EFFECTS OF pH ON ADSORPTION OF COPPER (II) ONTO GROUND PEANUT
HULLS

A thesis presented to the faculty of the Graduate School of Western Carolina University in
partial fulfillment of the requirements for the degree of Master of Chemistry.

By

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a_o	ionic radius
A	specific surface area
A	absorbance
ACS	American Chemical Society
ASTME	American Society for Testing Materials
ads	adsorbed
aq	aqueous
b	relative binding strength
b	path length
C_e	equilibrium concentration
c_i	concentration of ion i
C_o	initial concentration
c	concentration of absorbing species
C_A	concentration of acid needed to reach a point on the titration curve
C_B	concentration of base needed to reach a point on the titration curve
ε	molar absorptivity
F	Faraday's constant
FAAS	flame atomic absorption spectroscopy
γ	activity coefficient
$[H^+]$	concentration of protons (converted from pH)
HD	high density
I	ionic strength
l	path length
LD	low density
m	concentration of hull mixture
$m_{Cu\text{-}adsorbed}$	mass of copper adsorbed
m_{hulls}	mass of hulls
$m_{solution}$	mass of solution
MCB	Matheson Coleman Bell
$[OH^-]$	concentration of hydroxide (converted from pH)
pH_{pzc}	pH at the point of zero charge
pK_a	(-)log of the acid dissociation constant
q_e	surface coverage
Q_o	adsorption capacity
RMSE	root mean square error
σ	surface charge density
$\bar{\sigma}$	specific surface charge density
SCFM	surface complex formation model
Z_i	charge of ion i

ABSTRACT

EFFECTS OF pH ON ADSORPTION OF COPPER (II) ONTO GROUND PEANUT

HULLS

Stephen Adom, Master of Science in Chemistry

Western Carolina University (April 2020)

Advisor: Dr. Carmen Huffman

This study explores the influence of surface charge on the adsorption mechanism of Cu(II)

onto ground peanut hulls at different pH values. Ground hulls can be separated into two types

based on their density. For both types of hulls, adsorption capacity increases with pH, but low

density (LD) hulls adsorb more Cu(II) than high density (HD) hulls. The adsorption edge,

which represents the pH range where a great increase in percent adsorption as a function of

pH was observed, was lower for LD hulls than for HD hulls. For LD hulls, the maximum

adsorption of copper (II) ions onto hulls was 79.1 % at pH 4 and the minimum adsorption

was 65.2 % at pH 1 with a pH adsorption edge of 1.3-4.2. For HD hulls, the maximum

adsorption was 72.3 % at pH 5 and the minimum adsorption was 64.6 % at pH 2 with a pH

adsorption edge of 2-5.1. Measurements of pH before and after adsorption showed

approximately no change in pH when the initial pH was less than 3.5 and a decrease in pH

when the initial pH was > 3.5, suggesting a pH-dependent adsorption mechanism involving

physisorption and/or chemisorption at low pH and cation exchange at pH 3.5 or greater.

When pH was held constant using a buffer during adsorption, the maximum

adsorption of Cu(II) ions to hulls was 99.8 % at pH 6 and the minimum adsorption was 10.9

% at pH 2 for LD hulls. For HD hulls, the maximum adsorption was 99.4 % at pH 6 and the

minimum adsorption was 4.8 % at pH 2. A fit of the data to the Langmuir model gave

maximum adsorption capacities of 14.6 and 11.43 mg Cu/g hull at pH 6 for LD and HD hulls, respectively. The increase in adsorption with pH observed in both studies is likely due to a reduction of competition between H^+ ions and Cu(II) ions for binding sites on hulls at high pH values and also a more negative surface charge that binds positively charged Cu(II) ions at high pH values.

To better understand the adsorption mechanism, the hull surface charge was examined. Acidimetric-alkalimetric titrations were performed at varying ionic strengths. The exact pH_{pzc} could not be determined since acidimetric-alkalimetric titrations were not performed with high enough resolution. The value was however presumed to be between pH 4 and pH 11 based on the data acquired. The titration curves lacked variation with ionic strength which suggests surface charge on hulls may not be affected by ionic strength.

For both hull types, surface charge calculated from the titration data increased with pH. Though this result was not expected, the peanut hulls are somewhat soluble in basic solution, which could explain the anomaly. Previous studies have shown that the addition of hulls to basic solution increases the pH, which makes the hulls appear to be negatively charged. A more likely occurrence is that an alkaline substance is being leached into the solution causing the pH to increase. Despite these complications, a local maximum of surface charge was observed at pH 3.5, which coincides with the pH for which the proposed adsorption mechanism shifts. This suggest that something unique is occurring at the hull surface at this pH.

CHAPTER ONE: INTRODUCTION

Motivation

Mining activities are practiced in many river basins across the globe causing the release of heavy metal containing waste into those water bodies. For example, in Ghana, many rivers including the Pra River, Birim River, River Ankobra, River Tano, River Bia, River Offin, and River Oda are contaminated with heavy metals.[1] In 2017, a study was conducted to ascertain the level of contamination of heavy metals in the Pra River Basin.[1] Two hundred sixteen water samples were collected from 27 sampling points along the Pra River basin during the dry and wet seasons, and the concentrations of nine metals were determined. The research revealed that the concentrations of dissolved Pb, Cd, Cr, Ni, Fe, and Zn exceeded the safe drinking water guidelines given by the Nemerow's Pollution Index (NPI).[1] Duncan et al. recommended that continuous research be conducted on the presence of these pollutants to determine effective remediation measures.[2]

A similar study was also conducted in Dunkwa-on-Offin in the Central Region of Ghana where the mean concentrations of some selected metals (Pb, Cu and Hg) at 14 sites were compared to the safe levels established by the Environmental Protection Agency (EPA) in Ghana and the World Health Organization (WHO).[2] The mean recorded concentrations of the metals far exceeded the EPA and WHO limits.[2]

Additionally, high concentrations of mercury and zinc have been reported in the Wassa West and Talensi-Nabdam Districts in Ghana.[3,4] This pollution resulted from neglecting treatment of heavy metal waste generated during mercury amalgamation and roasting of gold to obtain pure gold. Untreated heavy metal wastes leached into water bodies contaminated the entire ecosystem by forming poisonous methyl mercury and mercury oxide.[3,4]

Some industrial activities also result in wastewater contamination with heavy metals. Among the major generators of heavy metal containing waste in water are the textile industries. The waste usually emanates from the dyeing process. Metals used in this process include copper, chromium, nickel and lead which are toxic and carcinogenic.[5] Nuclear power facilities also generate metal-containing toxic waste.[6] The metal containing waste can cause pollution if not treated before release into water bodies.[5]

Unlike other wastes, heavy metal containing waste are persistent and non-biodegradable and hence can accumulate to toxic levels with time.[7] These accumulated heavy metals in natural waters, if untreated, are capable of bioaccumulating through the food chain in nearby ecosystems and drinking water sources thus resulting in serious health problems.[8] There is therefore a need for wastewater to be treated for heavy metal contamination before being released into natural waters for human consumption.[9]

Although there are conventional methods of treating heavy metal contamination, including chemical precipitation, ion exchange, reverse osmosis, membrane electrolysis, and coagulation-flocculation,[10] these methods can be costly and have drawbacks such as toxic sludge generation, high chemical and energy consumption, metallic hydroxides production, scaling of $CaCO_3$ and $CaSO_4$, and the need for trained personnel and additional pretreatment procedures. [10]

Biosorption is an adsorption process that utilizes natural products.[11] Although less efficient than the current treatment methods, this alternative wastewater treatment process is reversible, rapid, simple, environmentally friendly, cost effective and can remove contaminants from water even at dilute concentrations.[12] Biosorption can also be used for large scale waste water treatment. The waste water can pass through a column packed with the biosorbent. As the sorbent gets saturated through the metal ion adsorption, high

concentrations of counter ions such as sodium can be passed through the sorbent to replace the metal ions, and the process can be repeated until the water is purified.

Background

Adsorption and Biosorption

Adsorption is a process in which a substance (the adsorbate) is removed from an aqueous state by becoming trapped on the surface of a solid (the adsorbent) through physical or chemical interactions.[13] Two main types of interactions describe how particles adhere to surfaces. In chemisorption, the binding forces involved are valence forces and intermolecular forces similar to those that operate in chemical compound formation. The binding forces can thus form ionic, covalent, metallic or hydrogen bonds. Regardless of the type of interaction, the bond is specific to the chemical nature of both the adsorbate and adsorbent.[14] Figure 1 shows an example of chemisorption of copper (II) ions onto alcohol groups. In contrast, physisorption involves adsorption of particles onto surfaces by weak non-specific Van der Waals forces and thus do not involve a significant change in the electronic structure of the species involved. (Figure 2). One major difference between the two adsorption processes is that, for chemisorption, the chemical nature of the adsorbate may be altered by the surface reaction such that the original species cannot be recovered while with physisorption, the adsorbed species are chemically identical with those in the fluid phase and therefore the chemical nature of the fluid is not altered by adsorption and subsequent desorption. [13]
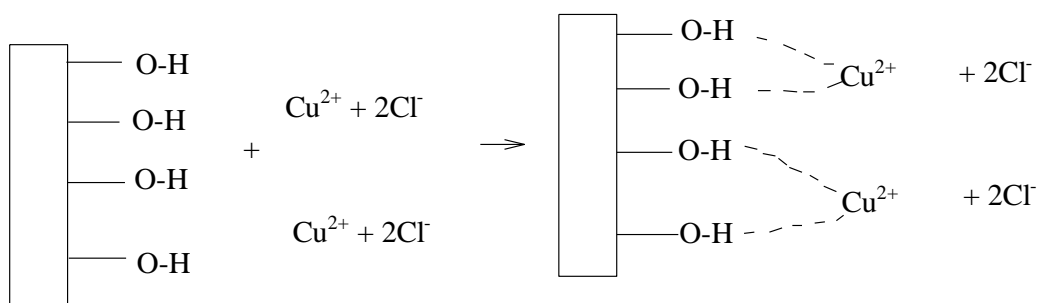
Figure 1. Schematic representation of chemisorption of copper (II) to alcohol groups on an adsorbent.

