

ADSORPTION OF COPPER(II) BY PEANUT HULLS IN A
FIXED-BED, CONTINUOUS FLOW COLUMN

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

By

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LIST OF ABBREVIATIONS

Presented in order of appearance:

Q_o	Adsorption capacity (mg Cu/g hulls)
k_2	Pseudo-second order rate constant (g hulls/mg Cu ²⁺ min)
τ	Breakthrough point (min)
q_e	Surface coverage at equilibrium (mg Cu ²⁺ /g hulls)
C_e	Concentration at equilibrium (ppm)
C_o	Concentration of stock solution (ppm)
V_{soln}	Volume of solution (mL)
m_{sorb}	Mass of adsorbent (g or kg)
K_F	Freundlich isotherm constant (mg Cu ²⁺ /g hulls ppm ^{1/n})
n	Freundlich, three parameter Clark, and four parameter Clark constant
b	Equilibrium constant (ppm ⁻¹)
α	Redlich-Peterson isotherm constant
q	Surface coverage at time t (mg Cu ²⁺ /g hulls)
C	Effluent concentration (ppm)
t	Time of sampling (min)
SSR	Sum of the squared residuals
C_{calc}	Calculated normalized effluent concentration
k_T	Thomas model rate constant (mL soln/mg Cu ²⁺ min)
ν	Flow rate (mL/min)
V_{eff}	Volume of effluent (mL)
A	Three and four parameter Clark model constant
r	Three and four parameter Clark model constant
a	Four parameter Clark model constant
KHP	Potassium hydrogen phthalate
FAAS	Flame atomic absorption spectroscopy
R^2	Correlation coefficient

ABSTRACT

ADSORPTION OF COPPER(II) BY PEANUT HULLS IN A FIXED-BED, CONTINUOUS FLOW COLUMN

Tyler Stephen Cook, Masters of Science in Chemistry

Western Carolina University (April 2017)

Advisor: Dr. Carmen L. Huffman

Heavy metal pollution is an important concern due to its adverse health and environmental effects. Biosorption is a way to remove heavy metals from aqueous systems with the use of biomaterials. There are many different types of biosorbents, such as algae, fungus, bacteria and lignocellulosic materials (wood, saw dust, peat, wheat bran, nut shells, etc.). Several studies have used peanut shells (hulls) as a heavy metal adsorption material. For instance, peanut hulls are an effective biomass for the removal of copper (II) from aqueous systems. However, these studies utilized equilibrium (batch) methods to quantify metal adsorption. These results are not comparable to an industrial setting, which utilizes a non-equilibrium flow system.

The biosorption of Cu^{2+} on unmodified and modified, high density, ground peanut hulls was investigated using equilibrium studies, kinetics studies, and dynamic adsorption studies. Adsorption models were applied to determine the adsorption capacity at equilibrium. A pseudo-second order rate law was applied to the kinetics data to determine the rate constant of adsorption. Dynamic sorption models were applied to the continuous flow studies to fit the experimental breakthrough curves.

It was determined that the alkaline peroxide modified, high density hulls had the highest

adsorption capacity, the fastest rate of adsorption, and latest breakthrough point. The alkaline modified hulls' adsorption capacity and breakthrough point are decreased from the alkaline peroxide modified hulls but perform better than the unmodified hulls. However, an improvement in the rate of adsorption was not seen in comparison to the unmodified hulls. The unmodified hulls had the lowest adsorption capacity and earliest breakthrough point.

The best fitting model for the equilibrium data for all types of hulls was the Redlich-Peterson model. However, the Langmuir model was the most useful as it yielded results with physically meaningful parameters as well as the best estimation of the adsorption capacity.

The four parameter Clark model was the best fitting dynamic adsorption model for each type of hulls, followed by the three parameter Clark, and finally the Thomas model. Although the four parameter Clark model resulted in the best fit, the model's parameters are empirical and are not physically meaningful. The Thomas model was the poorest fitting model tested.

Although the four parameter Clark model successfully fit the breakthrough data for each type of hull, the empirical nature of the model is not useful for comparing to the equilibrium and kinetics data. However, the more physically meaningful Thomas model does not successfully relate the equilibrium and kinetics parameters to the dynamic flow behavior of the Cu^{2+} /peanut hull adsorption system. There is a need for additional models to be tested and/or developed for these types of systems, as the models tested in this project were developed for other types of systems and applied to the biosorption of heavy metals with poor fit and predictive power.

CHAPTER ONE: INTRODUCTION

1.1 Motivation

1.1.1 Heavy Metal Pollution

Heavy metals, such as lead, chromium, copper, and cadmium, are toxic to human health and harmful to the environment. Industries typically introduce wastewater into natural bodies of water, and if metals are present, they bio-accumulate in the water system and can enter the food chain. Once these non-biodegradable metals have entered the food chain, they have the potential to accumulate in the human body leading to heavy metal poisoning.¹ Many different industries could release heavy metals into the environment via wastewater, such as iron and steel production, mining and mineral processing, pigment manufacturing, battery manufacturing, printing and photography, and others.^{1,2}

1.1.2 Effects of Copper

Copper is a common heavy metal pollutant and can enter the environment from many sources. In the United States copper is mined and processed, providing a potential source of copper to be released into the environment. Copper metal or a copper alloy is commonly used to manufacture materials like wire, sheet metal, and pipes. Copper compounds are also used as a preservative to treat plants, wood, leather, and fabrics. Some other sources of copper include landfills, smelters, mines, combustion of fossil fuels and waste disposal sites.³

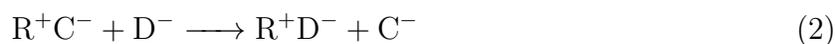
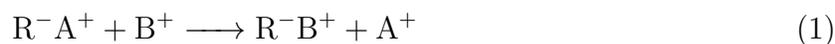
Copper is vital to human health and is found in many bodily processes. An adult human body needs approximately 900 μg of copper daily to function properly, but too much copper intake can wreak havoc on the body.³ Some signs of acute copper poisoning are irritation of the nose and mouth, headaches, dizziness, nausea, and diarrhea.³ Higher dosages of copper consumption can damage the kidneys and the liver and in the worst case, even cause death.

