stable than physical desorption, but will take some time to realize.

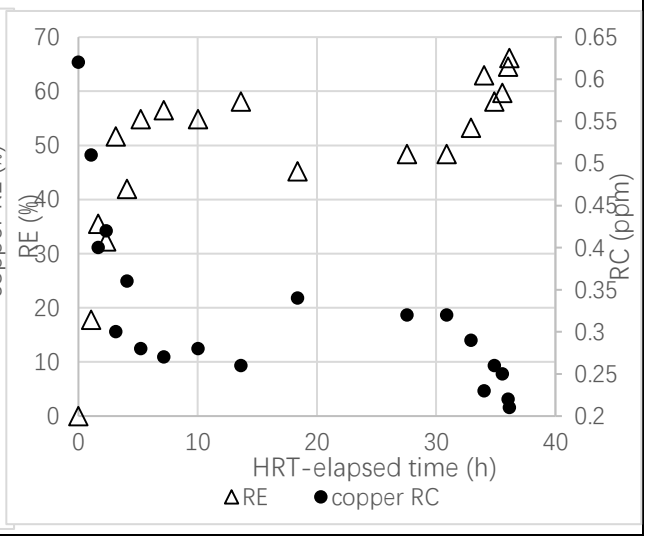
Whole oyster shells were proven to be less effective in removing chromium in the beaker experiment. In the mid-scale tank, no removal was seen at all whatever the circumstances of

continual inflow or longer contact times until seven days - which is likely because of competition among metal ions.

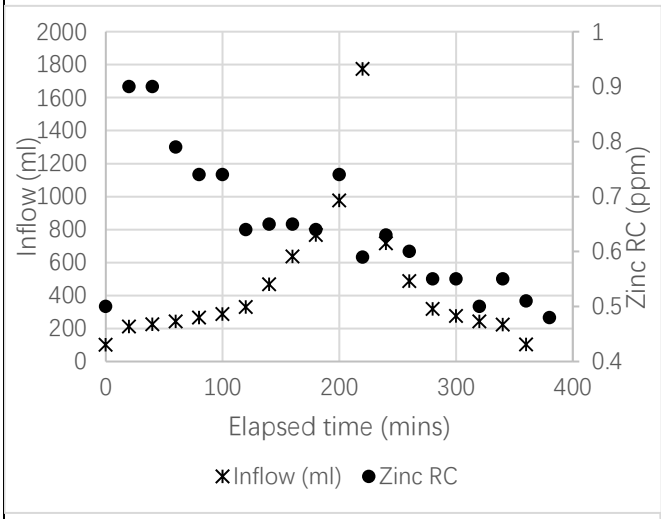
Cadmium (Figure 35(d)) was tested with a kit from LaMotte with code number 7839-02 and the value was given based on comparison to a color bar as part of the kit. Photos are given in Appendix 4. Despite the lower precision than the spectrophotometer, a rough tendency can be seen. RE of cadmium varied according to inflow amount and was stable at around 45% finally with low runoff. However, an RE of 85% can be reached in one day contact time, and RE also grew with later time to over 90% (Figure 36(a)). This means cadmium really needs a significant contact time with shells to reach high RE. For cadmium, one day is still the best time for removal.

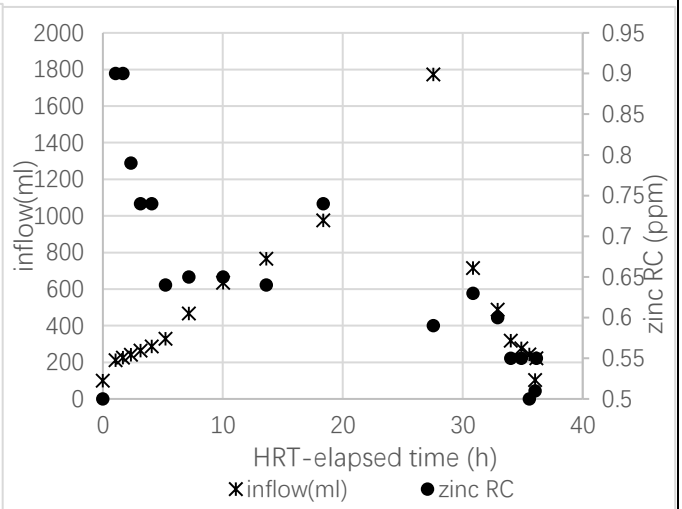
(a) Copper



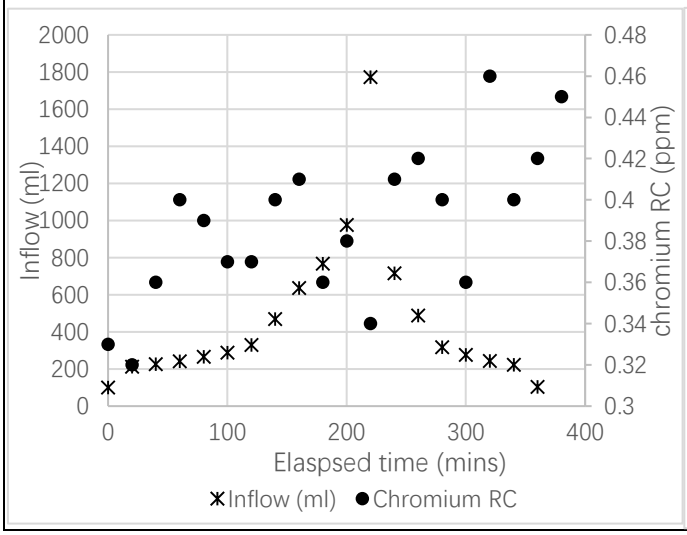


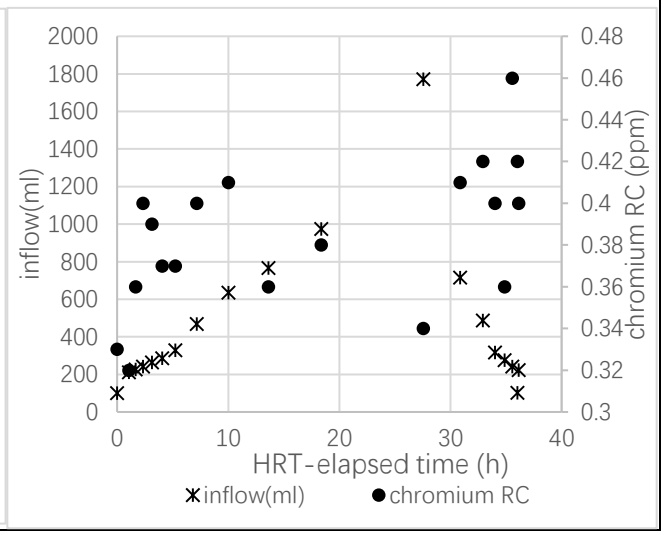
(b) Zinc





(c) Chromium





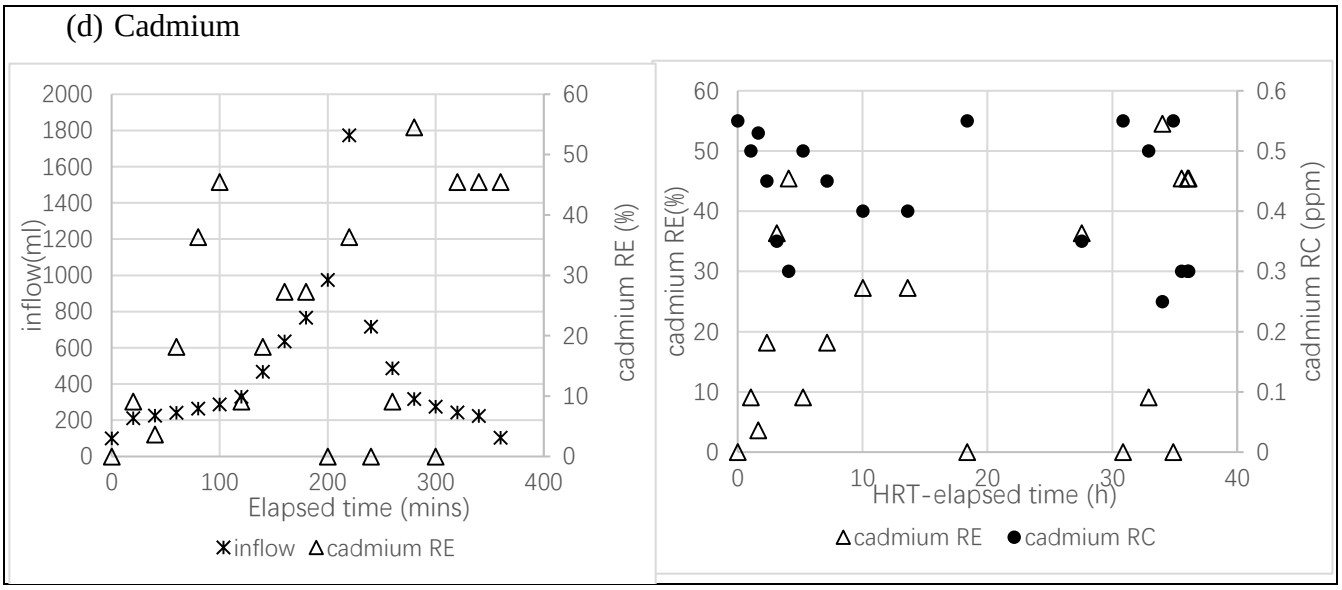


Figure 35 The relationship between Elapsed time and RE or RC, and between HRT-elapsed time and RC or RE.