Another proposed mechanism of adsorption is cation exchange. According to this mechanism of adsorption, metal ions with higher affinity for the adsorbent adsorb onto the binding sites as a replacement for ions on the adsorbent surface. As shown in Figure 3, cation exchange can be described as an extreme form of chemisorption in which the adsorbent is chemically altered. Cation exchangers are usually mixtures of salts and acids which enable them to exchange positively charged ions.[15]
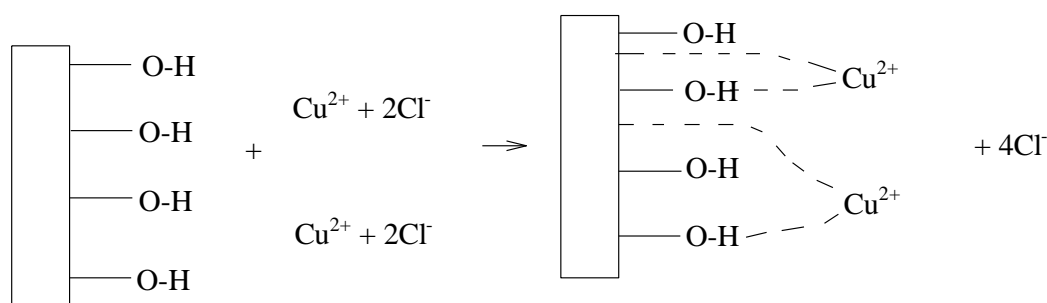
Figure 2. Schematic representation of physisorption of copper (II) to alcohol groups on an adsorbent with random interactions between the ion and the surface.
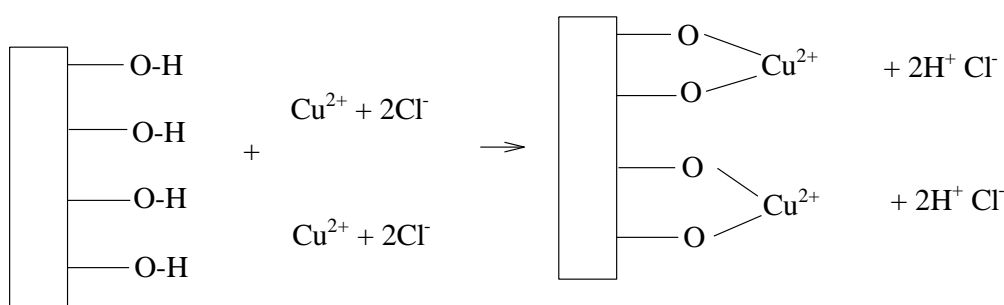
Figure 3. Schematic representation of cation exchange of copper (II) with H^+ ions in alcohol groups on an adsorbent.

Biosorption is a form of adsorption that uses biological materials to accumulate heavy metals (or other contaminants) from wastewater through metabolically mediated or physico-chemical pathways of uptake.[16] The process involves a solid phase (sorbent or biosorbent; adsorbent; biological material) and a liquid phase (solution, normally aqueous) containing a

dissolved species to be sorbate (adsorbate, metal). Due to the affinity of the adsorbent for the adsorbate species, the latter is attracted and bound to the adsorbent surface. The process is depicted by the equation

$$M \text{ (aq)} \rightleftharpoons M \text{ (ads)}$$
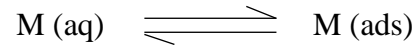
where M represents a metallic adsorbate, aq denotes the sorbate in an aqueous solution and ads represents the sorbate adhered to the adsorbent surface. The sorption of the adsorbate onto the adsorbent continues until equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases.[16]

Adsorption Models

Various adsorption theories including the Langmuir isotherm, the Freundlich isotherm, the Temkin isotherm, and the Dubinin–Radushkevich isotherm are used to model adsorption equilibrium.[17] The Langmuir model is specifically adopted for this research because it is a theoretical construct commonly used to describe the biosorption process and only two parameters are needed to fit data.[18] It describes in quantitative terms the equilibrium distribution of the formation of a monolayer adsorbate on the outer surface of the adsorbent.[19] One of the parameters, adsorption capacity (Q_o), indicates how much adsorbate can bind to adsorbent. Even if the adsorption capacity is not 100 % accurate, the relative adsorption capacity can be helpful in comparing adsorption from system to system.

This model is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.[17] Mathematically, the Langmuir model is represented as

$$q_e = \frac{b Q_o C_e}{1 + b C_e} \tag{1}$$

where C_e is the equilibrium concentration of adsorbate, q_e is the surface coverage [the amount of adsorbate per unit of adsorbent at equilibrium], Q_o is the adsorption capacity and b is the Langmuir isotherm constant, which is related to the binding strength.

The Langmuir isotherm is graphically represented as shown in Figure 4. As C_e increases, a corresponding increase in q_e values is observed because more metal ions are made available to occupy the binding sites on the adsorbent. As binding sites become saturated, q_e approaches the adsorption capacity, Q_o.
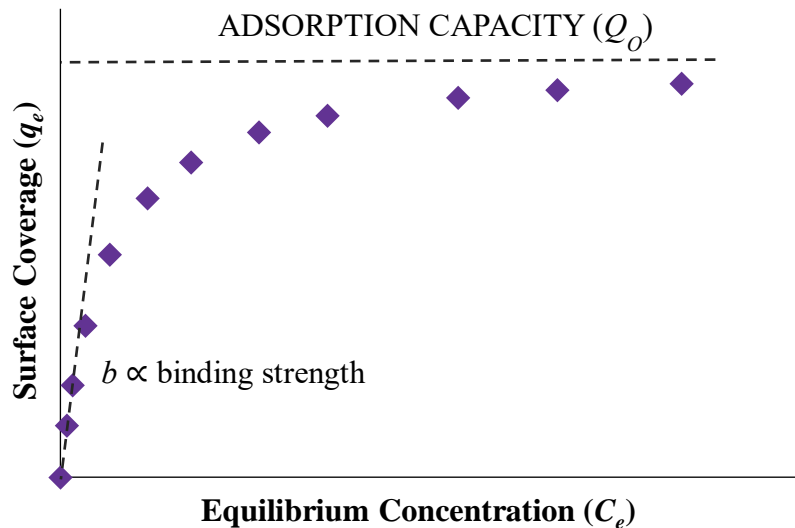
Figure 4. Graphical representation of the Langmuir adsorption isotherm.

The Langmuir model is an adsorption isotherm since it is developed for a specific temperature. Though it is useful, it has drawbacks. First, it is unable to accurately predict the adsorption equilibrium under changing ionic strength.[18] Also it fails to explain how and why adsorption occurs. Moreover, if the model parameters are obtained based on experiments under one set of conditions such as low pH, usually the same model parameters cannot give accurate predictions under different conditions such as high pH. In addition to the pH effect, it is experimentally shown that the type and concentration of electrolytes and complexing

agents play important roles in adsorption which are not considered with this model.[18] Nonetheless, the model is convenient for relative comparisons.

Surface charge density (σ) is related to the distribution of charged functional groups on a surface, which can be influenced by pH. As pH increases, surface charge decreases. An analysis of surface charge density as a function of pH can yield the point of zero charge (pH_{pzc}), which may elucidate the role of surface charge on adsorption. Generally, the surface charge is negative when pH of the solution is above pH_{pzc}, and positive when pH is below pH_{pzc}. This behavior implies that at higher pH, adsorption of metal ions will be higher.[18] While surface charge determination is helpful in determining the effects of pH on adsorption, modeling adsorption using a surface complex formation model (SCFM) is beyond the scope of this work.

Cation Exchange and pH

Many natural substances including proteins, cellulose, lignin and soil particles show ion exchange properties which influences how they function in nature.[20] Ion exchange materials are not soluble and contain loosely held ions which can be exchanged with other ions in solution. When a metal ion solution is mixed with an adsorbent, the ions make contact with the binding or exchange sites. Generally, affinity of exchangers for ion exchange materials is greatest for large ions with high valency.[15] For example, sodium ions on a resin surface can be exchanged for calcium ions in solution. Similarly, ion exchange materials bind to metal ions more readily than hydrogen ions. The metal ions are adsorbed onto the exchange site with the release of hydrogen ions into the solution, thus decreasing the pH of the solution.

The acid strength (pK_a) of ion exchange materials can also influence their surface charge at any pH and hence their adsorption capability. For example, if alcohol groups with a pK_a of about 10-18 form the major components of an adsorbent, then at pH 2-6, which is lower than the pK_a, the surface of the adsorbent will be acidic (neutral surface charge) and

cannot be an effective adsorbent. If high adsorption is observed with such an adsorbent, then the adsorption mechanism is not likely cation exchange, or other functional groups on the adsorbent are responsible for the adsorption. If a functional group such as alkanoic acid, with a pK_a of about 2-4, forms the major component of the adsorbent, then the surface will be acidic (neutral surface charge) at pH 1-2 resulting in low adsorption, or conjugate base (anionic surface charge) will predominate at pH 5-6 resulting in high adsorption in this pH range.