As copper is a potential threat to human health, it is necessary to monitor and control the levels of copper released into the environment.¹

1.1.3 Wastewater Treatment Methods

There are many techniques for removing harmful metals from water systems. These techniques include adsorption by activated carbon, membrane separation, reverse osmosis, electrodialysis, solvent extraction, chemical precipitation, and ion exchange.^{2,4,5} However, many are labor intensive, expensive, and generate large quantities of solid waste.² A more economic and environmentally friendly method of heavy metal removal is important for pollution prevention.

One of the most common ways for removing heavy metals from aqueous solution is to use ion exchange resins. An ion exchange reaction is a reversible reaction that removes dissolved cations or anions from solution and replaces them with cations or anions from the surface of the resin.⁶ Resins are typically small plastic beads that have charged functional groups on the bead's surface. The type of functional group and its charge dictate the efficiency and application of a particular resin.⁶ For instance, if the functional group has a -2 charge and a Ca^{2+} counterion, it would be best used for the removal of divalent cations from solution as they would be exchanged for the resin's Ca^{2+} counterion. Generic chemical reactions for a cationic (Equation 1) and anionic (Equation 2) ion exchange resin are shown below



where R represents the functional group on the resin, A^{+} and C^{-} are the counterions for the resin, and B^{+} and D^{-} are the ions in solution to be removed.

Ion exchange resins have a wide variety of applications like industrial wastewater treat-

ment and water filtration. They are most often applied to wastewater treatment by the use of a continuous flow, fixed-bed column, where contaminated wastewater flows through a column of resin and treated wastewater is emitted. Ion exchange resins are very efficient at the removal of all sorts of metals from wastewater. However, ion exchange resins require a large capital investment and on-going operational costs. Also as they are a synthetic product derived from petroleum, they are not the most environmentally friendly to produce.

1.1.4 Biosorption

Biosorption is a way to remove heavy metals from aqueous solution with the use of a biomaterial.⁷ There are many benefits to using biomaterials as a biosorbent. They can remove toxic ions from wastewater, are cost effective compared to traditional methods, and often allow for the concentrated metal to be recovered from the concentrated biosorbent.⁸ Since the material used is biodegradable, the amount of secondary waste produced will decrease with time, which is an advantage over the traditional sludge-producing methods of removing contaminants from water. There are many different types of biosorbents, such as algae, fungus, bacteria and lignocellulosic materials (wood, saw dust, peat, wheat bran, peanut hulls and others).^{8,9} All of these biomaterials have proven to have biosorption capabilities.^{8,10}

There are several studies that have used peanut hulls as a heavy metal adsorption material.^{9,11-14} For instance, ground peanut hulls are an effective biomass for the removal of copper(II) from aqueous systems.^{9,11-14} One study showed that oxidized peanut hulls are more effective at binding copper than unmodified hulls.¹¹ Peanut hulls exhibit a high and low density character. Some ground hull particles sink in water (high density hulls) and others float (low density hulls). No other study has focused on the performance of the different types of hulls or how they perform in a fixed-bed, continuous flow system.

The goals of this research are to study the equilibrium adsorption, the kinetics of adsorption, and the adsorption in a fixed-bed, continuous flow system of copper(II) by unmodified

and modified, high density peanut hulls. In addition, common mathematical models that describe equilibrium, kinetic, and dynamic flow behavior will be applied to test their modeling of this system.

1.1.5 Research Methodology

Figure 1 summarizes the goals of this research. From the equilibrium adsorption studies, the adsorption capacity (Q_o) can be determined, and from the kinetics studies, the rate law (and rate constant, k_2) of adsorption can be determined. Each is essential to understanding the effectiveness of peanut hulls at the removal of copper(II) in a water system. Experimental breakthrough curves will be determined by a fixed-bed, continuous flow study and will provide the breakthrough point (τ , time at which the effluent concentration is 50% of the stock solution concentration). The quality of the models for this system will be assessed. Quality modeling is essential as it is much faster and inexpensive to generate data with calculations than to gather experimental data. However, poor models can lead to erroneous predictions. This work will assess the feasibility of using existing models for an ion-exchange process involving ground peanut hulls.

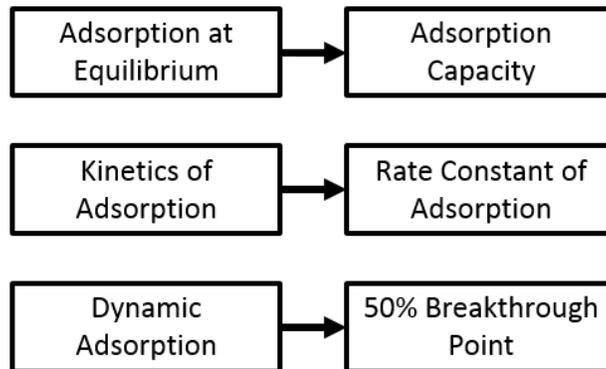


Figure 1. Research goals.

1.2 Background

1.2.1 Peanut Hulls

In 2014 there were more than 35.6 metric tons of in-shell peanuts produced worldwide.¹⁵ Peanut hulls are a natural, inexpensive, and renewable resource that have many potential uses. Currently peanut hulls are mainly used for roughage in cattle feed or are incinerated at the plant where peanuts are de-shelled.¹⁶ Peanut hulls are crude fiber (60 – 67 %) composed of mainly lignin and cellulose. The full composition of peanut hulls is shown in Table 1.^{12,17}

There are many materials that have been shown to be effective biosorbents because they are largely composed of cellulose and lignin.¹⁸ Cellulose is a naturally occurring polymer that consists of glucose units connected by ester linkages.¹⁹ Cellulose has alcohol functional groups on the glucose units.¹⁹ Lignin is a large polymer with a structure that varies from substance to substance and is not known for peanut hulls.¹⁹ Due to peanut hulls' fibrous composition, they show promise to be a low cost, effective biosorption material for the removal of heavy metals from aqueous systems.

Table 1. Composition of peanut hulls. (See Albrecht (1979) and Brown (2000).)