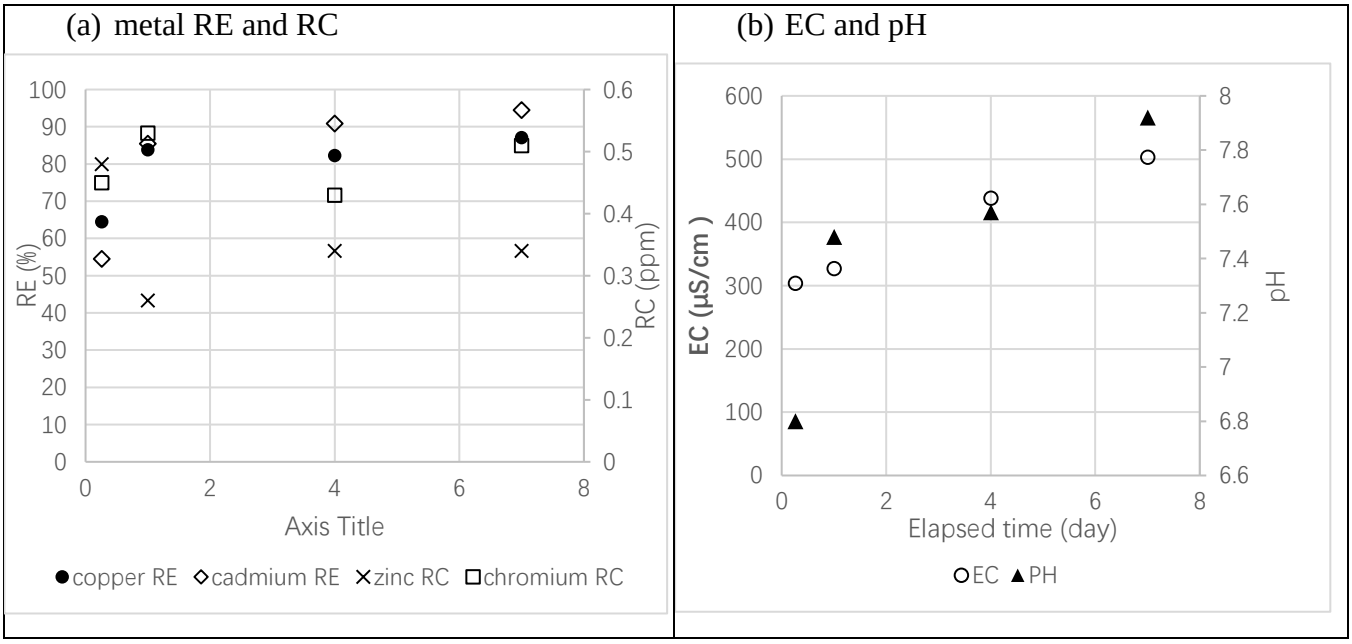


Figure 36 The relationship between metal concentration or RE, PH, EC and longer elapsed time

Table 3 Post 24 hour data

Elapsed Time (d)	pH	Temp (℃)	EC(µS/cm)	Cu con(mg/L)	Zn con(mg/L)	Cr con(mg/L)	Cd con(mg/L)
0.26	6.8	21.913	303.7	0.22	0.48	0.45	0.25
1	7.48	19.903	326.9	0.1	0.26	0.53	0.08
4	7.57	20.282	438	0.11	0.34	0.43	0.05
7	7.92	22.198	503	0.08	0.34	0.51	0.03

The modelling of the tank experiment data for the six hour storm design is not ideal. No data can be modeled based on first order decay of CMFR system as seen in Equation 6, where HRT was attempted with HRT calculated both from the concept used in wastewater and from the CMFR system formula. Another possibility of using HRT - elapsed time to be HRT in the relationship between HRT and concentration was explored. Unfortunately, none of this can be modeled in MATLAB. It is also likely because the process of oyster shells absorbing metal ions in co-existed metal solution is complicated and cannot be modeled based on a single mathematical expression. Maybe several stages can be divided for the whole process, and for each stage, a different corresponding model. However, for this model attempt, more data will be needed to interpolate and enrich the model.

Table 4 shows the modeling forms attempted for the mid-scaled experiment. Three equations were attempted and the second one uses the HRT and each individual k (the k for the best removal efficiency was chosen for each metal) as modelled by Equation 6 for a non-steady state, CMFR with first order decay. Table 5 shows the modelling results and Figure 37 and Figure 38 show the results for copper and zinc only as chromium and cadmium did not produce reasonable results.

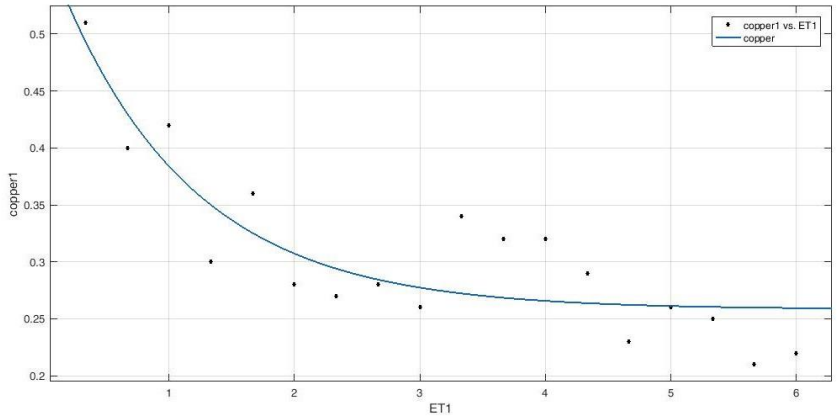
Table 4 Modelling Constructs and Equation Forms

Equation	General equation	x	y	z
a	y = a*exp(-b*x)+c	t	C(t)	
b	z = a + b*exp(-x*(y*c))	t	1/HRT+k	C(t)
c	ax^b+c	HRT	C(t)	

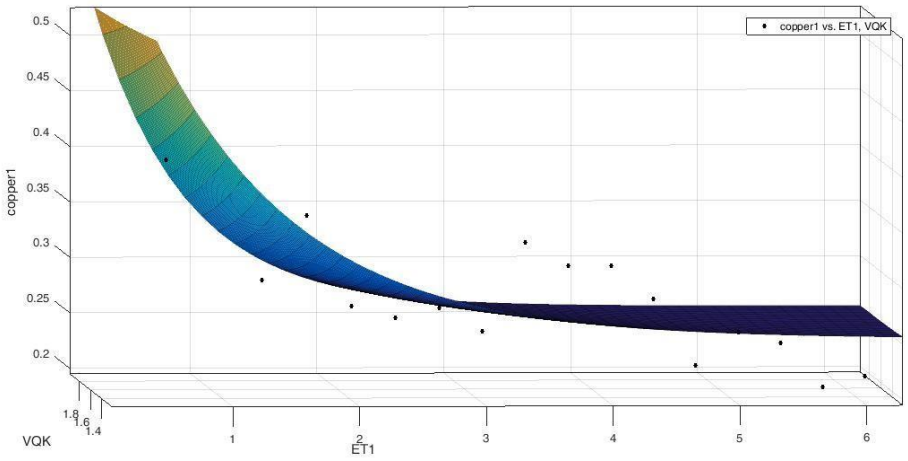
Table 5 Model Coefficients

	General Equation	Adjusted R^2	k	a	b	c
Cu	a	0.731	1.22	0.3223	0.9428	0.2583
	b	0.737	1.22	0.2549	0.38	0.7146
	c	0.72	1.22	0.3496	-0.8859	0.2499
Zn	a	0.865	0.032	0.4732	0.3671	0.4798
	b	0.872	0.032	0.4686	0.5327	0.3462
	c	0.824	0.032	0.7	-0.2328	0.2671
Cd	a	0	0.021			
	b	-0.13	0.021			
	c	-0.04	0.021			
Cr	a	0.186	0.0045	-0.0781	0.7525	0.4023
	b	-0.06	0.0045			
	c	0.217	0.0045	-0.1237	-1.519	0.3966

(a)



(b)



(c)

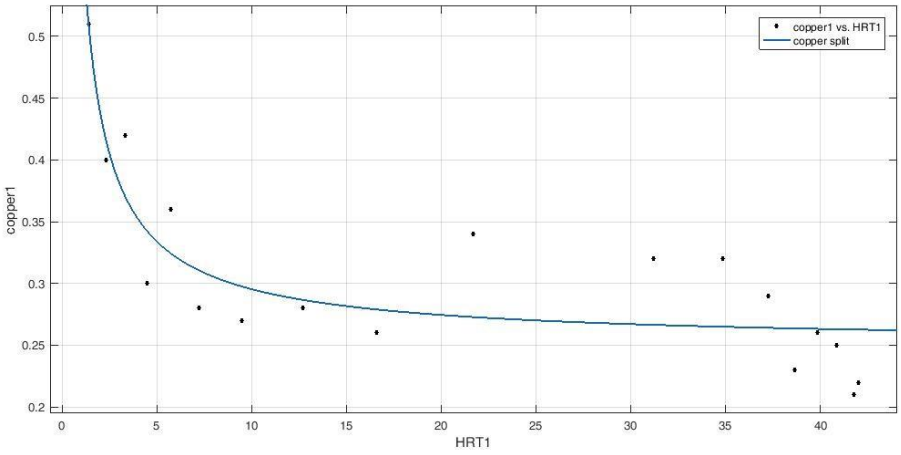
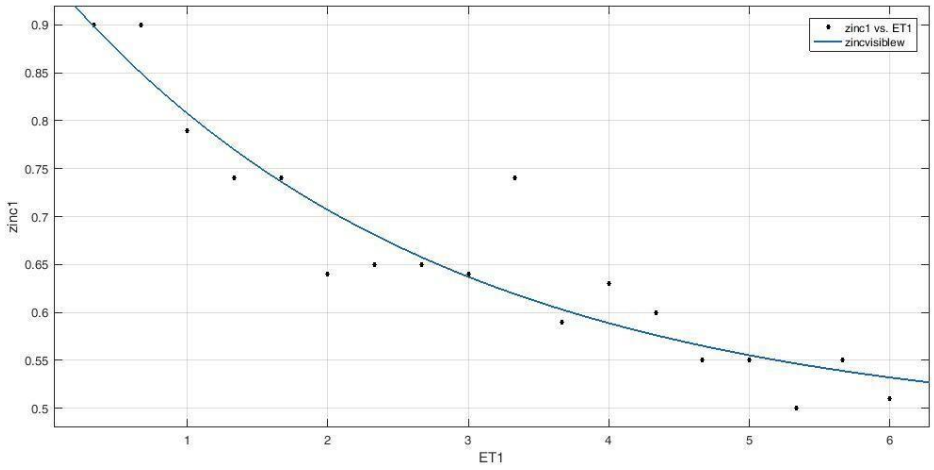
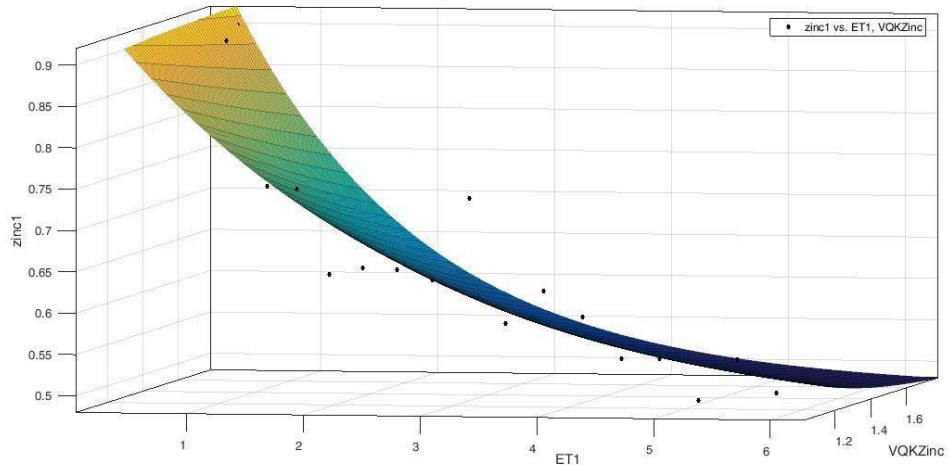