In cation exchange processes, decreasing the pH of a metal ion mixture decreases the adsorption capacity of adsorbent due to the competition between H^+ and metal ions for binding sites on the adsorbent.[21] Increasing pH increases the ability of metal ions to precipitate out of solution by forming metal hydroxides or oxides which cannot be adsorbed onto the adsorbent.[21] Determining the ideal pH where maximum adsorption is likely to occur is therefore important for waste water treatment.

Peanut Hulls

Previous research has indicated that peanut hulls are good biosorbents for heavy metal ions in waste water.[9,22–25] Peanut hulls contain a significant amount of cellulose and lignin.[26] Figure 5 and 6 represent cellulose and monomers of lignin, respectively, which form the major components of peanut hulls.[26]
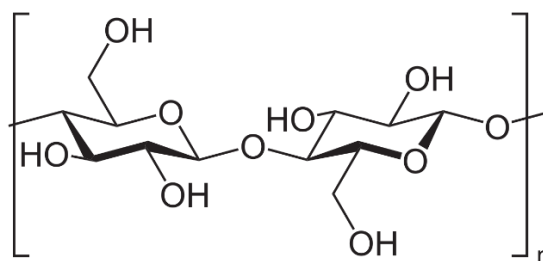
Figure 5. Molecular structure of cellulose.

The three monomers of lignin, *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which are synthesized via the phenylpropanoid pathway in plants, combine in different irregular patterns depending on the substance that contains it.[27] The structures show that lignin and cellulose have many –OH groups in which the H^+ ions are loosely held making them good candidates for use as cation exchangers via chemisorption, physisorption and cation exchange mechanisms.[26]

coniferyl alcohol   sinapyl alcohol   *p*-coumaryl alcohol
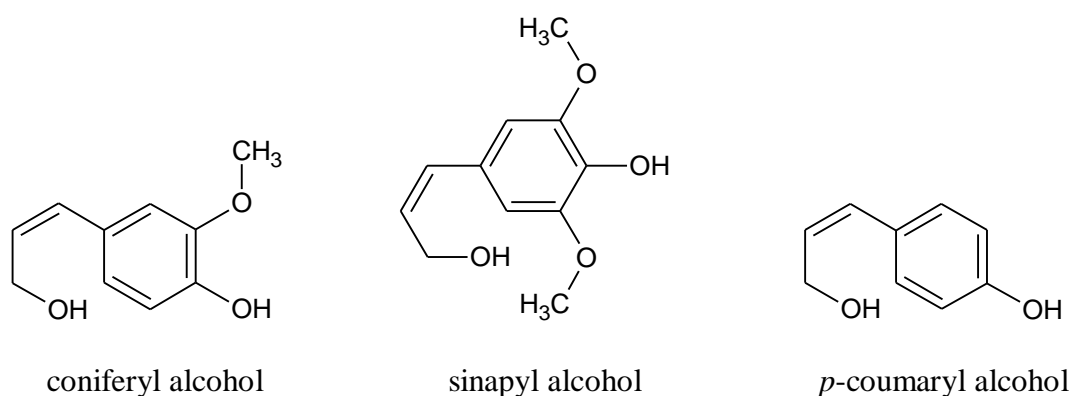
Figure 6. Molecular structures of the three monomers of lignin.

Research has shown that peanut hulls can be separated into high density hulls and low density hulls.[28,29] Researchers determined that low density hulls have more empty spaces and hence a higher surface area per gram than high density hulls. This results in a larger area over which to accumulate metals and for adsorption or ion exchange to occur.[28]

Research Goals and Methodology

In this research, adsorption of copper (II) ions onto low density and high density peanut hulls was studied. Copper was specifically used because it is safe to work with. It is less toxic and more environmentally friendly than other heavy metals such as arsenic, cadmium, chromium, lead, and mercury which are very toxic metals known to induce multiple organ damage, even

at lower levels of exposure.[6] It is also a common pollutant - associated with mining operations and Cu-based pesticides commonly used on vegetables. The goals of this research were to:

1) Determine the effect of pH on surface charge of low and high density peanut hulls.

2) Determine the effect of pH on adsorption of Cu(II) to low and high density peanut hulls.

3) Propose a mechanism for adsorption of Cu(II) to low and high density hulls.

An acidimetric-alkalimetric titration was carried out under varying ionic strength to determine the surface charge of hulls as a function of pH. This study helps to ascertain the distribution of ionizable functional groups on the hulls surface. A variable pH study in which the initial pH was set to a known value and allowed to fluctuate during adsorption was used to determine if cation exchange was occurring. Evidence of cation exchange includes a decrease in pH. Lastly, a constant pH study in which adsorption occurs in buffered acidic solutions is performed. Data was fit to a Langmuir isotherm to determine relative adsorption capacities and binding strengths.

CHAPTER TWO: EXPERIMENTAL

Materials

Ultrapure water with 18.2 cmΩ from a Barnstead water filtration system (Thermo Scientific, Model 7119) was used throughout. Roasted, unsalted peanuts in the shell were purchased from Ingles in Sylva, North Carolina, USA. Laboratory grade pHydrion buffer capsules were purchased from Fisher Scientific. Buffer capsules were dissolved in 100 mL ultrapure water to prepare buffer solutions to prepare pH 2 and 3 (potassium biphthalate and sulphamic acid), pH 4 (potassium biphthalate), pH 5 (sodium phosphate dibasic and potassium biphthalate) and pH 6 (potassium phosphate monobasic and sodium phosphate dibasic) solutions. Copper (II) chloride dihydrate (CAS 10125-13-0), nitric acid (trace metal grade), sodium hydroxide (reagent grade) and hydrochloric acid (ACS grade) were all purchased from Fisher Scientific and used without further purification. Potassium hydrogen phthalate (ACS grade, MCB brand), and sodium chloride (Puratronic 99.99% grade, Alfa Aesar brand) were used for acidimetric-alkalimetric titration. Compounds were used without further purification.

Flame atomic absorption spectroscopy (FAAS, Perkin Elmer PinAAcle 900F) was used to measure copper concentration. A tube revolver (Fisher, model #88881001) was used to mix copper solutions with hulls. A pH meter (Vernier software and technology, 5 V, 100 mA) was used to determine pH of solutions. Syringe (10 ml Luer Slip Tip) and syringe filters (Sartorius RC 0.45 μm) were purchased from Exel International and used to filter solutions for FAAS. All samples and standards were stored in centrifuge tubes (Polypropylene and polythene) purchased from Fischer Scientific.

Hull Preparation

The method used for hull preparation was adapted from previous research.[28–31] A single batch of hulls was prepared and used to avoid batch to batch variation. Hulls were manually

separated from the seed coats and peanuts. They were then ground using a Hamilton Beach Fresh Grind Coffee Grinder (#80335). Ground hulls were separated by size using U.S.A. Standard stainless steel test sieves (ASTM E-11 Specification, Fisher Scientific Co.) with mesh sizes 1 mm and 500 µm on a sieve shaker (Model SS-15, Gilson, Inc.). The hulls retained by the 500 µm sieve were collected and used for the study. The collected hulls were washed with 60 ºC water, followed by ice cold water, and then dried at 50 ºC in an air oven (VWR International, Model 1300U).

A known mass of hulls were mixed with water with slight stirring. As shown in Figure 7, floating (low density, LD) and sinking (high density, HD) hulls were separated by decantation. Hulls were then vacuum filtered and placed to dry on a watch glass in a 50 ºC oven until a constant mass was achieved. The hulls were stored in labelled plastic bags for future use.
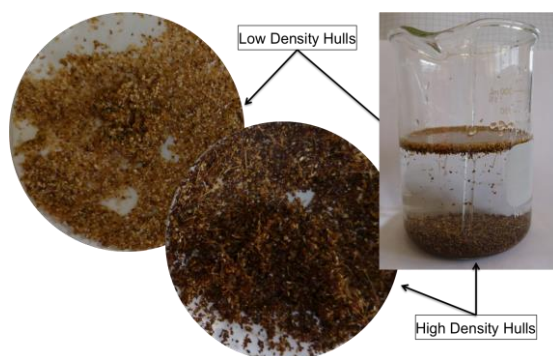
Figure 7. Separation of low and high density hulls.

Acidimetric-Alkalimetric Titration

Boiled ultrapure water was used to prepare 0.05 M sodium chloride solution. Peanut hulls (0.5 g) were added to a conical flask containing 50 mL of 0.05 M sodium chloride. The conical flask was covered with parafilm and the hulls were kept in solution for 24 h. A standard solution of potassium hydrogen phthalate was used to standardize 0.5 M NaOH solution. The NaOH solution was also used to standardize 0.05 M HCl. Two separate

titrations, one each for acidimetric and alkalimetric titration, were performed. The hulls in the NaCl solution were titrated using 0.142 M NaOH during which the pH of the hull mixture was recorded at 10 min intervals. Similarly, a separate hull mixture was also titrated with 0.008 M HCl. The conical flask was covered with parafilm during the titrations to avoid dissolutions of carbon dioxide and the equilibrium time needed to establish surface charge was assumed to be 10 min. The titrations were repeated for both hull types using 0.5 M and 0.005 M sodium chloride to soak the hulls.