Chemical Characteristics	Percent
Crude Fiber	60-67 %
Cellulose	(35-45 %)
Lignin	(27-33 %)
Moisture	8-10 %
Protein	6-7 %
Ash	2-4 %
Fat	1 %
Physical Characteristics	Percent
Porosity	61.7 %
Solubility in water	0.74 %
Bulk density	5 – 7 lb/ft ³

1.2.2 Equilibrium Adsorption Models

Adsorption isotherms illustrate the relationship between the amounts of free and bound adsorbate (solute) in the presence of an adsorbent (solid) at a given temperature.²⁰ In this study the isotherms show the relationship between the amounts of free and bound divalent copper in the presence of peanut hulls. Figure 2 shows an adsorption isotherm, which is a plot of surface coverage (q_e) vs. equilibrium concentration (C_e). Surface coverage is the amount

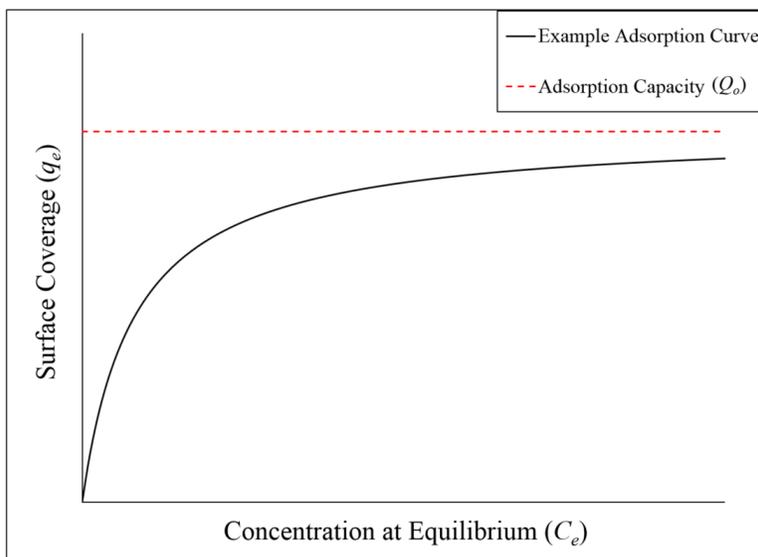


Figure 2. Example adsorption isotherm.

of adsorbate bound to a unit amount of adsorbent at a given equilibrium concentration of adsorbate in the solution. Surface coverage is calculated using

$$q_e = \frac{(C_o - C_e)V_{\text{soln}}}{m_{\text{sorb}}} \quad (3)$$

where C_o is the stock (initial) concentration (ppm), V_{soln} is the volume of stock solution (mL), and m_{sorb} is the mass of sorbent (g). Surface coverage initially increases sharply as equilibrium concentration increases, then begins to gradually level off as the surface of the adsorbent becomes saturated. As the adsorbent becomes fully saturated, the curve

approaches a horizontal asymptote, which represents the maximum surface coverage, the adsorption capacity (Q_o). The three isotherm models that will be discussed in this paper are the Freundlich, Langmuir, and Redlich-Peterson models. These are the three most commonly used models used for fitting isotherms.

The Freundlich model is one of the earliest known sorption isotherms. It describes non-ideal, heterogeneous, multilayer sorption.²⁰ The Freundlich equation is

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F and n are the Freundlich constants. K_F and n can be calculated from the slope and y-intercept of the linearized Freundlich equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

The Langmuir model is one of the most common models applied to biosorption studies because of its ability to predict a wide range of experimental data with good agreement. The Langmuir model is a two parameter equation that assumes the surface of the adsorbent is homogeneous, all binding sites are equivalent, and that there is no interaction between adjacent adsorbate molecules on the surface.²⁰ Equation 6 shows the Langmuir equation

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \quad (6)$$

where b is the equilibrium constant (related to energy of adsorption).²¹ As shown in the linearized equation below (Equation 7), a plot of C_e/q_e vs. C_e yields a straight line if the data is described by the Langmuir model, and the slope and y-intercept can be used to calculate Q_o and b .

$$\frac{C_e}{q_e} = \frac{1}{b Q_o} + \frac{1}{Q_o} C_e \quad (7)$$

The usefulness of the Langmuir model stems from the meaningful value of Q_o , which gives the maximum amount of adsorbate that can be held by the adsorbent.

The Redlich-Peterson isotherm is a three parameter model that incorporates the Freundlich and Langmuir isotherms into one model. The Redlich-Peterson model bridges the gap between heterogeneous, multilayer adsorption and homogeneous, monolayer adsorption. The combination of these two models yields a much better fit of most data than the use of the Freundlich or Langmuir models. However, the Redlich-Peterson model loses some applicability as the units of the adsorption capacity are raised to a power, which is not physically meaningful. The Redlich-Peterson equation is

$$q_e = \frac{Q_o b C_e}{1 + b C_e^\alpha} \quad (8)$$

where α is a unitless parameter between 0 and 1. Equation 8 reduces to the Langmuir equation when $\alpha = 1$, and it reduces to the Freundlich isotherm when α is small and $1/bQ_o$ approaches zero.²² This suggests that the adsorption process is best described by the Langmuir model as α approaches 1 and the Freundlich model as α approaches 0. The linearized Redlich-Peterson equation is

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{1}{Q_o} C_e^\alpha \quad (9)$$

and a plot of C_e/q_e vs. C_e^α will provide the parameters Q_o and b . However, the units for the Redlich-Peterson parameters are not equivalent to the units of the Langmuir parameters with the addition of the third parameter α . The addition of α makes the Redlich-Peterson a more empirical model, which allows for a better fit to a wider range of adsorption curves.

1.2.3 Adsorption Kinetics

Rate studies determine how fast an adsorbate attaches to the surface of an adsorbent. Kinetics studies will be used to determine the rate at which the hulls and copper solution reach equilibrium. Like most biosorption processes, copper adsorption to peanut hulls follows pseudo-second order kinetics.^{9,23,24} The rate law is

$$\text{Rate} = k[\text{Cu}^{2+}][\text{sites}]^2 \quad (10)$$

where k is the rate constant and “sites” are the available binding sites on the hulls.¹¹ Assuming the copper concentration is in such excess that the initial concentration and the final concentration is essentially unchanged, Equation 10 reduces to a pseudo-second order rate law:

$$\text{Rate} = k_2[\text{sites}]^2 \quad (11)$$

where $k_2 = k[\text{Cu}^{2+}]$. The rate constant (k_2) can be calculated using the linearized, integrated rate law equation for pseudo-second order kinetics,

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

by plotting t/q vs. t , where t is time and q is the surface coverage at time t . The slope is equivalent to $1/q_e$ and the y-intercept is $1/k_2 q_e^2$, which yields k_2 .