Figure 37 Modelling Results for Copper. (a) basic equation; (c) unsteady CMFR with k; (c) power law

(a)



(b)



(c)

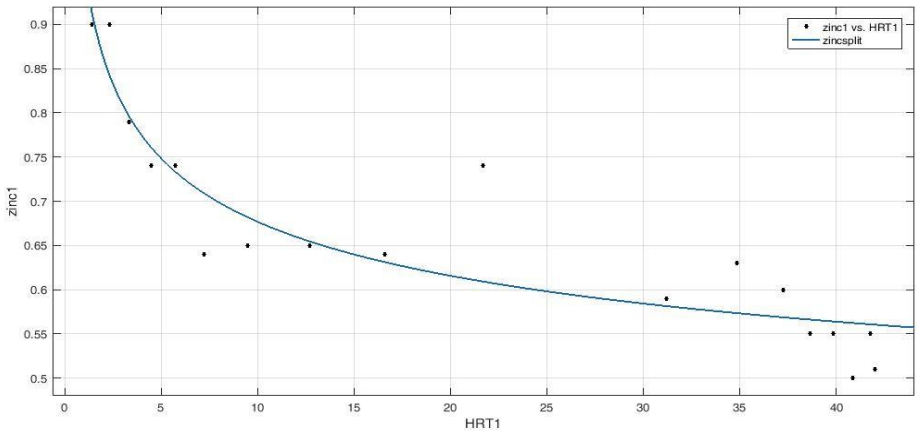


Figure 38 Modelling Results for Zinc

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

This research investigated the ability of whole, untreated oyster shells in stormwater treatment removing heavy metals. The focus of this project was to study the effect of initial concentration, surface area of shells and exposure time (ET) on removal efficiency and the role of hydraulic retention time in stormwater.

6.1 OYSTER SHELLS PERFORMANCE

Generally, the whole oyster shells have the ability to remove specific metal ions even in low concentration stormwater. In preliminary experiments, high concentrations of one-liter mixed solution with 5mg/L trivalent iron, ammonium, 50mg/L phosphate, 2.3mg/L copper, 24.1mg/L nitrate and 10mg/L zinc were treated with one single shell with a surface area of 115.7cm^2. Among all elements, iron showed the fastest removal rate and best removal efficiency of 94% at 24 hours, followed by copper, 67.7% at two days. No obvious reduction was seen for other elements. In this mixed solution, there are three metal ions and they were preferred to be absorbed in the following sequence: $Fe^{3+} > Cu^{2+} > Zn^{2+}$, based on the strip testing results. A desorption was observed for iron after one day.

There are four targeted metal ions in the beaker and mid-scale device experiment: Cu^{2+}, Zn^{2+}, Cr^{6+} and Cd^{2+}. Oyster shells are highly effective in copper removal, whether in the beaker or scaled-up experiment. They are also effective for removing zinc and cadmium with longer treatment times, but less effective in removing hexavalent chromium. At lowest initial concentration with 24 hours of contact, 79.2% can be reached for copper in a beaker, 33.3% RE for zinc, 57.7% RE for cadmium and 14.3% RE for chromium. Therefore, under similar conditions, the adsorption rate of metals is rated as follows: copper > cadmium > zinc > chromium. This sequence is the same as what happened in the mixed solution sample under continuous inflow, where at the end of runoff (six hours), copper had the highest RE of 64.5%, and cadmium was the next with 45.5%. Desorption occurred in zinc and chromium, but an obvious reduction can be seen for zinc after an initial sharp increase, while chromium has no signs of adsorption. A dramatic increase in pH accompanied the shells in the first few hours or days, and then slowly reduced to an almost neutral value.

6.2 THE EFFECT OF *IC*, *SA* AND *ET* ON *RE*

Initial concentration, surface area and exposure time were the effective factors monitored in this research. Generally, exposure time is positively related to removal efficiency, longer times can increase removal efficiency. However, desorption is easy to occur over longer times. Also, for most of the metals, the most effective reaction time is the first few hours or few days, after that, although an increase can be seen with longer times, the increase can be negligible. For metal solutions with the lowest initial concentration closer to real stormwater concentrations, the fast reaction time was 6 hours for copper to 79.2%, 3 days for zinc to 55.2%, 3 days for cadmium to 61.5% and 7 days for chromium to 61.9%. However, under the condition with inflow and coexisting ions, the best exposure time would be one day, when cadmium and copper can reach RE of 85.5% and 83.9%, respectively.

There is positive relationship between initial concentration and removal efficiency for copper and zinc, but negative relationship was found for hexavalent chromium. No clear relationship between IC and RE was seen for cadmium. Copper showed a removal efficiency of 80% when IC is 2.4ppm compared to 60% when IC is 0.65ppm under the same condition. The middle-sized shells (154cm^2) showed am increasing tendency of RE 70%, 75%, 83%, with increase of initial concentration from 0.3ppm to 1.07ppm. Chromium removal demonstrated a reducing tendency from 60%, 37.3% to 26%, when IC was 0.2ppm, 0.5ppm and 1.0ppm, respectively.

Surface area of shells is an important parameter in this research, because instead of mass of shell powder that was used in other research, it provides an idea to answer the question: how many whole oyster shells should the stormwater be exposed to for treatment? In the beaker experiment, SA of 38cm^2 to 550cm^2 of shells were used to treat 2-liter copper solution; for other metals, appropriate 40cm^2 to 300cm^2 SA of shells were used to treat 1-liter metal solution. For mid-scale experiment, a total SA of over 9000 cm^2 was used to treat a cumulative volume of 8.645-liter inflow. A strong positive relationship was observed between SA and RE for all metals, however, the effect seems negligible when SA is between a certain range and smaller when surface area is over certain amount. When surface area is from 69cm^2 to 108cm^2, no clear increase of RE can be seen, but when the span is between 38cm^2 to 121cm^2, the difference is quite obvious. Also, there was no big difference of shells for removing copper with a surface area between 320 cm^2 and 550

cm^2. It was also found that, the smaller shell can also reach high removal efficiency but will take a longer time than a bigger shell.

6.3 THE ROLE OF *HRT*

Hydraulic retention time is a significant parameter used in lots of fields, even in wastewater treatment. A definition of HRT was used in CMFR system that normally mimics a lake system, etc. The author attempted three variations including the non-steady state, CMFR reactor with first order decay, which includes HRT in the exponent along with the decay rate found in the experiments. Copper and Zinc provided the best results indicating that to some degree, this model is applicable to stormwater, but the degree needs to be explored further.

6.4 RECOMMENDATIONS FOR FUTURE RESEARCH

One of the limitations of this project is the spectrophotometer doesn't have a very low detection limit that might be required for real stormwater. The sample solution used in this project was prepared with relatively high concentrations of metals. Also, the samples' pH were not adjusted to the similar pH as natural stormwater because of the high concentration of solution. Lower detection limit devices and samples should be used for more precise data in future research. In addition, although one day is considered as the best exposure time for metal removal, the side problem, like high pH, should be dealt with as well. More exposure time can bring up pH a little bit, or some chemicals will be needed to adjust pH afterwards.

In this project, several methods were used to test metal concentration including easy strips, test kits and a spectrophotometer. The easiest method is the strips; however, it has a threshold for testing low concentration solutions. When concentration is below 1ppm, the strips cannot tell us an obvious concentration change, but when concentration is over 1ppm, the color change of the strips is easy to differentiate. For many field tests, strips will be an effective and cheap method to give an idea of concentration change when initial concentration of sample water is over 1ppm.

The reuse and disposal of treated oyster shells will be a serious problem for future research. When applied in real applications, the timing at which point the oyster shells need to be changed and then how to deal with the treated shells as a waste product, are two key questions waiting to be answered. In this project, only four metal ions were included. However, other normal metals like

lead, manganese etc. should be also tested with oyster shells, to see if they also work for removing these metals. Meanwhile, different kinds of shells (e.g. clam shells, lobster shells etc.) should be compared with parallel experiments to find the one type that is most effective in removing most metals.

Further experimentation with the mid-scale and higher scales should be undertaken to explore the meaning of HRT in this application. Where to place the oyster shells for stormwater treatment has not been decided - probably in a catch basin or stormwater treatment pond. Based on the targeted place, specific experiments can be undertaken to explore the removal efficiency under different conditions. If in a catch basin, then HRT will be better to follow the definition of CMFR system or PFR system, so a stable inflow and outflow rate should be controlled. If in a pond, then HRT will be a key to determining the size of the pond. According to the data from this tank experiment, metal ions need to be in contact with oyster shells at least one day to reach a relatively good removal. Therefore, a stormwater pond would be better for treating with oyster shells, but a related experiment to verify this should be conducted in the future.