Variable pH Adsorption

Drops of 25 % HCl were added to ultrapure water (pH 7) amid constant stirring to prepare 50 mL of a pH 1 HCl solution. Approximately 0.03 g of $CuCl_2.2H_2O$, 0.5 g of ground peanut hulls and 10 g of the HCl solution were added to a 15 ml centrifuge tube. The process was repeated using HCl solutions with pH values of 2, 3, 4, 5 and 6. Mixtures were allowed to equilibrate for 24 h on a revolver, filtered and diluted with 5 % HNO_3 before analysis using FAAS.

Constant pH Adsorption

In each adsorption experiment, solutions of $CuCl_2$ were prepared in the concentration range of 10-1000 ppm by serial dilution in pH 2, 3, 4, 5, and 6 buffer solutions. Approximately 10 g of each copper (II) solution was allowed to equilibrate with 0.5 g of peanut hulls. After equilibrating on a revolver for 24 h, the solutions were filtered, diluted with 5% HNO_3, and measured using FAAS.

Flame Atomic Absorption Spectroscopy

Determination of metal concentrations was carried out using a Perkin Elmer flame atomic absorption spectrometer (FAAS, PinAAcle900F). Three replicate absorption measurements were collected for each sample at a flow rate of 2.5 L/min and the mean was used to calculate the concentration.

The FAAS measured the absorbance of Cu(II) standards in the concentration range of 0.5-12 ppm and determined the equilibrium concentrations of the samples using the Beer-Lambert law:[32]

$$A = \varepsilon l c \qquad (2)$$

where l is the path length in centimeters, c is the concentration of the absorbing species and ε is the molar absorptivity.

The margin of error of the FAAS measurements was experimentally determined by repeated measurements of standards and found to be less than 10 %. The error in each FAAS measurement and the percent adsorption values were determined by error propagation using equations in Appendix.

CHAPTER THREE: RESULTS AND DISCUSSION

Acidimetric-Alkalimetric Titration

In adsorption studies, pH is one of the relevant impact factors that affect the binding of heavy metal ions to an adsorbent surface. This is because, for experimental conditions with pure waters, pH of solution affects the binding sites on the surface of the adsorbent, the chemical nature of the adsorbent and the amount of hydrogen ions that can compete with the metal ions for binding sites.[33]

Acidimetric-alkalimetric titrations were conducted with each hull type at three different ionic strengths to probe the surface charge of the hulls, which can dictate how the hulls interact with ions in solution. Figure 8 and 9 show the results obtained using LD hulls and HD hulls, respectively. The acid volumes are listed as negative values so that the addition of acid lies to the left in the plot.. The positive values on the x-axis represent volumes of NaOH added.

The pH_{pzc} is the pH for the point of zero charge and is defined by the pH at which all three curves intersect. However, for both LD and HD hulls, there is almost no difference in the titration curves with a change in the ionic strength, so the pH_{pzc} is taken as the inflection point, which is between pH 4 and pH 11 for both hull types. The inability to get the exact pH_{pzc} values may be due to the use of a high concentration of salt. Previous research which used 0.001 M, 0.01M and 0.1 M ammonium chloride solutions identified an exact pH_{pzc} value.[34] Also, since the titration was manual, pH values for small additions of acid or base (such as 0.001 mL) could not be obtained which accounted for poor resolution. A lack of

variation in the titration curve with ionic strength suggests the surface charge may not be
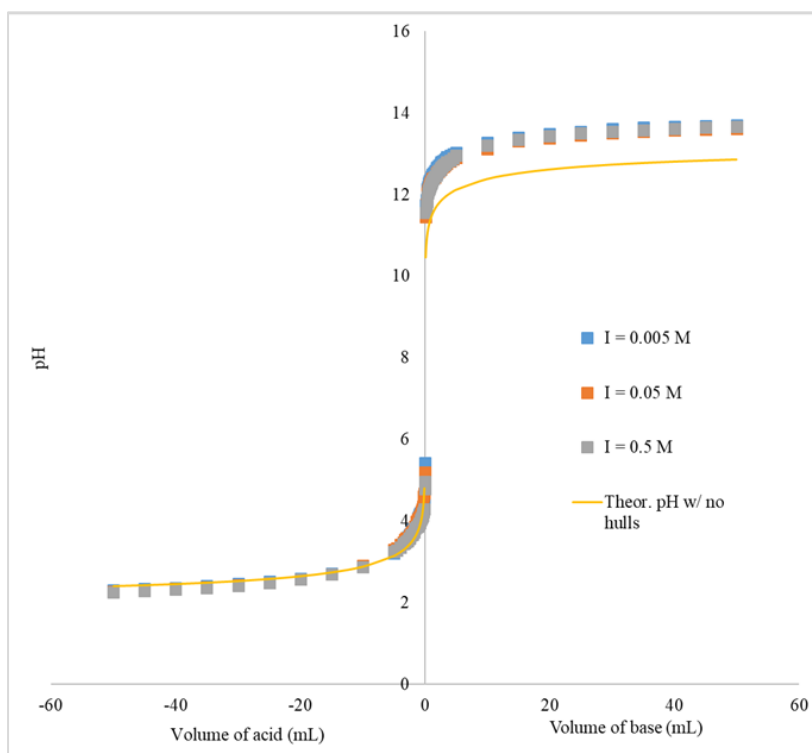
affected by ionic strength.

Figure 8. Acidimetric-alkalimetric titration curve for LD hulls. The yellow solid line represents where pH points would lie when no hulls are present in titration.
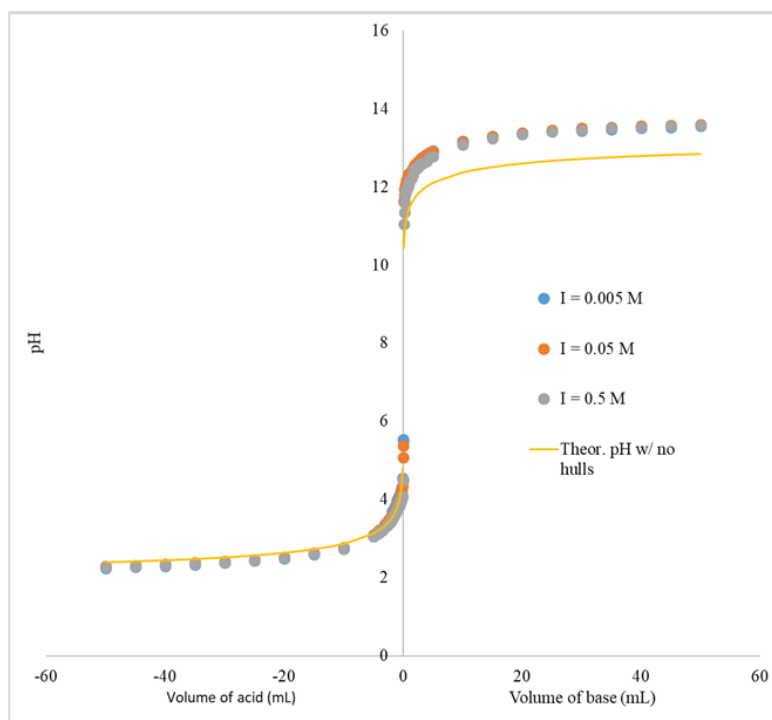

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Figure 9. Acidimetric-alkimetric titration curve for HD hulls. The yellow solid line represents where pH points would lie when no hulls are present in titration.

A yellow line in Figure 8 and 9 indicates the theoretical value for the pH based on the amount of acid or base added as if no hulls were present. For the alkalimetric titrations, the actual titration curves with hulls showed higher pH values than the theoretical pH values without hulls, suggesting the hulls give off hydroxide ion. This has been observed previously when the pH of an alkaline solution increased when hulls are added. This is likely due to the dissolution of some alkaline compounds within the hulls. Indeed, the basic solution in the alkalimetric titration turned lightly yellow. For the acidimetric-alkalimetric titration data to indicate surface charge, the substrate must be insoluble, so it is likely the alkalimetric portion of these results is invalid. Nonetheless, surface charge was calculated for the entire pH region, and the focus on the acidic region is pertinent for this pH study, which focuses on a pH range of 2-6..

The surface charge density is determined using the equation,

$$\sigma = \frac{(C_A - C_B + [OH^-] - [H^+])F}{Am} \tag{3}$$

where C_A and C_B are the concentrations of acid and base, respectively, needed to reach a point on the curve in mol/L, $[H^+]$ and $[OH^-]$ are the concentrations of acid and base, respectively, converted from pH in mol/L, F is the Faraday constant (C/mol), A is the specific surface area in m^2/g and m is the concentration of hull mixture in g/L. Since the surface area of peanut hulls is not known, A in the denominator is omitted, resulting in the specific surface charge in C/g:

$$\bar{\sigma} = \sigma A \tag{4}$$

Also the extended Debye-Huckel theory was used to determine $[H^+]$ and $[OH^-]$ after converting from pH. First, the ionic strength from all ions in the solution at any point was