1.2.4 Continuous Flow Models

A breakthrough curve describes the adsorption of an adsorbate as it flows through an adsorbent. The curve is a plot of effluent concentration (C) as a function of either time (t) or volume of solution that has passed through the adsorbent (V_{eff}). An example breakthrough curve is show in Figure 3. This ideal breakthrough curve has a symmetrical, sigmoidal shape

(S-shape). Initially, there is little or no adsorbate in the effluent as it is adsorbed by the adsorbent. As time increases the concentration of adsorbate in the effluent increases. This is called “breakthrough.” Adsorbate breakthrough occurs as the binding sites on the adsorbent become increasingly saturated and allow the adsorbate to pass through the adsorbent unbound. Eventually, the effluent concentration begins to level off, approaching the stock concentration (C_o). Once all of the binding sites are filled, the adsorbate can no longer be retained by the adsorbent, so the effluent concentration is equal to the stock concentration. Often, breakthrough curves are compared and quantified with the breakthrough point (τ), which is the time at which the effluent concentration is 50 % of the stock concentration.

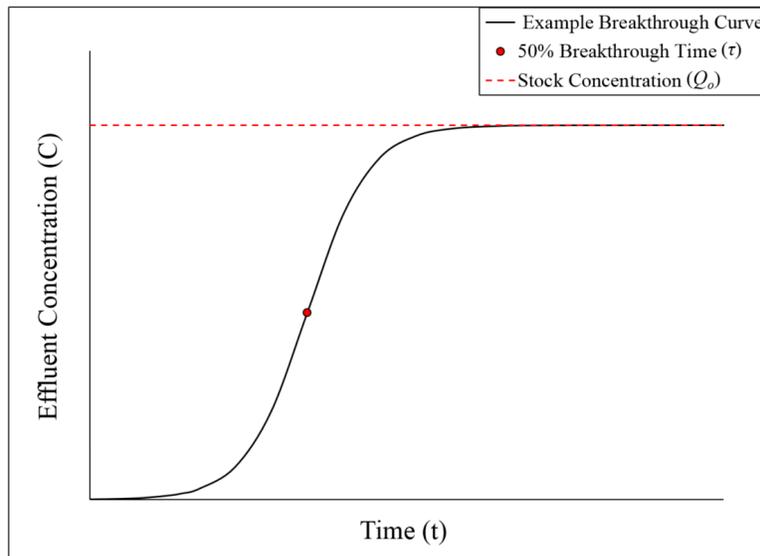


Figure 3. Example breakthrough curve.

Over the past century many continuous flow models have been developed to predict the performance of different adsorbate/adsorbent systems.^{8,10,18,25–32} Some of these models include the Bohart-Adams,³³ Thomas,²⁸ Clark,³¹ Modified Dose-Response,³⁴ and Wolborska³⁵ models. In this paper the focus will be on the Thomas, three parameter Clark, and four parameter Clark models which are some of the most commonly used models. The quality of the fit is determined by comparing the sum of the squared residuals (SSR). The formula for

the sum of the squared residuals is

$$\sum \left(\frac{C}{C_o} - C_{\text{calc}} \right)^2 \quad (13)$$

where C_{calc} is the normalized effluent concentration predicted by the model.

The Thomas model is one of the most widely used models for the prediction of breakthrough curves. The Thomas model assumes that adsorption is best described by a Langmuir adsorption model, there is no axial dispersion, and that the rate is best described by second order kinetics.^{18,28-30} The adsorption breakthrough model by Thomas is

$$\frac{C}{C_o} = \frac{1}{\exp\left(\frac{k_T}{\nu}(Q_o m_{\text{sorb}} - C_o V_{\text{eff}})\right) + 1} \quad (14)$$

where k_T is the Thomas rate constant (mL soln/mg Cu²⁺ min), m_{sorb} is the mass of adsorbent (kg), V_{eff} is the volume of effluent (mL), and ν is the flow rate (mL/min).

One of the most recently developed continuous flow models is the Clark model.³¹ The Clark model was developed using the mass transfer concept (movement of mass of adsorbate) along with the Freundlich isotherm while neglecting dispersion (ability of adsorbate to disperse evenly throughout the adsorbent). The Clark model is a purely empirical model as its parameters do not have any physical meaning.³¹ The three parameter Clark model is as follows:

$$\frac{C}{C_o} = \left(\frac{1}{1 + Ae^{-n}} \right)^{1/n-1} \quad (15)$$

where n is related to the Freundlich constant, and A and r are Clark constants. The Clark model was developed as a three parameter equation, but in a recent study a fourth parameter (a) has been added to improve fitting for asymmetric breakthrough curves.³² The four

parameter Clark model is as follows:

$$\frac{C}{C_o} = \left(\frac{a}{1 + Ae^{-n}} \right)^{1/n-1} \quad (16)$$

where the addition of a allows the model to predict a wider variety of experimental data.

CHAPTER TWO: EXPERIMENTAL

2.1 Materials

All solutions were prepared using ultrapure water with a resistivity of 18.2 M Ω from a Milli-Q water filtration system purchased from Millipore. Copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), hydrogen peroxide (H_2O_2 , 35%), sodium chloride (NaCl, 99.9%), and nitric acid (HNO_3 , 69.5%), potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{KOH}_4$, 99.98%), and potassium hydroxide (KOH) were purchased from Fisher Scientific. Sodium hydroxide (NaOH, 98%) was purchased from Sigma Chemical Co. All chemicals were used without further purification.

2.2 Peanut Hull Preparation

Roasted, unsalted, whole peanuts were purchased from Ingles, a local grocery store in Sylva, North Carolina. The peanuts and seed coats were separated from the hulls by hand. The hulls were ground with a coffee grinder (Hamilton Beach, 80370) and sieved with USA stainless steel test sieves (Fisherbrand) with pore sizes of 2 mm, 1 mm, 0.5 mm, 0.25 mm, and 0.125 mm. The hulls utilized in all experiments were the hulls retained by the 0.5 mm sieve and therefore are between 0.5 mm and 1 mm in their widest dimension. These hulls were mixed with 70 °C ultrapure water for 5 min, filtered, rinsed with cold ultrapure water and left to dry in air on a watch glass. The dried hulls were transferred to a large plastic bag filled halfway with ultra pure water. The hulls that floated (low density hulls) were separated from the hulls that sank (high density hull) by decantation, filtered and left to dry in air. The hulls used in all experiments were high density hulls.