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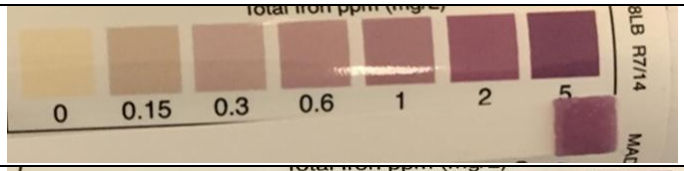
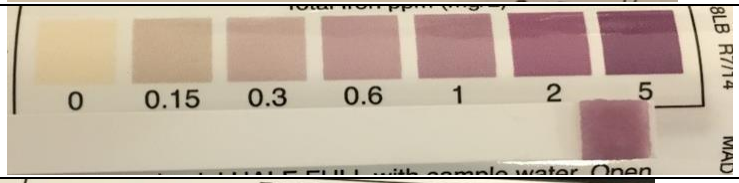
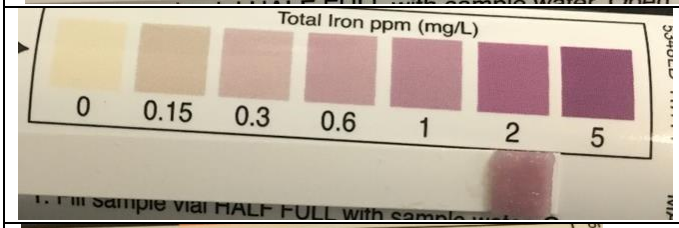
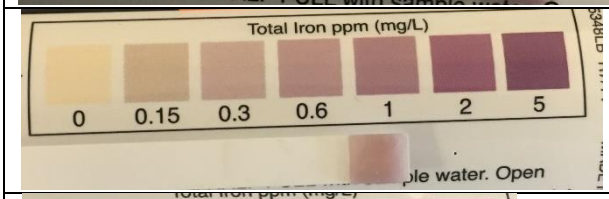
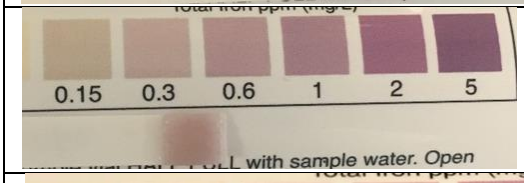
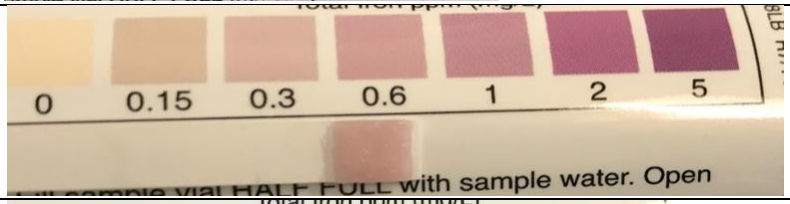
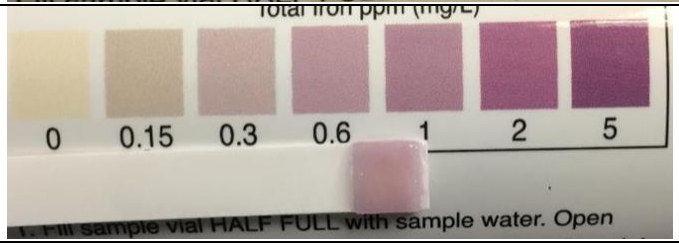
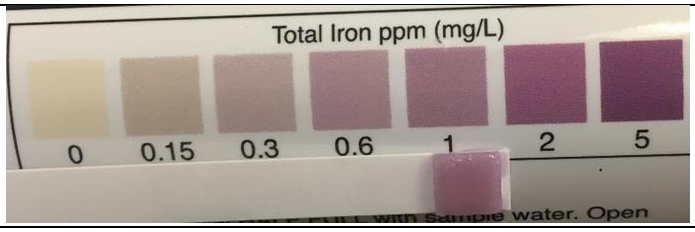
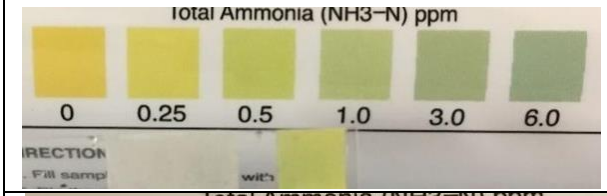
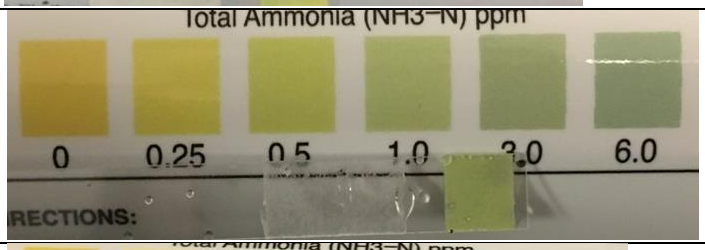
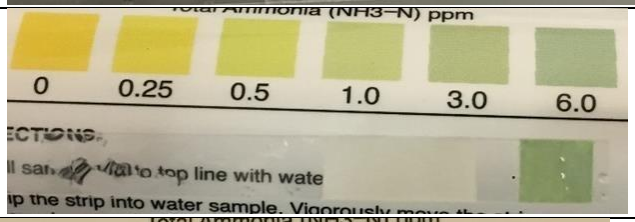
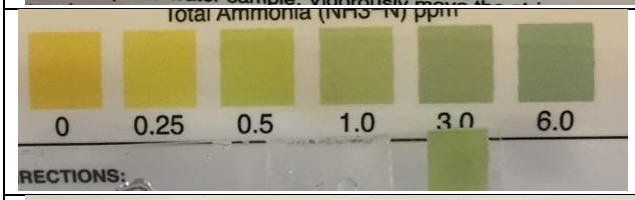
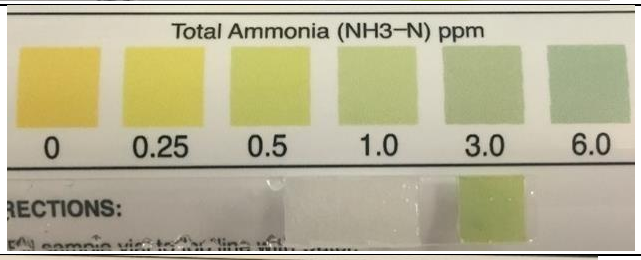
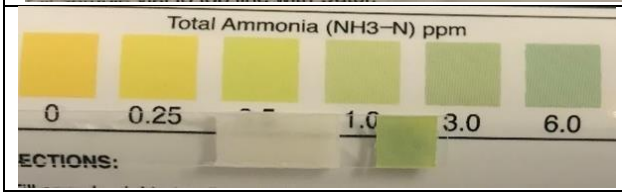
APPENDIX 1 PRELIMINARY RESULTS

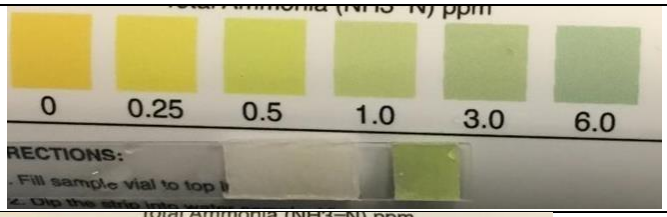
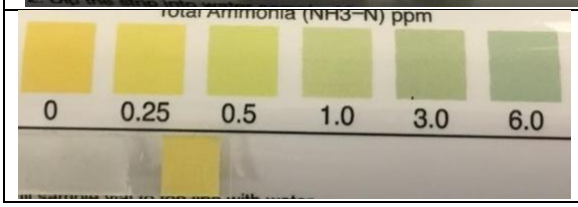
Total Iron PPM (mg/L)

Photos	Results
	ET=0h, 5mg/L
	ET=1h, 4-5mg/L, say 4.5
	ET=6h, 1-2mg/L, say 1.5
	ET=18h, 0.6-1mg/L, say 0.8
	ET=24h, 0.3-0.6mg/L, tend to 0.3, say 0.3
	ET=48h, 0.3-0.6mg/L, tend to 0.6, say 0.5
	ET=4 days (96h), 0.6-1mg/L. say 0.6

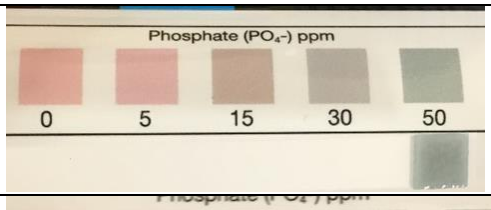
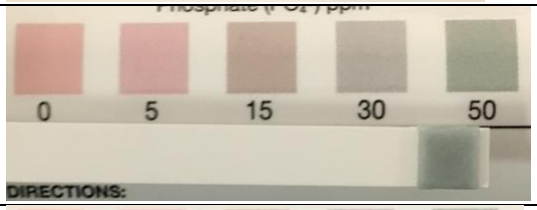
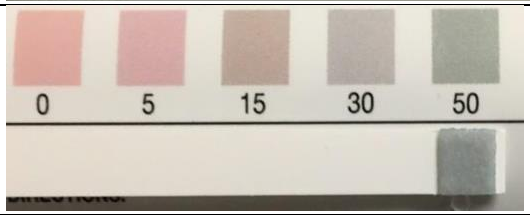
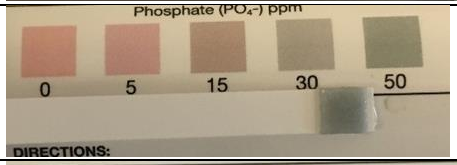
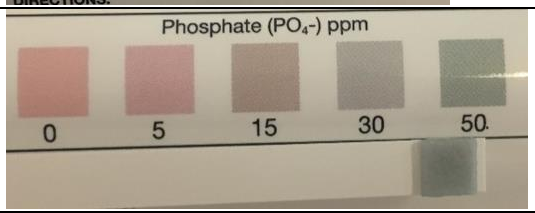
	ET=9 days (216h), 1-2mg/L, say 1.5

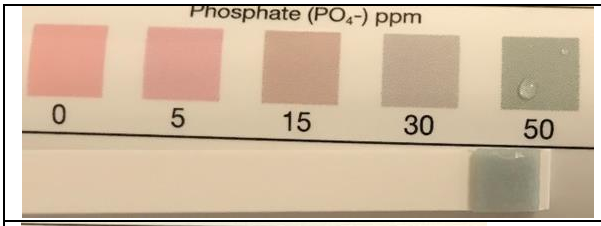
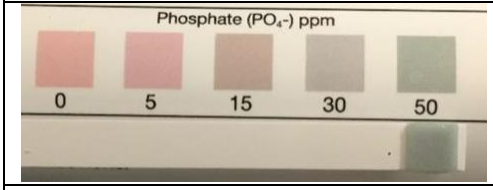
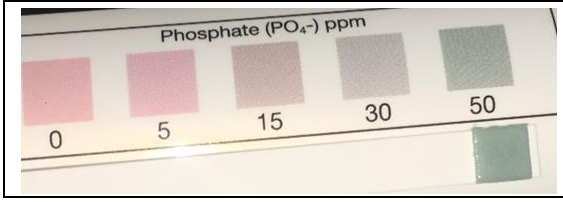
Total Ammonia (mg/L)

Photos	Results
	ET=0h, 5mg/L, however, the strip showed between 0.5-1mg/L, say 0.5ppm
	ET=1h, 1-2mg/L, say 2ppm
	ET=6h, 3-6mg/L, tend to 6, say 5ppm ((should be initial concentration))
	ET=18h, 3-6mg/L, tend to 3, say 3ppm
	ET=24h, 3-6mg/L, tend to 3, say 3ppm
	ET=48h, 1-3mg/L, tend to 3, say 3ppm