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calculated. The ions that contributed to ionic strength were: H^+ and Cl^- from the acidic titration, Na^+ and OH^- from the basic titration, and Na^+ and Cl^- from the initial salt concentration. The formula for ionic strength is

$$I = \frac{1}{2}\sum_i c_i Z_i^2 \tag{5}$$

where c_i is the concentration of ion i and Z_i is the ion's charge. The $[H^+]$ and $[OH^-]$ are then divided by the activity coefficient (γ):

$$\log \gamma = \frac{-A\sqrt{I}}{1+Ba_o\sqrt{I}} \tag{6}$$

where A and B have constant values of 0.5085 and 0.3281 for water as the solvent at 25 °C, and a_o is the ionic radius for hydrogen or hydroxide, taken to be 9 or 3.5 Å, respectively. The specific surface charge as a function of solution pH in the acidic region is shown in Figure 10 and 11 for LD and HD hulls, respectively.
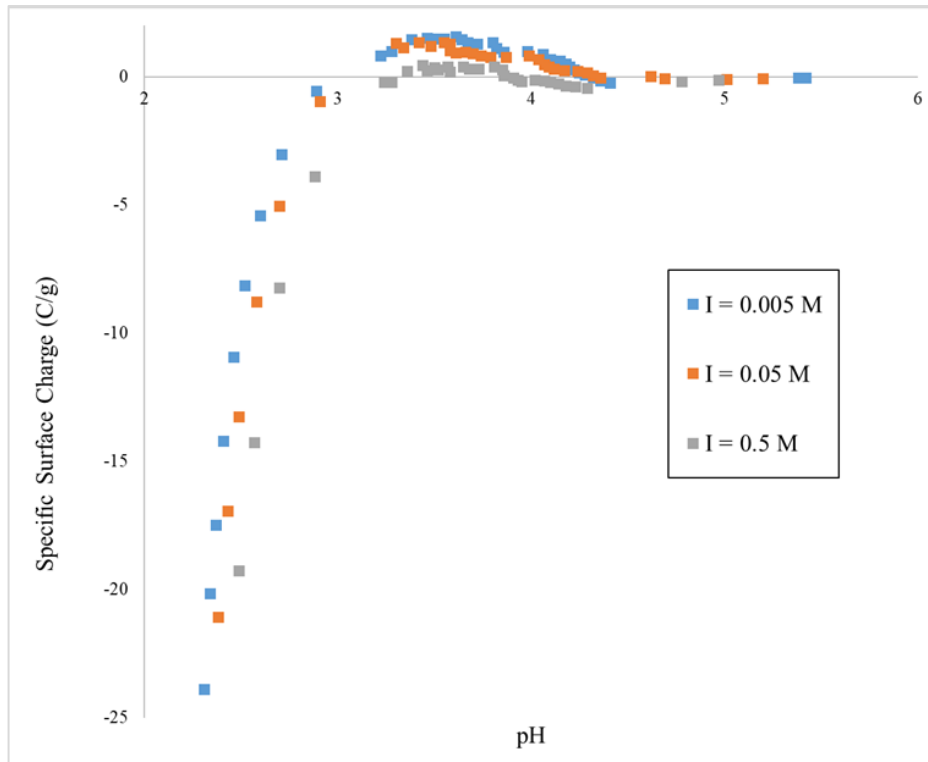
Figure 10. Surface charge as a function of pH for LD hulls.

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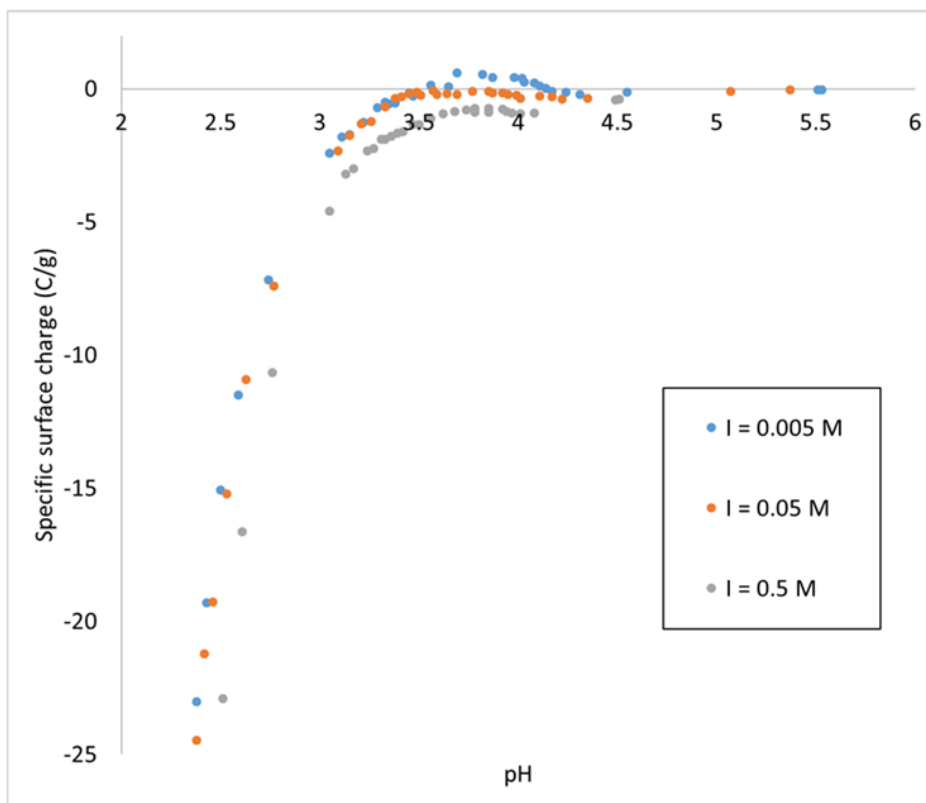
Figure 11. Surface charge as a function of pH for HD hulls.

From previous research, surface charge is negative when the solution pH is above pH_{pzc}, and positive when pH is below pH_{pzc}. Since negative surface charge creates binding sites for Cu(II) adsorption by cation exchange, adsorption will be higher at pH values above the pH_{pzc}. However, for both hull types, specific surface charge increases with pH. This unusual result may be explored further but is more likely the result of hull solubility than the experiment itself. Though this result wasn't expected, it suggests that the pH_{pzc} may be higher than pH 6 so greater adsorption should be observed for solutions with pH 6 and above. Also there is a noticeable local maximum of the specific surface charge at pH 3.5. This suggest that the hull surface electronic structure at this pH, which may result in a change in adsorption mechanism at that point.

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Variable pH Study

Data obtained from the FAAS was used to determine percent of copper (II) ions adsorbed onto the hulls which was then plotted against the initial pH values. The percent of copper (II) ions adsorbed onto each hull type was calculated using the relation

$$\% \, Cu_{adsorbed} = \frac{m_{solution} \times (C_o - C_e)}{C_o \times m_{solution}} \times 100 \tag{7}$$

where $m_{solution}$ is the mass of copper (II) solution added to hulls, C_o is the initial copper (II) concentration, C_e is the concentration of copper (II) solution at equilibrium.

Figure 12 helped identify the likely pH with maximum Cu (II) adsorption by peanut hulls. For HD hulls, percent adsorbed was lower than that of LD hulls at all pH values which is consistent with what has been observed previously.[30] LD hulls have a greater surface area per gram than HD hulls, making available binding sites for adsorption greater in LD hulls.[28] For LD hulls, the maximum adsorption of copper (II) ions was 79.1 % at pH 4 and the minimum adsorption was 65.2 % at pH 1 with a pH adsorption edge of 1.3-4.2. For HD hulls, the maximum adsorption was 72.3 % at pH 5 and the minimum adsorption is 64.6 % at pH 2 with a pH adsorption edge of 2-5.1. The uncertainties in the measurements were 5.1-6.7 % for LD hulls and 4.3-7.4 % for HD hulls. (See Appendix). The pH values with the maximum and minimum percent adsorption agree with results from previous research.[35] The location of the adsorption edges was also consistent with results reported in previous research that studied adsorption of Cu(II) onto activated carbon, which was pH 3-5.[36] These results confirm that there is low adsorption for low pH solutions. This is expected because at low pH, there is greater competition between copper (II) ions and hydrogen ions for binding sites on hulls, which eventually reduces the percent of copper (II) ions adsorbed. Also, low pH makes the overall surface charge of hulls positive which is likely to repel positively charged copper ions and thereby decrease adsorption.