2.2.1 Alkaline Modification

A 0.97 M solution of NaOH was prepared and transferred to a jacketed beaker connected to a constant temperature water bath set to 20 °C. For every 100 mL of NaOH solution, 2 g of hulls were added. The temperature was maintained at 20 °C for 1 h. The mixture was heated to 60 °C and then left to cool to room temperature for 24 h. The dark brown reaction liquid with fine particulate matter was generated during the modification and was decanted leaving only the hulls. The hulls were then rinsed repeatedly with ultrapure water until decanted rinse water was clear and free of fine particulate matter. The hulls were transferred to a large Büchner funnel and rinsed with ultrapure water until the effluent was reduced to neutral pH. Alkaline modified hulls were left on a watch glass to dry.

2.2.2 Alkaline Peroxide Modification

The procedure for the alkaline peroxide modification is the same as the alkaline modification, except the reaction solution contains 0.97 M NaOH in 30 % H₂O₂, and the reaction mixture did not need to be heated to 60 °C. The reaction mixture is exothermic (reaching max temperature of ~60 °C) and bubbles vigorously as the hydrogen peroxide is consumed, creating a foam layer (comprised of hulls and solution) above the reaction mixture. To prevent the loss of hulls from the foam layer in the reaction vessel, a nylon stocking was placed around the beaker opening and was held in place by a large rubber band. The reaction liquid is yellow instead of dark brown as observed in the alkaline modification and much more fine particulate matter was generated with this modification.

2.3 Adsorption Study

All copper(II) chloride solutions in this study were prepared in a pH 4 buffer. The buffer was prepared by first dissolving 0.957 g potassium hydrogen phthalate (KHP) into 100 mL

of ultrapure water. In a separate container potassium hydroxide pellets were dissolved into 3 mL of ultrapure water. The pH of the KHP solution was monitored with a pH probe. Potassium hydroxide solution was added dropwise to the KHP solution until the solution pH increased to 4.

Copper(II) chloride solutions were prepared using pH 4 buffer with concentrations ranging from 0-2500 ppm. Approximately 0.5 g of hulls was added to a 15 mL plastic conical tube along with 10 g of copper solution. The conical tubes were placed on a tube revolver (Thermo Scientific) and rotated at 40 rpm for 24 h. After the samples were mixed, each sample was filtered using a 10 mL syringe and a 0.45 μ m syringe filter. Each sample was then diluted with 5% nitric acid for metal analysis.

The concentrations of copper(II) and sodium before and after mixing were determined by flame atomic absorption spectroscopy (FAAS) using a PinAAcle 900F Atomic Absorption Spectrometer (Perkin Elmer). To reduce the amount of possible matrix effects between copper(II) and sodium, standards of copper(II) were prepared with a range of 0-12 ppm while keeping the concentration of sodium constant at 50 ppm. A second set of standards with a concentration range of 0-12 ppm were prepared while keeping the copper(II) concentration constant at 5 ppm. The adsorption wavelengths for copper(II) and sodium were 216.51 nm and 330.24 nm, respectively. New standards were prepared for each experiment using the same method.

2.4 Kinetics Study

A stock copper(II) chloride solution of 1000 ppm was prepared in KHP/KOH pH 4 buffer. Approximately 0.5 g of hulls was placed in a 15 mL conical tube along with 10 g stock copper(II) solution. The sample was placed on a tube revolver (Fisher Scientific) set to 40 rpm to agitate the mixture. Aliquots (0.1 mL) were collected from the reaction conical tube at different intervals for 24 h. The aliquots were transferred to a tared 15 mL conical tube

and diluted with 5% nitric acid for metal analysis. Each sample was filtered using a 10 mL syringe and a 0.45 μm syringe filter. These samples were analyzed with FAAS using the method described above.

2.5 Continuous Flow Study

A home-built flow system was used to control the loading rate of the column. A peristaltic pump (GHH) was controlled by an adjustable DC motor speed PWM controller (Rio Rand) with a DC 12 V 1 A power supply (NKC Electronics). All components were purchased from amazon.com.

The experimental setup for the fixed-bed column study is shown in Figure 4. The average column parameters and uncertainties are shown in Table 2. The column has an internal diameter of 1.75 cm. Dry peanut hulls (5.04 ± 0.03 g) were soaked in KHP/KOH pH 4 buffer solution for 10 min. The slurry of buffer solution and hulls was then transferred to the column in sections and tamped with a nylon rod periodically to ensure a consistent packing density. The hulls were packed to a bed height of 6.3 ± 0.2 cm. The hull material was then followed by layers of glass wool, glass beads, more glass wool, and a ground glass joint adapter. Glass beads and glass wool were used as supporting material to ensure that the packing density of the peanut hulls was constant throughout the experiment. The column was then inverted and connected to the flow system.

Table 2. Average column parameters and uncertainties for the continuous flow, fixed-bed studies.

Column Parameters	
Bed Height (cm)	6.3 ± 0.2
Mass of Hulls (g)	5.04 ± 0.03
Stock Concentration (ppm Cu^{2+})	97 ± 1
Flow Rate (mL/min)	4.99 ± 0.05

The column was mounted vertically and excess buffer solution was removed. A 97 ± 1 ppm

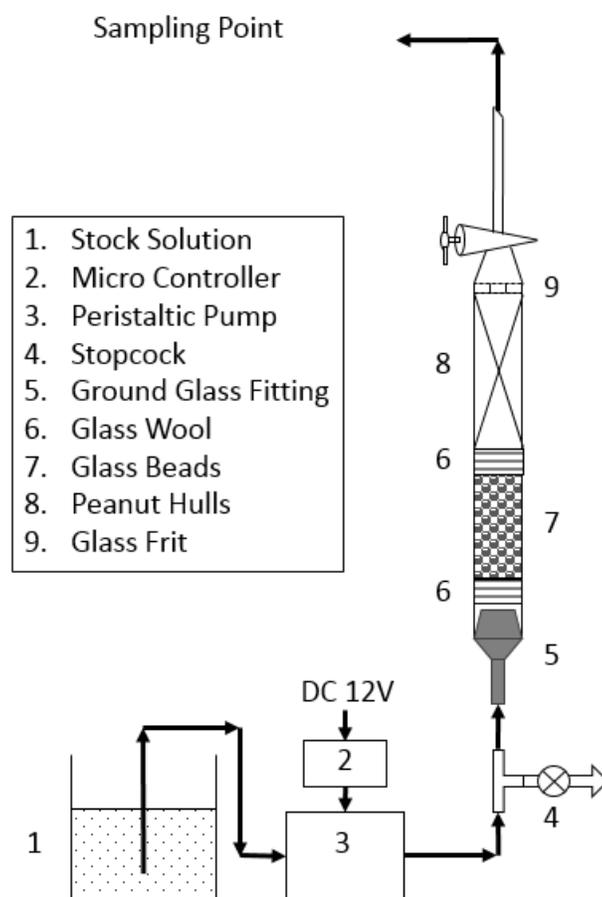


Figure 4. Experimental set up for continuous flow, fixed-bed study.