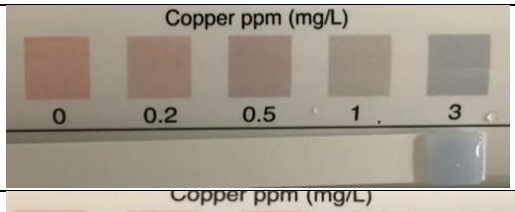
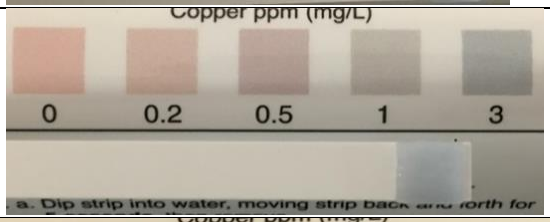
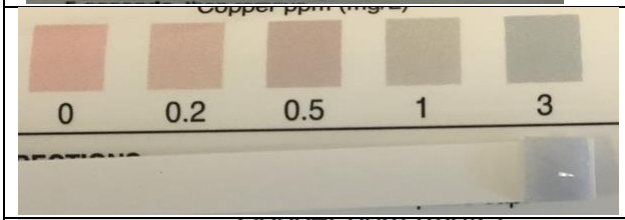
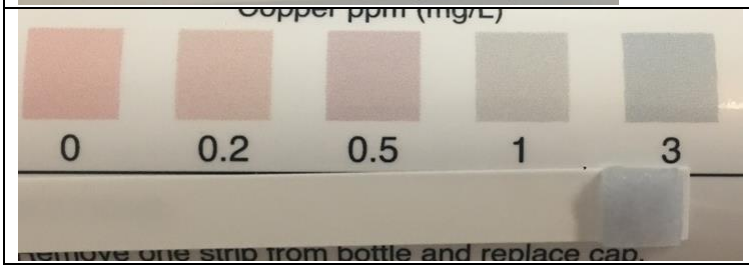
	ET=4 days (96h), 1-3mg/L, tend to 3, say 3ppm
	ET=9 days (216h), 0- 0.25mg/L, say 0.2ppm

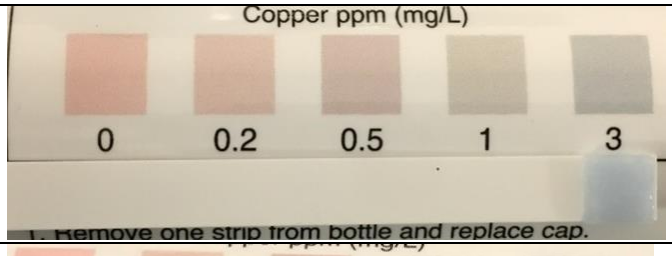
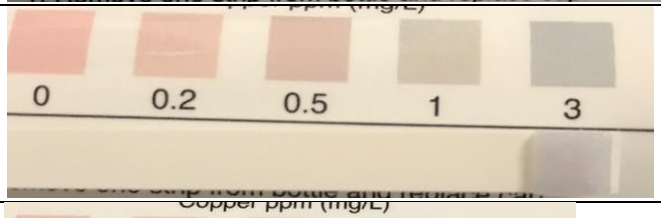
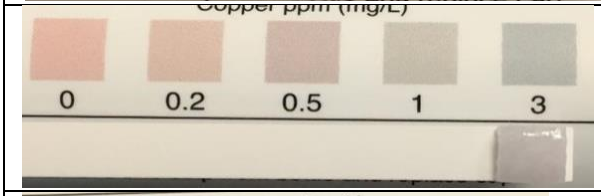
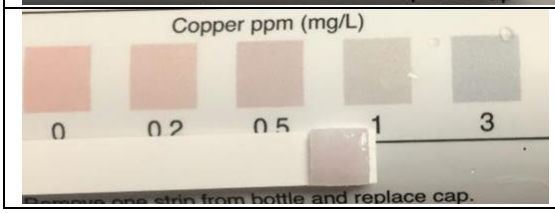
Phosphate (mg/L)

Photos	Results
	ET=0h, 50mg/L
	ET=1h, 30-50mg/L, tend to 50mg
	ET=6h, 30-50mg/L, tend to 50mg
	ET=18h, 30-50mg/L, tend to 50mg
	ET=24h, 30-50mg/L, tend to 50mg

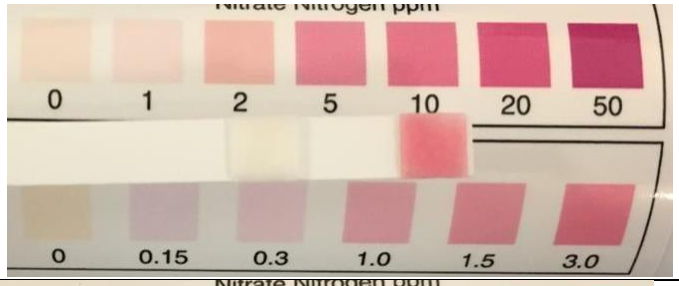
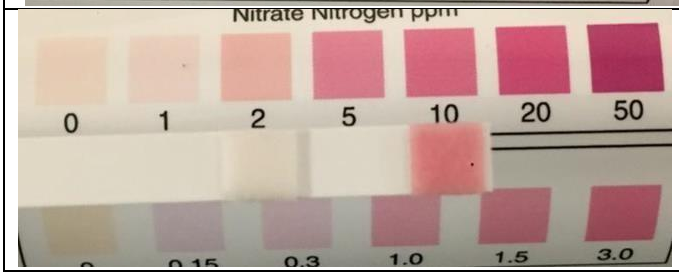
	ET=48h, 30-50mg/L, tend to 50m
	ET=4 days (96h), 30-50mg/L, tend to 50
	ET=9 days (216h), 30-50mg/L, tend to 50(took with the lighter, so the color is kind of brighter than others)

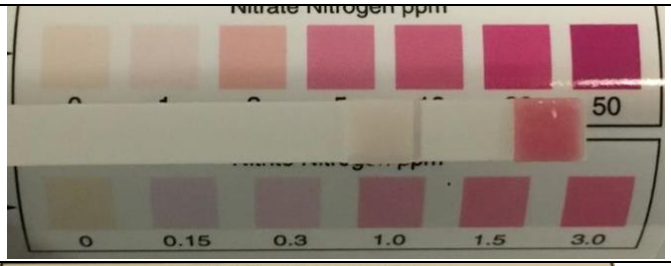
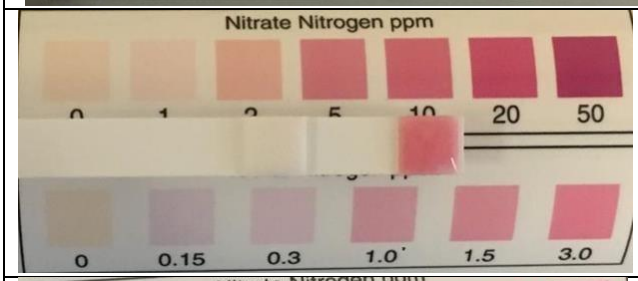
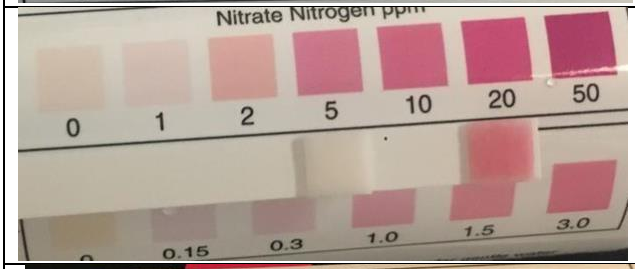
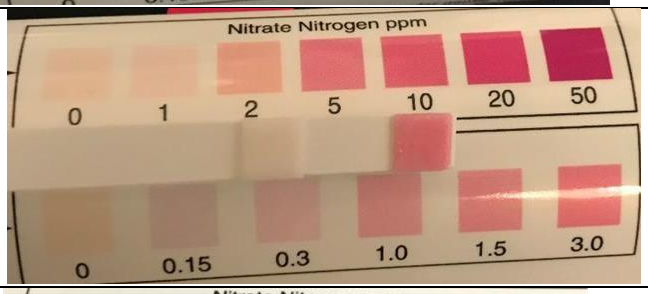
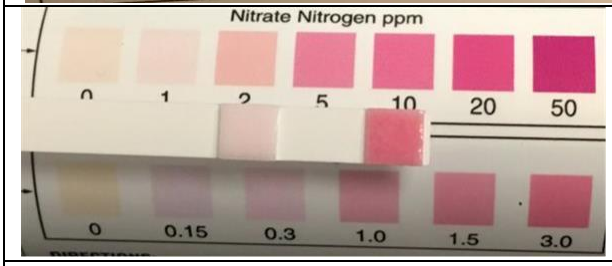
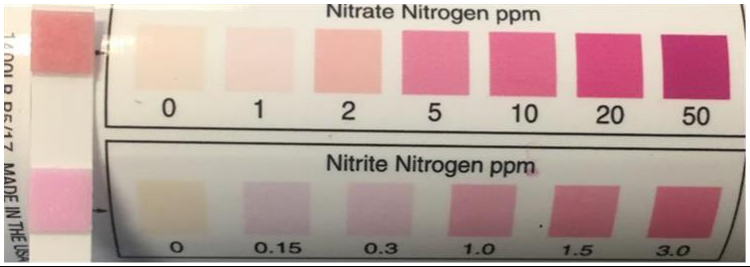
Copper (mg/L)

Photos	Results
	ET=0h, 2.325mg/L
	ET=1h, 1-3mg/L, tend to 3mg
	ET=6h, 1-3mg/L, tend to 3mg
	ET=18h, 1-3mg/L, tend to 3mg