The pH after adsorption was also measured, and Figure 13 shows the plot of initial pH versus pH at equilibrium. The gray diagonal line on the plot shows where data points would fall if no change in pH were observed. Little difference in pH was observed for highly acidic solutions after adsorption. For solutions with initial pH of about 1.2 to 3.2, all have a resulting pH that is about the same or slightly higher. There is still significant adsorption of Cu(II) at these low pHs (as observed in Figure 12), but if pH does not increase, then hydrogen ions are not being released from the hulls, so the mechanism at this pH range is likely not cation exchange. Rather, it could be chemisorption and/or physisorption.
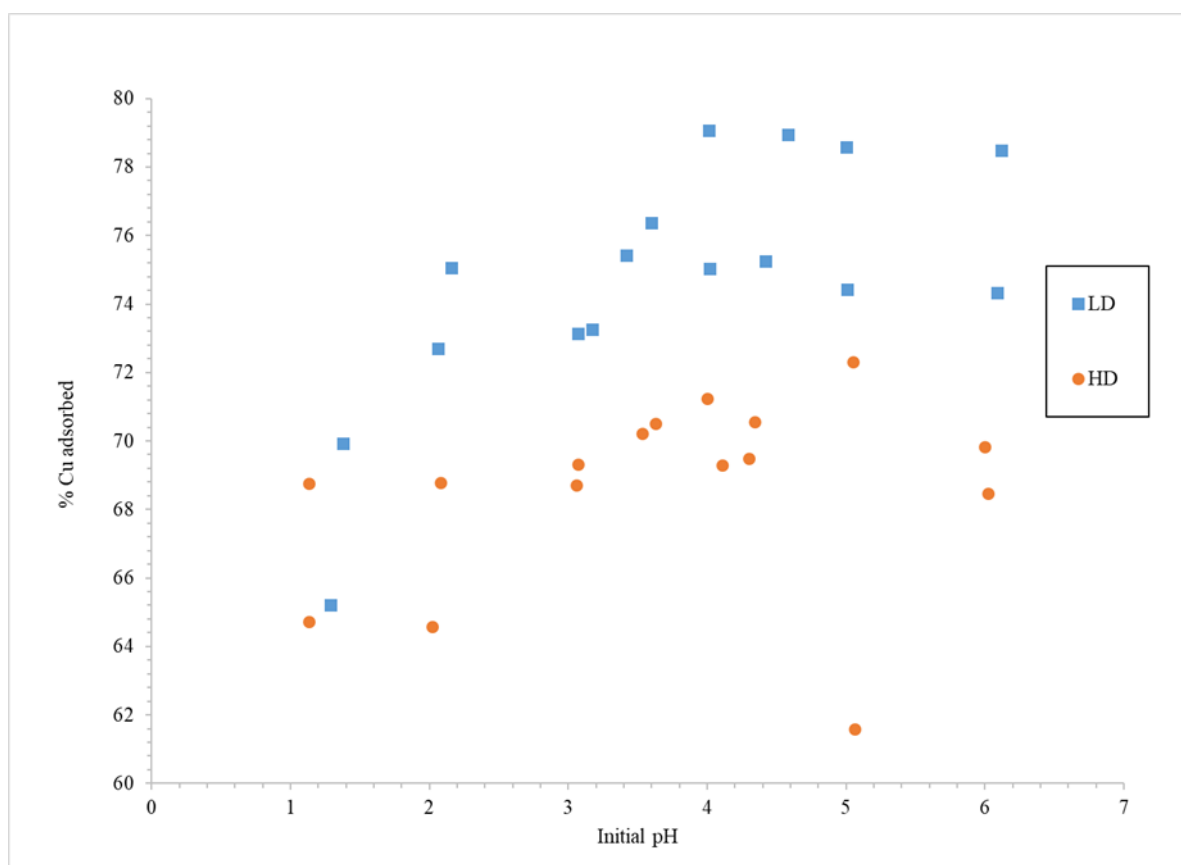
Figure 12. Percent of Cu adsorbed as a function of initial pH. The data shown represents two trials each for high density hulls and low density hulls. Initial copper concentration ranged 2750-2950 ppm; the mass of hulls was 0.5 g for each trial.

In contrast, high pH solutions tended to become more acidic during the adsorption process as indicated by the reduction of pH. For solutions with an initial pH from about 3.5-6

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all have a resulting pH of about 3.5. This indicates that during adsorption, copper (II) ions

bind to hulls and cause the hulls to release hydrogen ions into the solution, thereby

decreasing the pH of the solution. The release of hydrogen ions suggests cation exchange

may be the adsorption mechanism at these pH values. For experiments with initial pH greater

than 3.5, the resulting pH is constant at about 3.5 regardless of the initial pH. This is

consistent with the somewhat constant percent adsorption shown in Figure 12 over this pH

range. This suggests that a threshold amount of hydrogen ions is released regardless of the

initial pH. This is likely due to the local maximum specific surface charge at this same pH,

which represents an equilibrium condition.

Figure 13. Equilibrium pH vs. initial pH for adsorption of Cu(II) to LD and HD hulls. The
solid line shows where points would lie for no change in pH.

Constant pH Study

Constant pH adsorption studies were conducted to investigate the effect of pH on adsorption

of copper (II) ions onto LD and HD hulls. Figure 14 and 15 show the percent Cu adsorbed

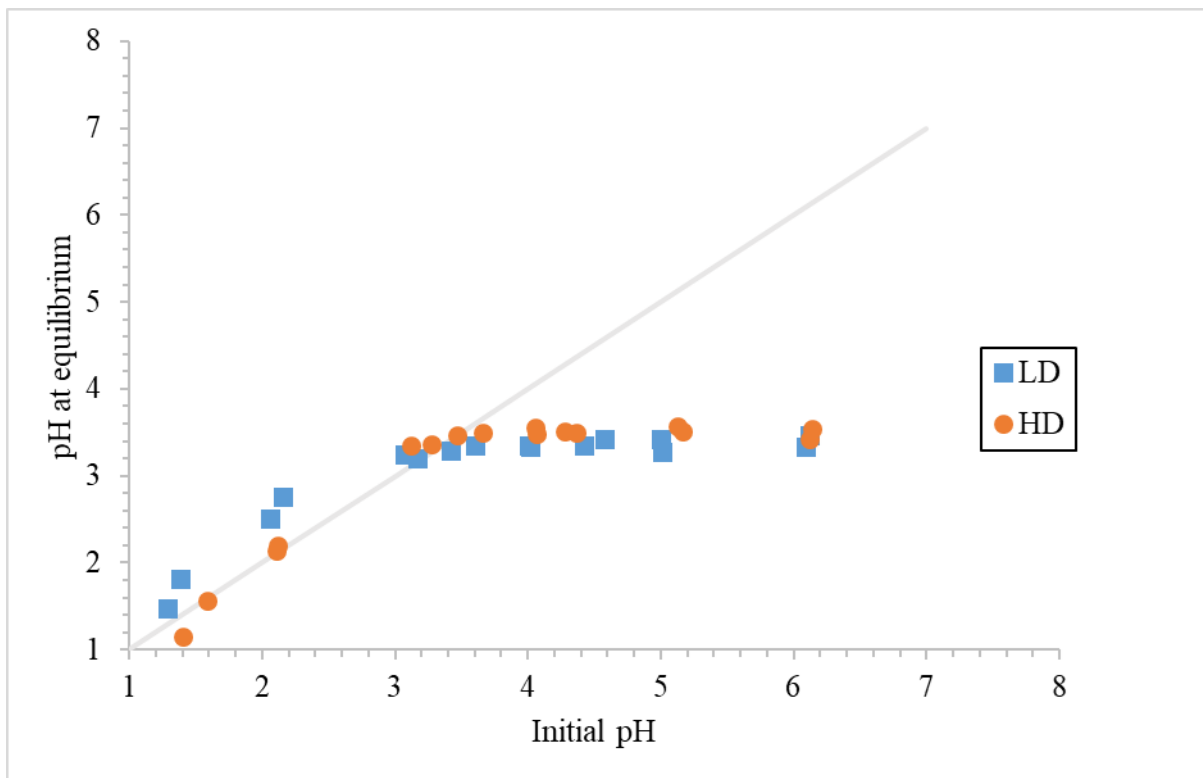onto LD and HD hulls, respectively, as a function of different equilibrium Cu concentration. The uncertainties in the percent adsorbed values were determined with error propagation (see Appendix), and their values were 0.2-19 % for LD hulls and 0.2-24 % for HD hulls. Generally, the largest uncertainties were associated with low pH solutions and adsorption onto HD hulls.

A greater percent adsorption of copper (II) was observed for LD hulls than HD hulls. A similar pattern was observed with the variable pH studies and in previous research.[30] For LD hulls, the maximum adsorption of copper (II) ions to hulls was 99.8 % at pH 6 and the minimum adsorption was 10.9 % at pH 2. For HD hulls, the maximum adsorption was 99.4 % at pH 6 and the minimum adsorption was 4.8 % at pH 2. The minimum adsorption for constant pH study was far lower than that for the variable pH study because of the higher concentration of copper (II) ions used for the variable pH study, which was about 3000 ppm. Figure 14 and Figure 15 show that percent Cu adsorbed generally increases from pH 2 to 6 for both hull types. This is consistent with what is observed for variable pH measurements and previous research[37–39] and is likely attributed to the decreased competition of copper and hydrogen ions for binding sites at higher pHs. Also, increasing pH makes the overall hull surface less positive, which may enhance the attraction of the positively charged, divalent copper ions.

Figure 14. Percent of Cu(II) adsorbed for LD hulls as a function of equilibrium Cu(II) concentration at different buffered pHs.

The same data obtained from the constant pH adsorption studies was modeled with the Langmuir isotherm (Equation 1). The amount of metal adsorbed to the surface, or surface coverage (q_e), was calculated by

$$q_e = \frac{m_{Cu-adsorbed}}{m_{hulls}} = \frac{(C_o - C_e)m_{solution}}{m_{hulls}} \tag{8}$$

where $m_{Cu\text{-}adsorbed}$ is the mass of copper adsorbed and m_{hulls} is the mass of hulls used. For each set of samples for a single hull type and pH, q_e was plotted as a function of C_e, and LoggerPro was used to fit the data to the Langmuir isotherm (Equation 1). The results for LD and HD hulls are shown in

Figure 16 and Figure 17, respectively. The fitting parameters for both sets of data are provided in Table 1.