copper(II) solution was pumped out of the first stopcock (4) to adjust to the desired flow rate of 4.99 ± 0.05 mL/min. The stopcock was then turned to allow the stock solution to flow up through the column and out the top. 1.5 mL aliquots of the effluent were collected at different time intervals for 2 h. The aliquots were diluted with 5% nitric acid and then filtered using a 10 mL syringe and 0.45 μ m syringe filter for metal analysis. Copper(II) and sodium concentrations were determined using FAAS as described previously.

CHAPTER THREE: RESULTS AND DISCUSSION

3.1 Equilibrium Adsorption of Copper

Figure 5 shows adsorption isotherms (surface coverage, q_e , vs. equilibrium concentration, C_e) for Cu^{2+} bound to unmodified, alkaline modified, and alkaline peroxide modified hulls. The data represents one trial for each type of hull, and connecting lines have been shown to guide the eye.

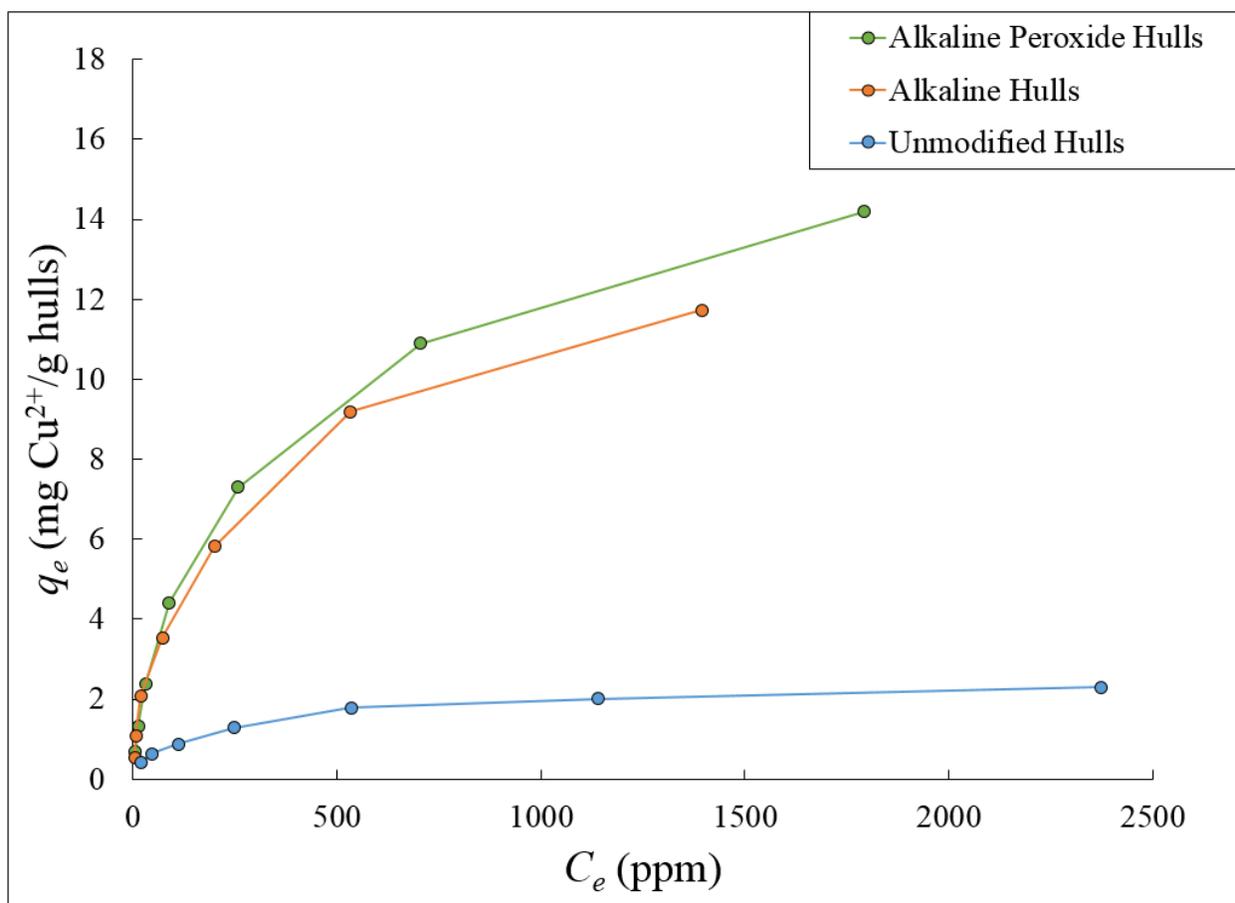
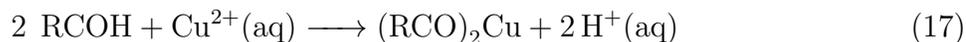


Figure 5. Adsorption isotherm data. Connecting lines have been added to guide the eye.

For each type of hull, initially the adsorption curve begins with an increase in surface coverage as solute concentration increases and eventually begins to level off. In cases when

the data approaches a horizontal asymptote, the asymptote represents the maximum possible surface coverage, also known as the adsorption capacity (Q_o). A comparison of adsorption curves for the different types of hulls shows that the unmodified hulls have the lowest adsorption capacity and the modified hulls have a higher adsorption capacity. The alkaline peroxide modified hulls have a slightly higher adsorption capacity when compared to the alkaline modified hulls. The adsorption curves show that the modification process increases the adsorption capacity of unmodified hulls.