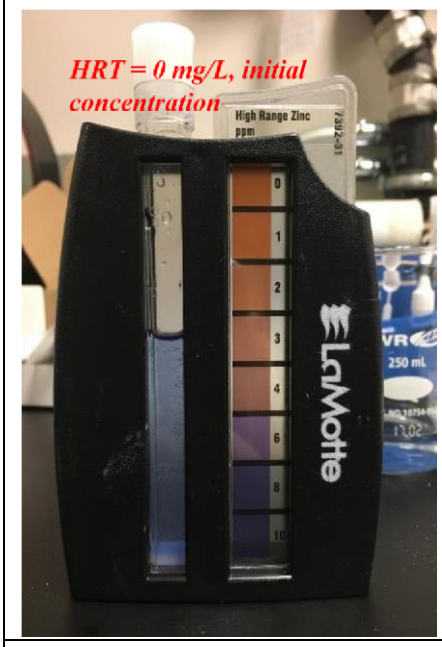
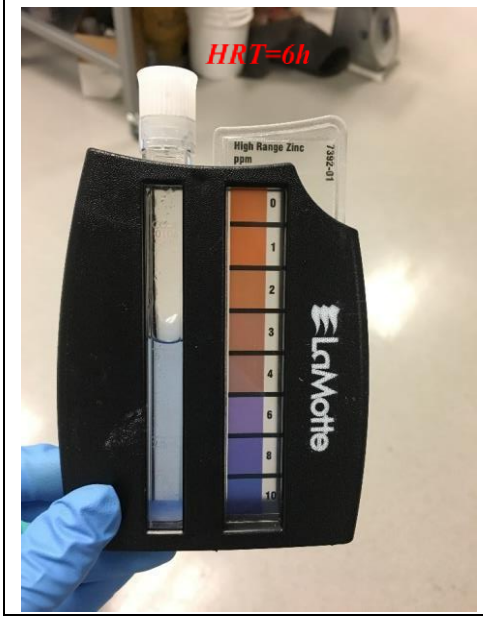
	ET=24h, 1-3mg/L, tend to 3mg
	ET=48h, 0.5 – 1 mg/L, tend to 1mg, say 0.75 ppm
	ET=96h, 0.5 – 1 mg/L, tend to 1mg, say 0.75 ppm
	ET=216h, 0.5-1mg/L, tend to 1mg, say 0.5 ppm

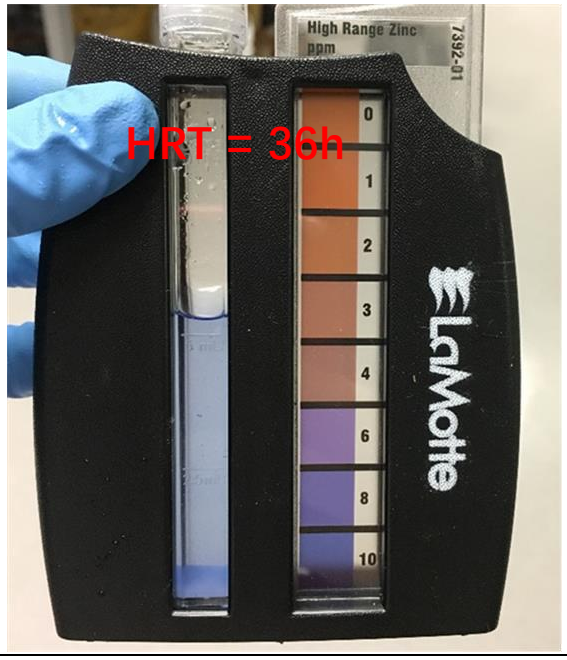
Nitrate PPM

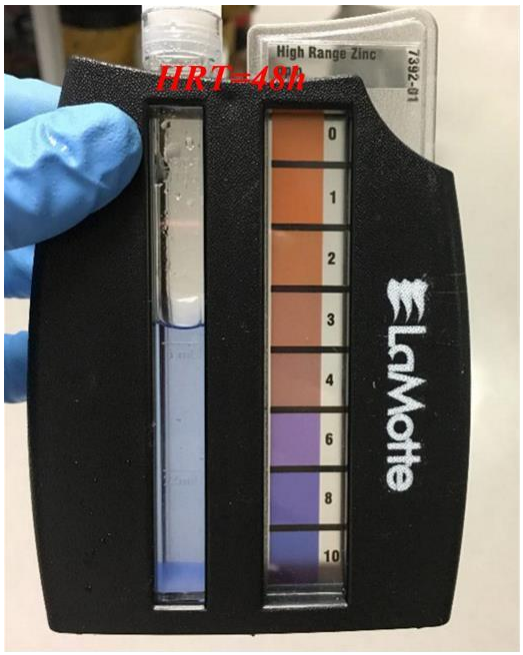
Photos	Results
	ET=0h, Nitrate nitrogen: 24.1mg/L (The strip showed like between 10 and 20mg/L), say 15ppm Nitrite nitrogen: 0mg/L
	ET=1h, 10-20mg/L, say 15 ppm

	ET=6h, 10-20mg/L
	ET=18h, 10-20mg/L
	ET=24h, 10-20mg/L
	ET=48h, 10-20mg/L
	ET=96h, Nitrate nitrogen:10-20mg/L; Nitrite nitrogen: 0.15-0.3mg/L
	ET=216h, Nitrate nitrogen:10-20mg/L; Nitrite nitrogen: 0.3-1mg/L, tend to 1mg

Zinc (mg/L)

Photos	
	
	





APPENDIX 2 MATLAB CODE FOR CALCULATING *SA*

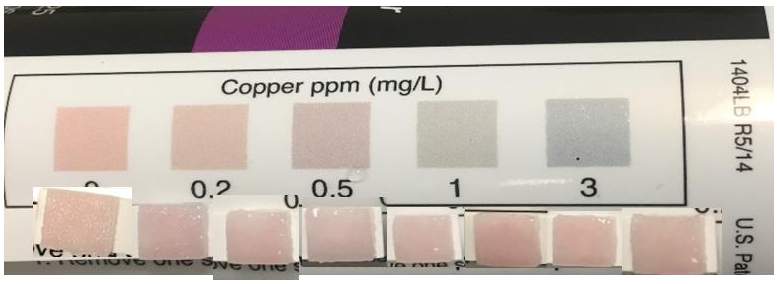
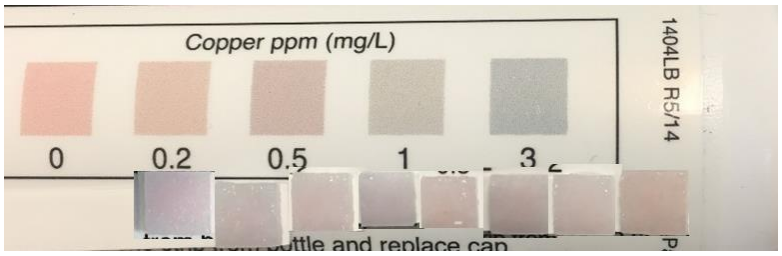
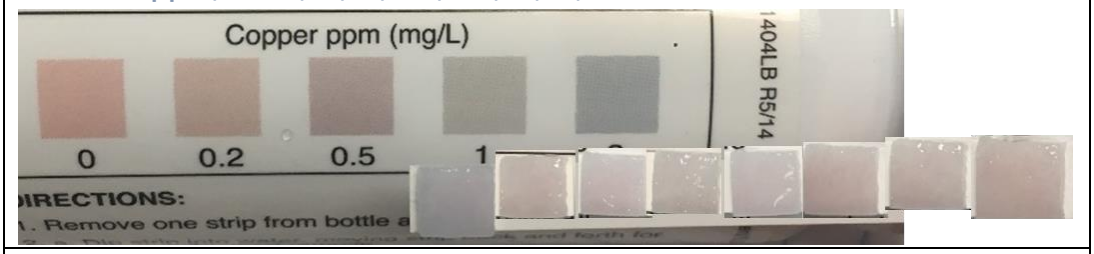
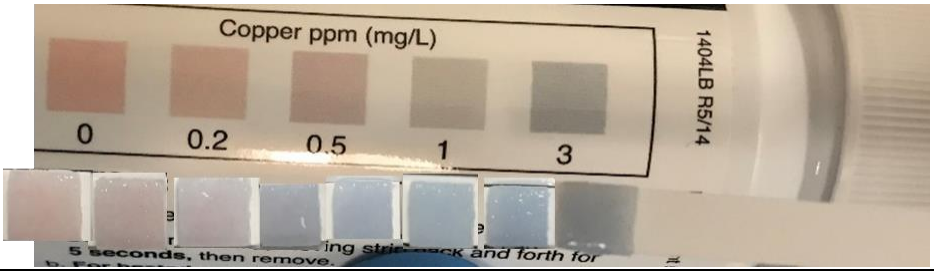
% This file creates a binary image of an image, and calculates the %

percentage of black (0) pixels.

```
% Open the image and set as a variable %
Need to add file location
uiopen('101A.JPG',1);
I = imread('101A.JPG');

% Convert image to grayscale image(GI), then remove any lone dark spots:

GI = rgb2gray(I);

% Convert image to grayscale image(GI), then remove any lone dark spots
% The value of 26 can be adjusted, or this step can be skipped
GI= imfill(GI,26);

% Convert grayscale image to binary image (BI) with adjutable sesnitivity
BI = imbinarize(GI);
% Remove any lone white spots smaller than specified number of pixels
% The value of 20 can be adjusted, or this step can be skipped
BI = bwareaopen(BI,20);
% Show grayscale and binary side by side imshowpair(GI,BI,'montage')
% Calculate and display the percentage of voids
N = numel(BI);
% NT = sum(BI(:));
% P = (1-
(NT/N)); %
display(P);
display(N); %
display(NT);
```

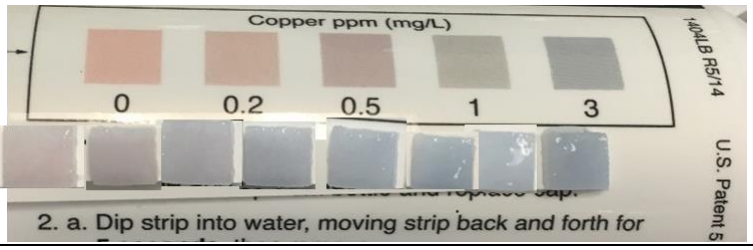
APPENDIX 3 COPPER INDIVIDUAL EXPERIMENT

The concentration tested by strips

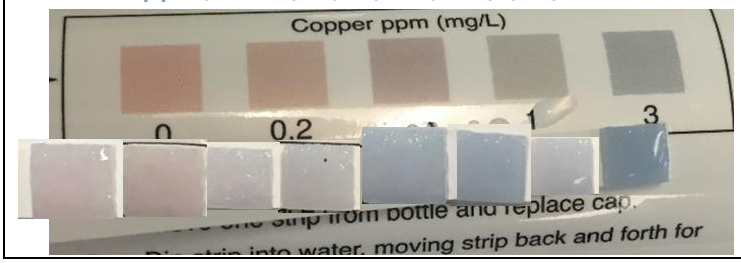
Photos
C0 = 0ppm, ET:0h,1h,6h,18h,36h,3d,5d,7d 
C0 = 0.63ppm, ET:0h,1h,6h,18h,36h,3d,5d,7d 
C_0 = 0.71ppm, ET:0h,1h,6h,18h,36h,3d,5d,7d 
C_0 = 2.4 p pm, ET:7d,5d,3d,36h,18h,6,1h,0h 