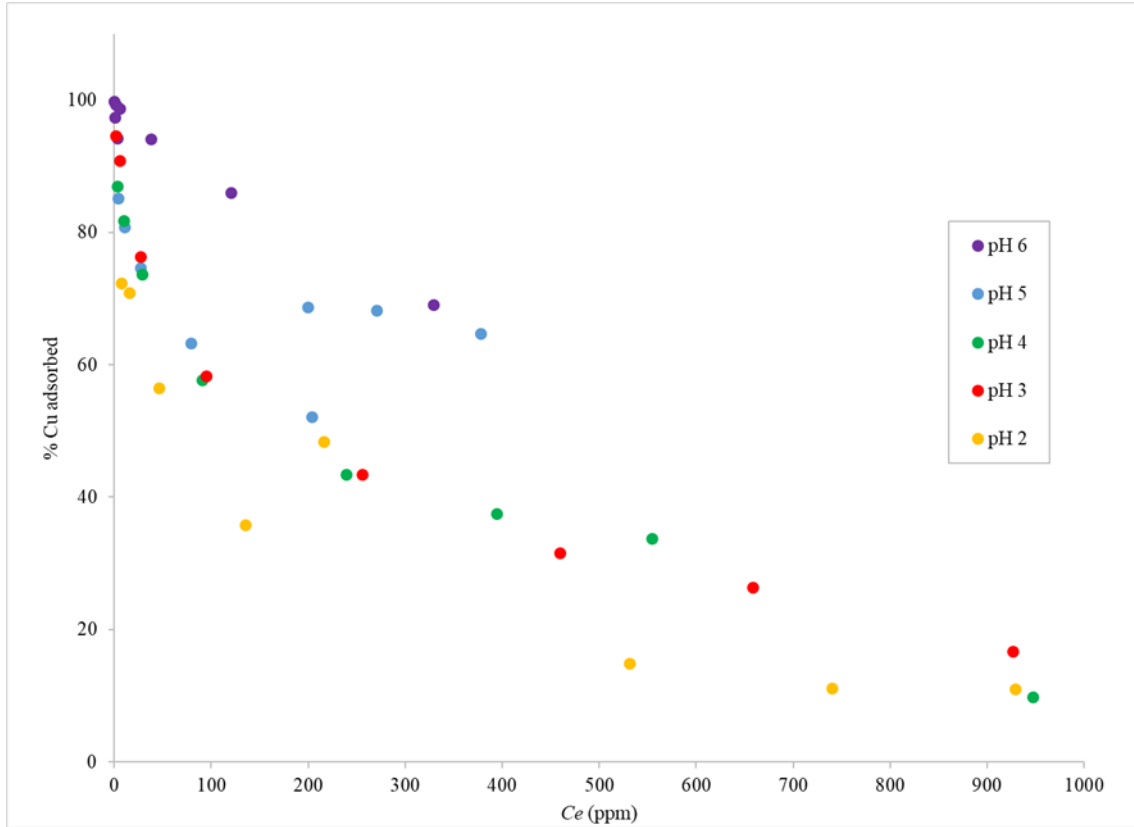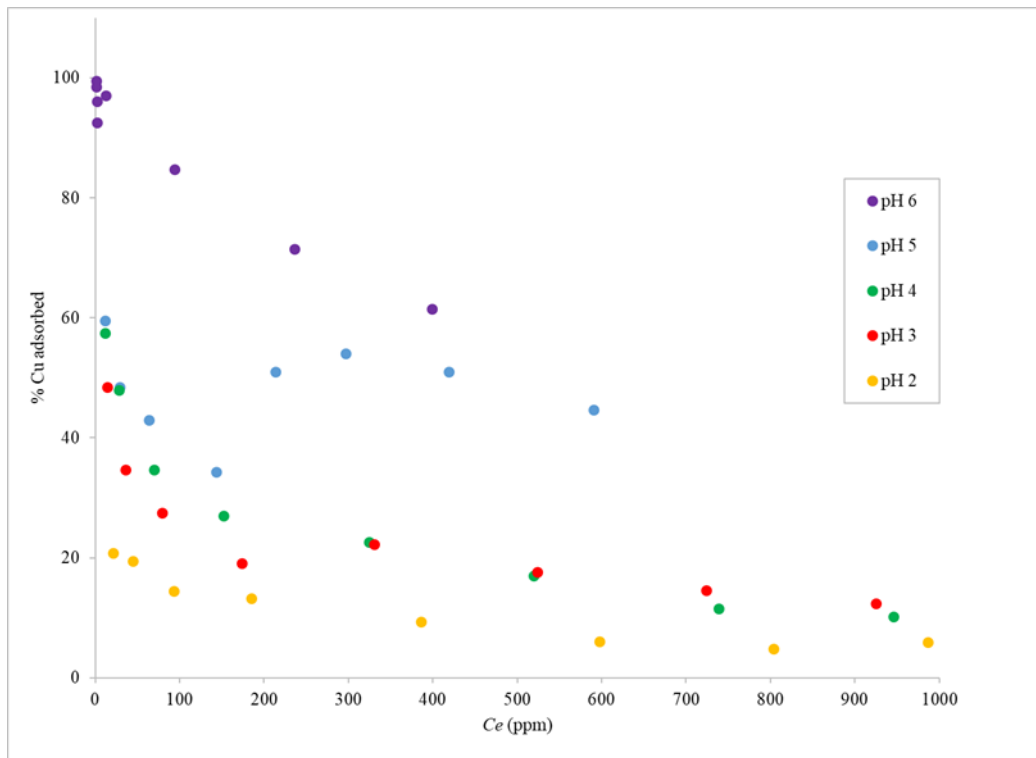Figure 15. Percent of Cu(II) adsorbed for HD hulls as a function of equilibrium Cu(II) concentration at different buffered pHs.
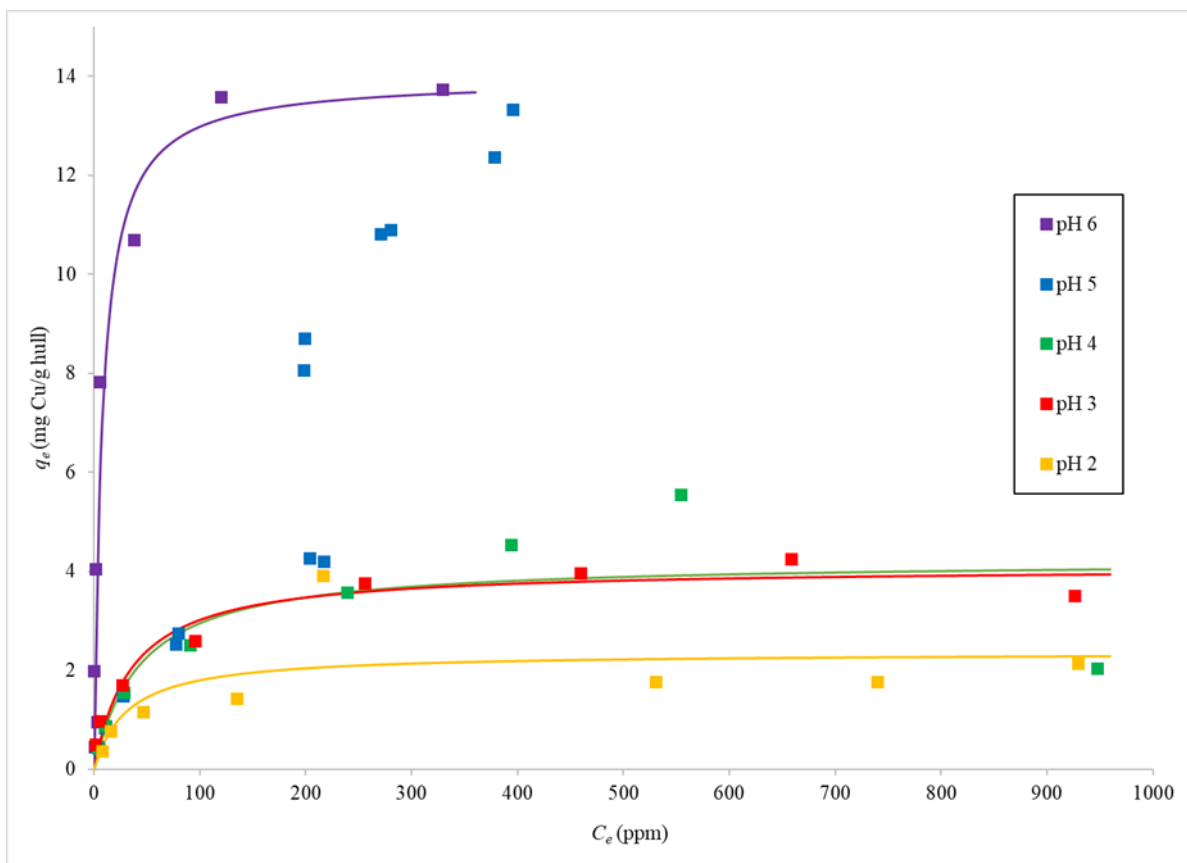
Figure 16. Adsorption isotherms for adsorption of Cu(II) to LD hulls as a function of pH. The data represents a single trial at each pH except for pH 5 which was a two trial experiment. The solid lines are fits to the Langmuir equation (Equation 1).
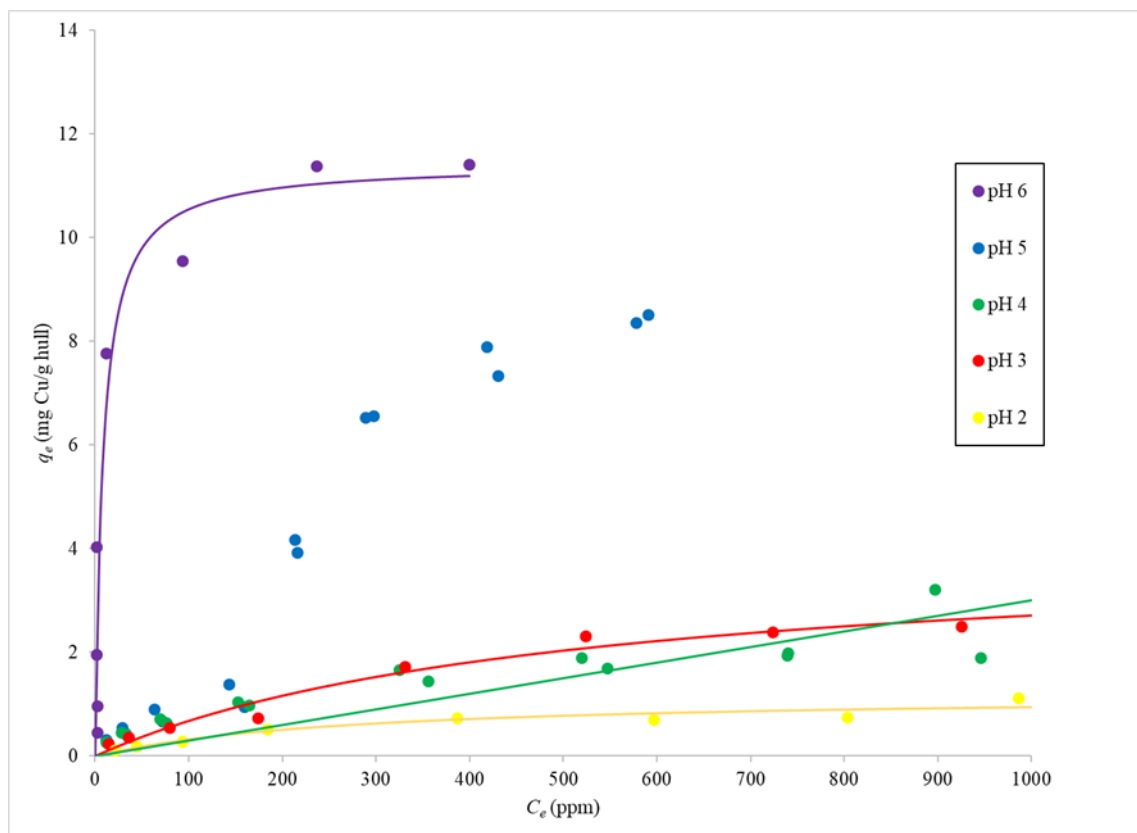
Figure 17. Adsorption isotherms for adsorption of Cu (II) to HD hulls as a function of pH. The data represents single trial at each pH except for pH 5 which was a two trial experiment. The solid lines are fits to the Langmuir equation.