As the unmodified peanut hulls are largely composed of cellulose, it is likely that the alcohol functional groups on the glucose units act as the binding sites for the Cu^{2+} . Binding is believed to occur via an ion exchange mechanism where the hydrogen on the alcohol group dissociates and is replaced with a Cu^{2+} ion:



The increase in adsorption capacity for the alkaline modified hulls can be associated with the delignification process that occurs when the hulls are subjected to the extremely basic alkaline modification solution.³⁶ As the lignin is removed from the peanut hulls, the surface area increases, which increases the number of available binding sites per gram of hulls. The basic solution also converts the alcohol binding sites into anionic alkoxide binding sites:



The sodium in this ion exchange system is weakly bound to the alkoxide binding site and will be exchanged for a stronger associating ion. The order of ion affinity for weak acid exchangers is $\text{H}^+ > \text{Cu}^{2+} > \text{Na}^+ > \text{K}^+$.⁶ As Cu^{2+} comes into close proximity of the binding sites, it is bound to the surface of the hulls, displacing the Na^+ counterions. This modification increases the amount of Cu^{2+} ions that can bind to the surface of the hulls. In addition, it

has been shown that chemically altering the binding sites with an alkaline peroxide solution can improve the hulls' ability for binding copper ions.^{11,14,21} The use of an alkaline peroxide solution converts the alcohol binding sites on cellulose to a carboxylate anion with a sodium counterion. The carboxylate ion is a common functional group used with ion exchange resins since it chelates strongly to cations, so the conversion to this functional group would increase the hulls' ability to adsorb Cu^{2+} .⁶ The modification turns the cellulose functional groups into a stronger cationic exchanger:^{14,21}



The alkaline peroxide modified hulls have a slightly higher adsorption capacity than the alkaline modified hulls for the adsorption of copper. The carboxylate functional group is a stronger acid than the alkoxide functional group, which allows the sodium to be weakly associated and exchange with stronger associating ions more readily. The increase in adsorption capacity is likely due to the combination of creating binding sites that are both more accessible and have a higher affinity for Cu^{2+} .

Adsorption models were applied to estimate or quantify (depending on the model) the adsorption capacity for each type of hull. The three most commonly used models are the Freundlich, Langmuir and the Redlich-Peterson, and these are the models that have been applied in this research. Figures 6, 7, and 8 show the nonlinear fits of at least two trials of experimental data using the Freundlich, the Langmuir, and the Redlich-Peterson models, respectively. Figures 9, 10, and 11 show the data fit to their respective linearized equations. A plot of the residuals is shown below each linear plot to show quality of fit. The linearized equations for each model were applied to each data set and the fitting parameters were determined using the LINEST function in Microsoft Excel. The parameters for each fit are provided in Table 3. The variable related to the adsorption capacity (Q_o for the Langmuir and

Redlich-Peterson isotherms and K_F for the Freundlich isotherms) is lowest for the unmodified hulls and larger for the modified hulls with the alkaline peroxide modified hulls having a slightly larger capacity than the alkaline modified hulls. This trend matches what was observed in the single trial data (Figure 5).

Table 3. Fitting parameters for Freundlich, Langmuir and Redlich-Peterson isotherms for unmodified, alkaline modified, and alkaline peroxide modified hulls. Uncertainties were calculated with error propagation.

Freundlich Isotherm	Unmodified Hulls	Alkaline Modified Hulls	Alkaline Peroxide Modified Hulls
K_F (mg Cu ²⁺ /g hulls ppm ^{1/n})	0.15 ± 0.01	0.38 ± 0.03	0.42 ± 0.06
n	2.7 ± 0.1	2.05 ± 0.07	2.0 ± 0.1
R^2	0.978	0.972	0.965
Langmuir Isotherm	Unmodified Hulls	Alkaline Modified Hulls	Alkaline Peroxide Modified Hulls
Q_o (mg Cu ²⁺ /g hulls)	2.54 ± 0.09	12.6 ± 0.4	14.2 ± 0.4
b (ppm ⁻¹)	0.0049 ± 0.0009	0.0060 ± 0.0009	0.007 ± 0.001
R^2	0.985	0.972	0.989
Redlich-Peterson Isotherm	Unmodified Hulls	Alkaline Modified Hulls	Alkaline Peroxide Modified Hulls
Q_o (mg Cu ²⁺ ppm ^{α-1} /g hulls)	0.436 ± 0.009	1.80 ± 0.04	4.6 ± 0.1
b (ppm ^{-α})	0.08 ± 0.03	0.09 ± 0.02	0.030 ± 0.006
$α$	0.7763	0.7414	0.8507
R^2	0.994	0.985	0.993

Figure 9 shows the plot of C_e/q_e vs. C_e fit with the linear Freundlich equation (Equation 5). The Freundlich model is the poorest fitting isotherm out of the three utilized, with R^2 values of 0.978, 0.972, and 0.965 for unmodified, alkaline modified, and alkaline peroxide modified hulls, respectively. The residuals plot shown in Figure 9 shows a similar curvature for all types of hulls studied. This suggests that the Freundlich fit does not describe the