C_0 = 2.4 p pm, ET:7d,5d,3d,36h,18h,6,1h,0h

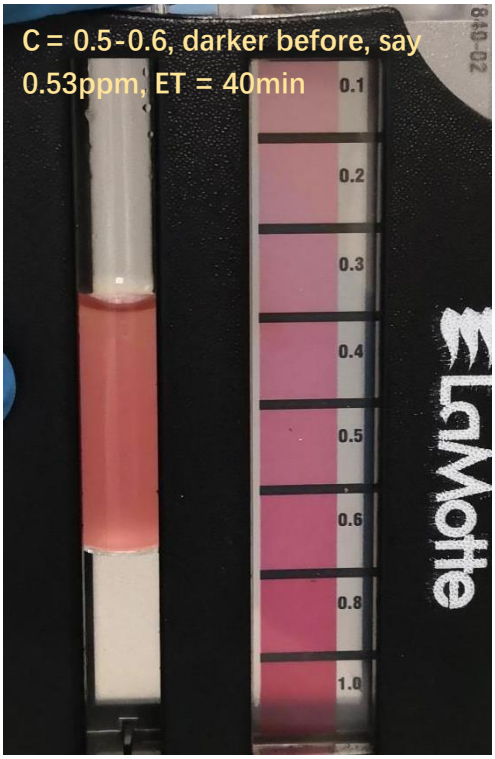
C_0 = 2.4 ppm, ET:7d,5d,3d,36h,18h,6,1h,0h



C_0 = 2.4 ppm, ET:7d,5d,3d,36h,18h,6,1h,0h

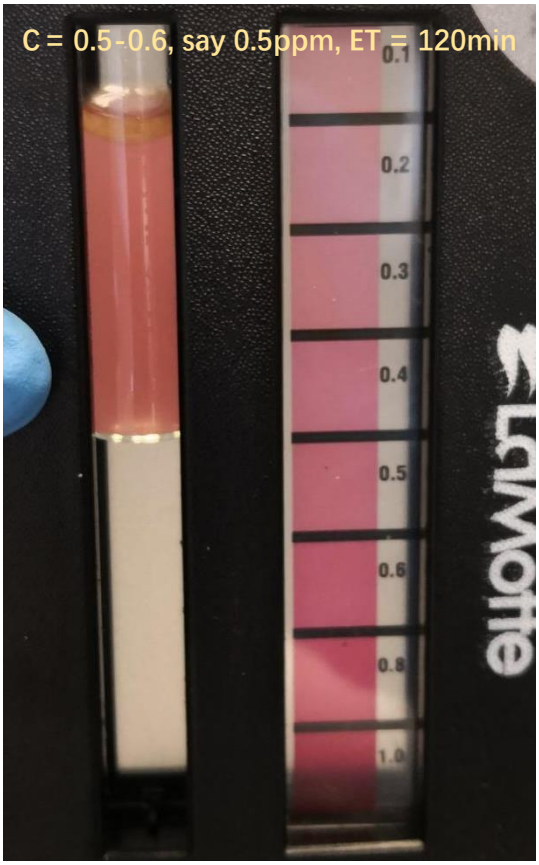


APPENDIX 4 CADMIUM TESTED BY LAMOTTE KIT IN MID-SCALE EXPERIMENT

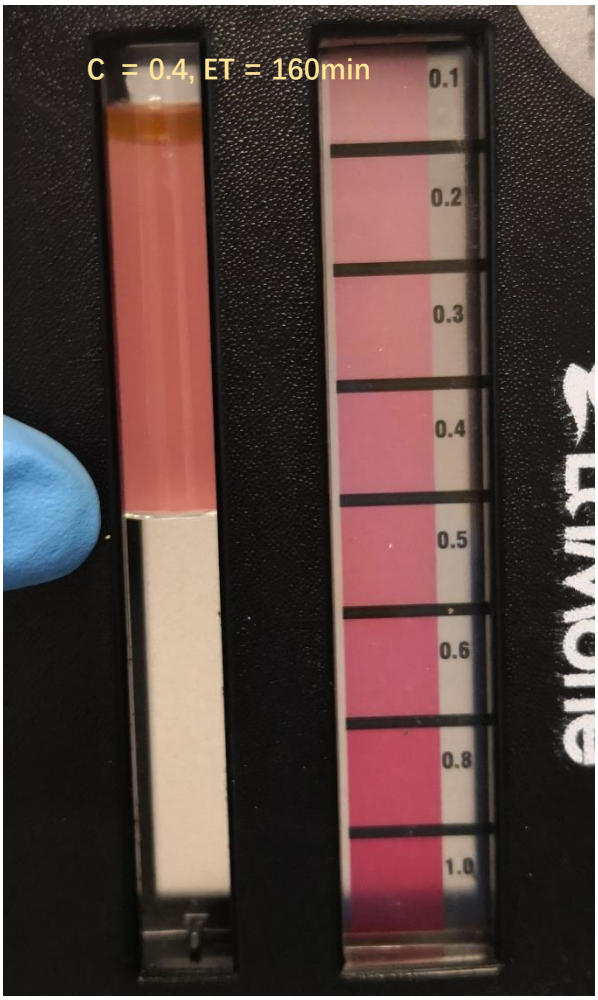
 C = 0.5-0.6, darker before, say 0.53ppm, ET = 40min 0.1 0.2 0.3 0.4 0.5 0.6 0.8 1.0 LaMotte	 C = 0.5-0.6, lighter than before, say 0.45ppm, ET = 60min 0.1 0.2 0.3 0.4 0.5 0.6 0.8 1.0

C = 0.3-0.4, lighter than first one, say 0.35ppm, ET = 80min

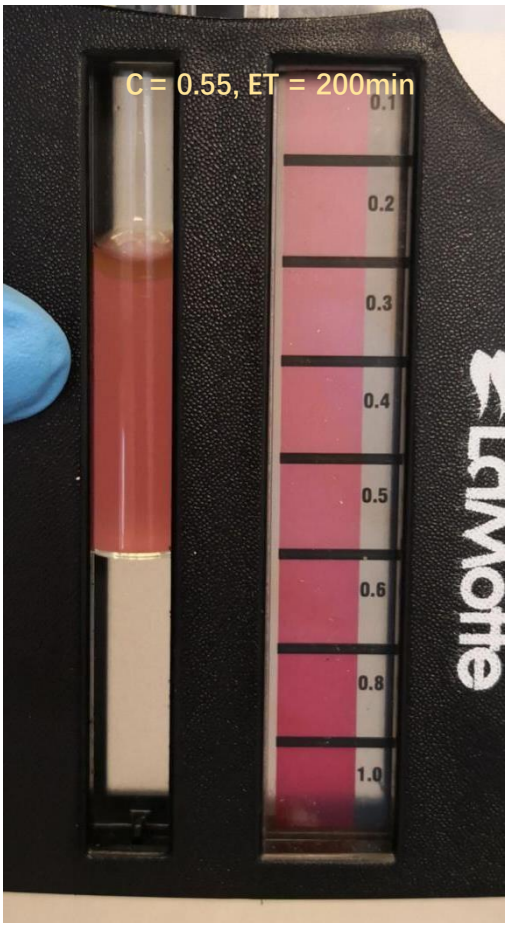
C = 0.3-0.4, lighter than before, say 0.3ppm, ET = 100min

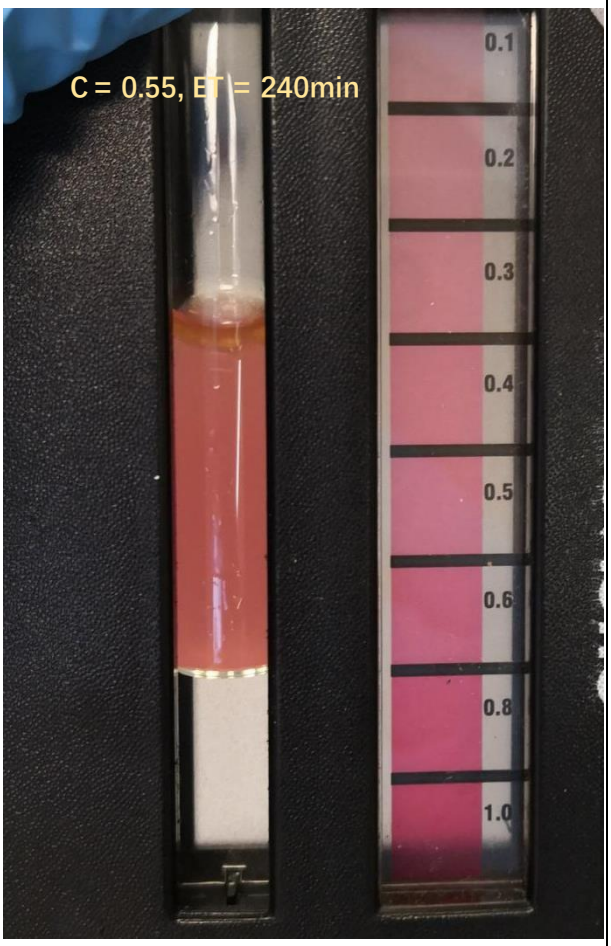

C = 0.5-0.6, say 0.5ppm, ET = 120min
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0
Lamotte


C = 0.45, ET = 140min
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0
Lamotte

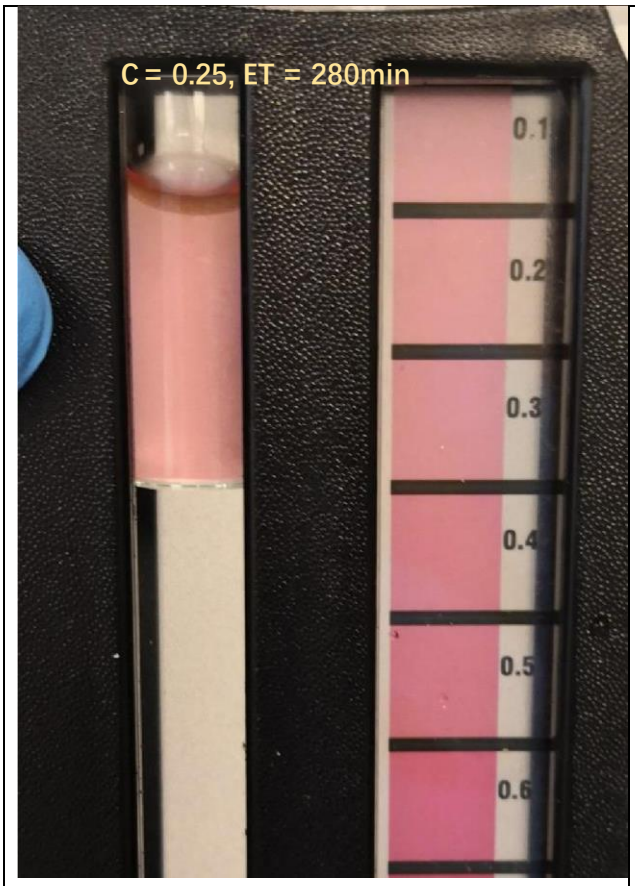

C = 0.4, ET = 160min
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0
LaMotte