Table 1. Langmuir isotherm parameters for LD and HD hulls at different pH values.

	LOW DENSITY HULLS			HIGH DENSITY HULLS		
	Q_o	b		Q_o	b	
pH	(mg Cu/g hull)	(L/mg hull)	RMSE	(mg Cu/g hull)	(L/mg hull)	RMSE
2	2 ± 2	0.03 ± 0.04	0.83	1.2 ± 0.4	0.004 ± 0.01	0.11
3	4 ± 1	0.02 ± 0.01	0.34	4.05 ± 0.8	0.002 ± 0.0007	0.19
4	4 ± 4	0.02 ± 0.02	1.21	2.99 ± 0.8	0.003 ± 0.001	0.31
5						
6	15 ± 4	0.08 ± 0.02	0.53	11.43 ± 4.3	0.12 ± 0.05	1.54

The pH 5 data obtained for both LD and HD hulls do not follow Langmuir-type behavior. Despite repeating the experiments for this pH, the data does not align with trends observed for the other pH experiments, although the results were repeatable. Although no

mistake could be identified, the difference may be due to a systematic error rather than a unique behavior at this pH. Further trials are needed.

Also, adsorption capacities are higher for LD hulls than HD hulls, which is likely due to the greater porosity within the LD hulls.[28] The high porosity results in a greater surface area to mass ratio in the hulls, making more binding sites available per gram of hull. Generally, Q_o increases with pH, although it is about the same (within the limit of uncertainty) for pH 3 and 4, and there was a large increase from pH 4 to pH 6. This is consistent with the observation of the proposed change in binding mechanism that occurs around pH 3.5. Possibly, adsorption capacity is low for physisorption and chemisorption mechanisms, but a switch to cation exchange greatly increases the number of binding sites.

Relative binding strengths of copper (II) ions are greatest at pH 6 for hulls. This increase may be due to the fact that the binding sites, which may be hydroxyl groups on the lignin and cellulose in hulls, are made readily available by the release of hydrogen ions into the aqueous copper-hull mixture as pH increases. Thus, alkoxide-metal interaction increases the bond strength that can form between copper (II) and the binding sites on the hulls during cation exchange than the relatively weaker interaction that would result from physi- or chemisorption at lower pH. The *b* values and their uncertainties at pH 2, 3 and 4 are almost the same, and thus *b* values at these pHs need to be verified by making more measurements at low equilibrium Cu(II) concentrations.

CHAPTER FOUR: CONCLUSIONS AND FUTURE DIRECTIONS

The acidimetric-alkalimetric titrations for both hull types gave a pH_{pzc} between pH 4 and pH 11. The inability to get the exact pH_{pzc} values may be due to the use of high concentration of salt and large increments in volume of acid and base added amid pH recording. In addition, the solubility of hull components may have invalidated some of the results. A lack of variation in the titration curves with ionic strength suggests the surface charge is not affected by the ionic strength or a much lower ionic strength may vary the titration curves.

For both hull types, surface charge increased with pH. This suggests that the pH_{pzc} may be higher than 6 where greater adsorption was noticed for constant and variable pH studies. Also, the noticeable turning point of the surface charge at pH 3.5 suggests that a change in the hull surface electronic structure occurred at the hull surface at pH 3.5. This may cause a change in adsorption mechanism at that pH.

This percent adsorbed values for both variable and constant pH studies confirmed that there is low adsorption for low pH solutions. This is expected because at low pH, there is greater competition between copper (II) ions and hydrogen ions for binding. High pH solutions tended to become more acidic during the adsorption process whereas the pH of low pH solutions remained almost constant during and after adsorption. This suggests that adsorption of copper (II) onto hulls may occur by the cation exchange mechanism whereby hydrogen ions on components of hulls are exchanged with Cu^{2+}.

For both hull types, the adsorption capacities increases as pH increases from 2 to 6. This is due to the decrease in hydrogen ions available to compete with copper (II) ions for binding sites on hulls. LD hulls have greater adsorption capacities than HD hulls which might be due to the porosity of the LD hulls giving them an increased surface area and more binding sites for adsorption. Binding strengths of copper (II) ions generally increase from pH

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2 to pH 6 for hulls with the exception of pH 4 which decreased unexpectedly. This might result from a change in the pK_a of hulls with increasing pH. Adsorption capabilities of peanut hulls under all pH conditions indicated that peanut hulls are good biosorbents under controlled laboratory conditions. For waste water treatment, a wide range of trace metals and numerous other ions such as calcium and carbonate ions can compete and complicate adsorption mechanisms. Therefore, further testing of the biosorption process under conditions that more closely mimic real effluent is needed before the viability can be confirmed.

Future studies could incorporate additional models such as Freundlich and SCFM to fit data and results could be compared to the Langmuir fit. The rate of adsorption can also be monitored by performing some kinetic studies. The kinetic studies would focus on change in pH with concentration of hull and copper (II) mixtures at certain time intervals. Similar adsorption experiments as described in this work can also be performed to determine the effects of pH on adsorption of copper (II) ions onto modified LD and HD hulls. Actual waste water or contaminated river water can also be used to assess the adsorption of hulls

Other method modifications can be tested to increase the reliability of adsorption results. For example, it was proposed by previous research that, HD polythene or Teflon containers which have been pre-cleaned by soaking in dilute HCl, distilled water and sample rinse should be used during adsorption studies to reduce sample contamination and adsorption losses.[40] It was also recommended that filters should be pre-washed with acid, distilled water and sample before use.[40]

Desorption studies can be performed with all hull types to determine if adsorbed copper (II) ions can be removed. The efficiency of desorption can be studied as well. Furthermore, research can be conducted to determine if hulls used for adsorption studies can be recycled. If recycling of hulls is found to be possible, its regenerative capacity can be determined.

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APPENDIX

Uncertainty in $x = \delta x$, C_{stock} = concentration of stock solution, m = mass, A = absorbance, C = concentration, i and f represents initial and final respectively

Stock concentration

$$\delta C_{stock} = C_{stock} \sqrt{\left(\frac{\delta m}{m_{CuCl2.2H2O}}\right)^2 + \left(\frac{\delta m}{m_{soln}}\right)^2}$$

Sample concentration

$$\delta C_f = C_f \sqrt{\left(\frac{\delta m}{m_i}\right)^2 + \left(\frac{\delta C_i}{C_i}\right)^2 + \left(\frac{\delta m}{m_f}\right)^2}$$

FAA sample concentration

$$\delta C_{FAA} = C_{FAA} \sqrt{\left(\frac{\delta A}{A}\right)^2 + \left(\frac{\delta slope}{slope}\right)^2}$$

To determine the uncertainties in the final reported Q_e values, percent of copper (II) adsorbed were determined for each pH and hull type using the relation

$$\% \, Cu \, adsorbed = \frac{(C_i - C_e)m_{soln}}{C_i \times m_{soln}} \times 100$$

The uncertainty values obtained for C_i and $(C_i - C_e)$ were then used to determine the uncertainties in the final reported percent copper (II) ions adsorbed.

$$\delta Cu \, adsorbed = \%Cu \, ads \sqrt{\left(\frac{\delta \Delta C}{\Delta C}\right)^2 + \left(\frac{\delta C_i}{C_i}\right)^2}$$