C = 0.4, ET = 180min
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0
LaMotte

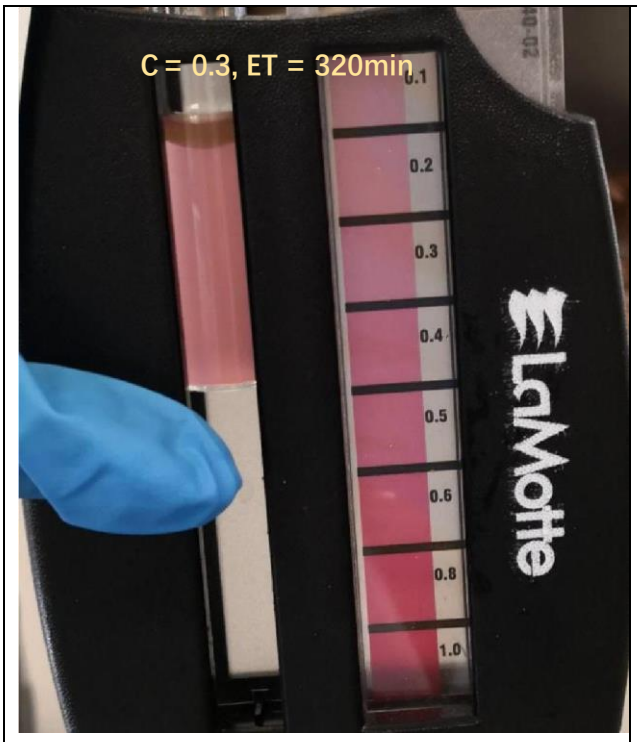
 C = 0.55, ET = 200min 0.1 0.2 0.3 0.4 0.5 0.6 0.8 1.0 LaMotte	 C = 0.35, ET = 220min 0.1 0.2 0.3 0.4 0.5 0.6 0.8 1.0 LaMotte

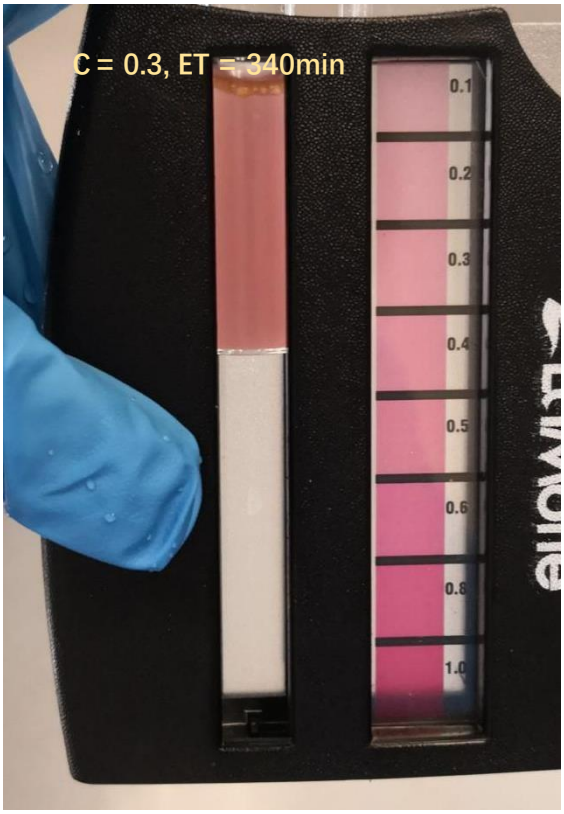

C = 0.55, ET = 240min
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0

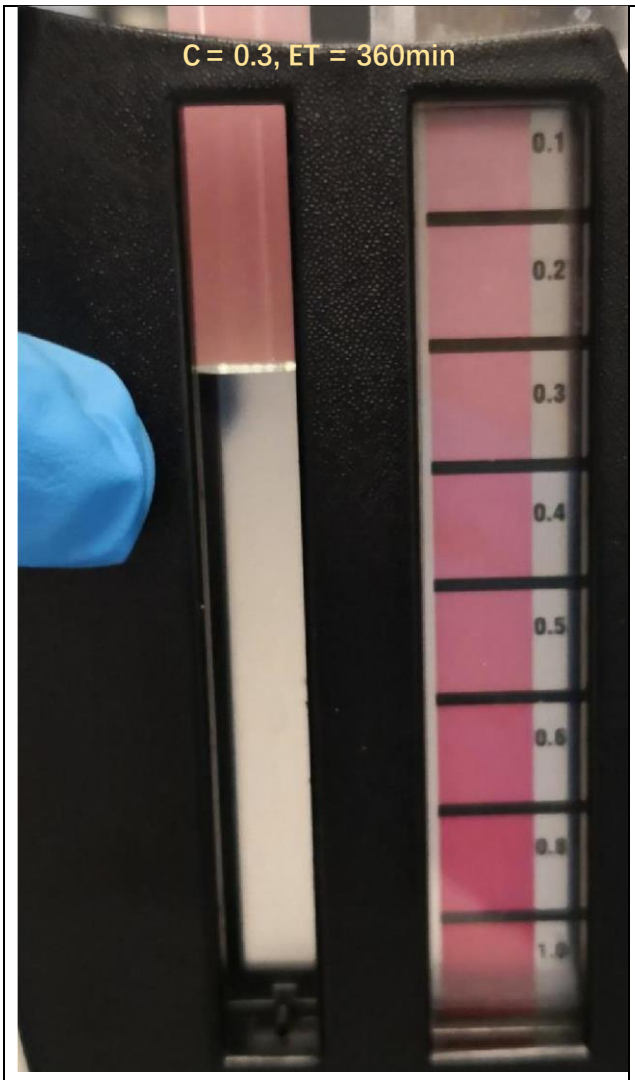

C = 0.5, ET = 260min
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0
LaMotte

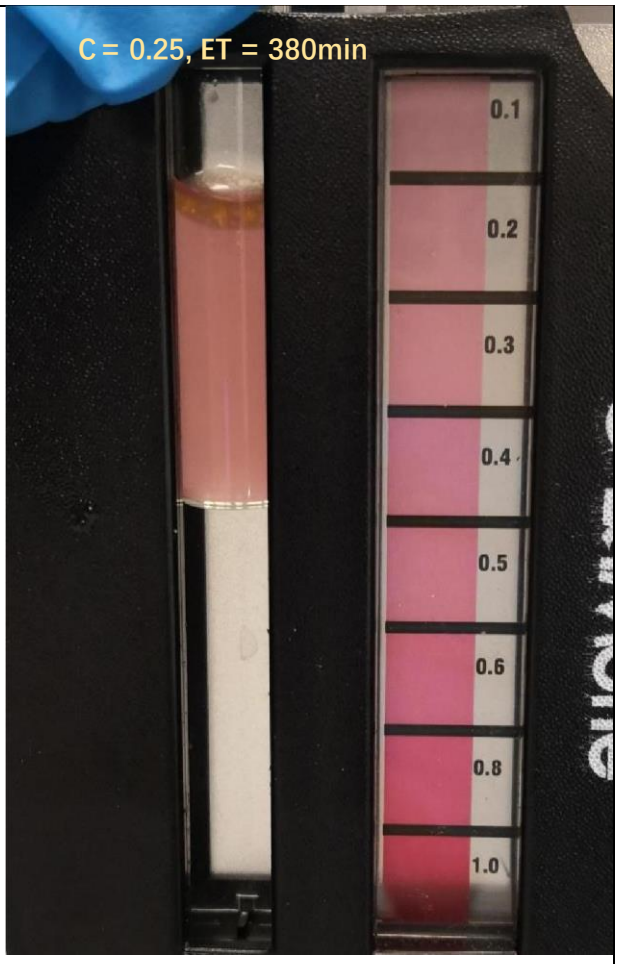

C = 0.25, ET = 280min
0.1
0.2
0.3
0.4
0.5
0.6


C = 0.55, ET = 300min
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0
LaMotte


C = 0.3, ET = 320min
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0
LaMotte

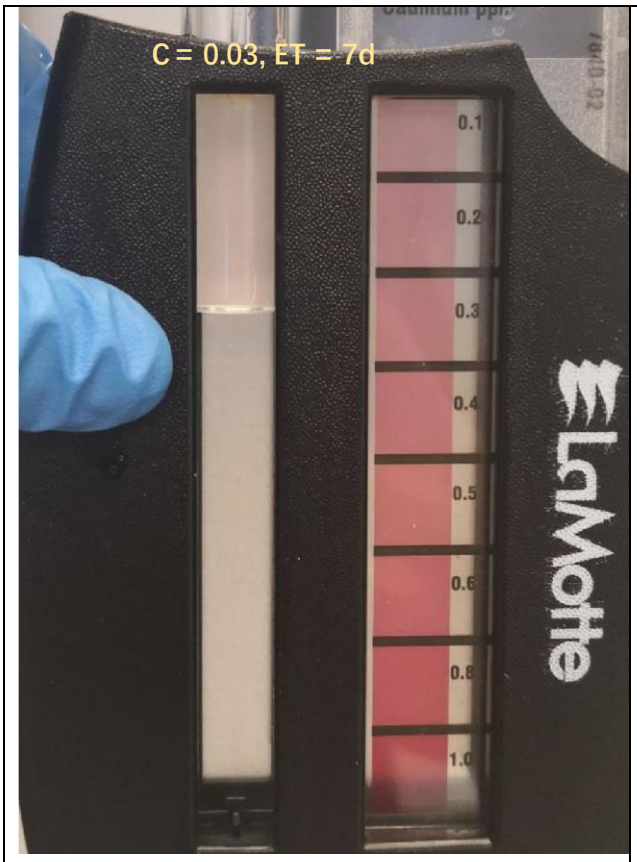

C = 0.3, ET = 340min
0.1
0.2
0.3
0.4
0.5
0.6
1.0


C = 0.3, ET = 360min
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0


C = 0.25, ET = 380min
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0


C = 0.08, ET = 1d
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0
LaMotte


C = 0.05, ET = 4d
7840-02
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0
LaMotte


C = 0.03, ET = 7d
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0
LaMotte