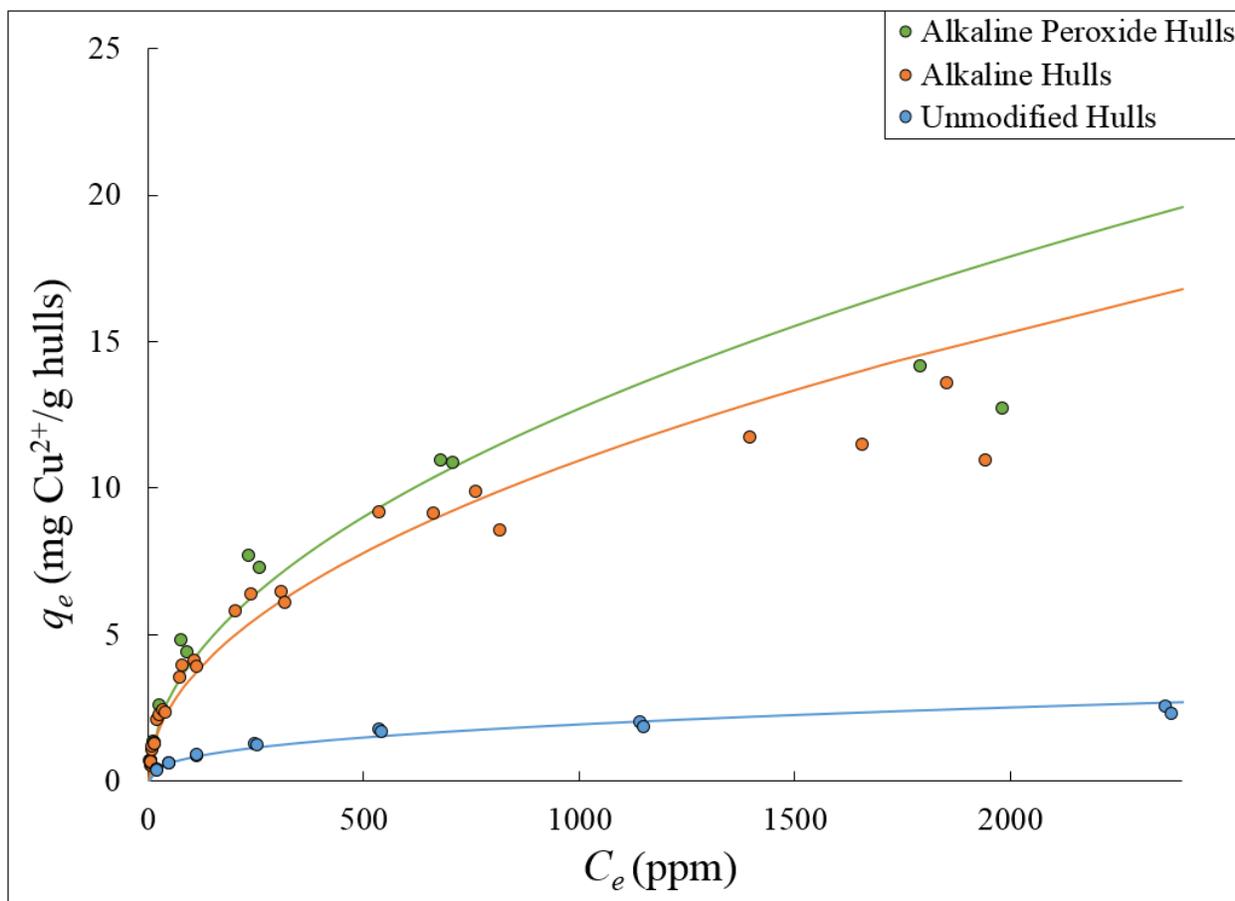


Figure 6. Equilibrium data fit with the Freundlich nonlinearized equation.

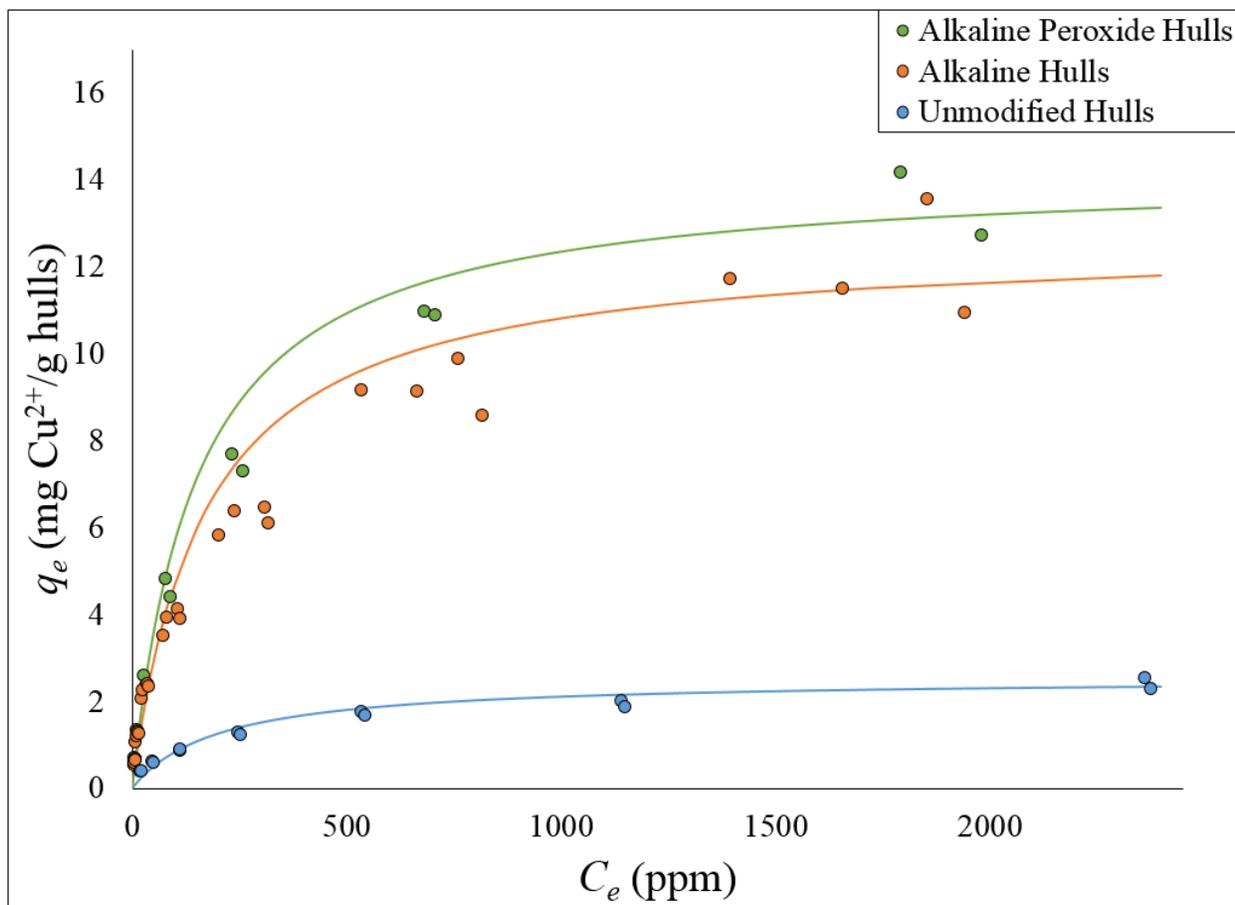


Figure 7. Equilibrium data fit with the Langmuir nonlinearized equation.

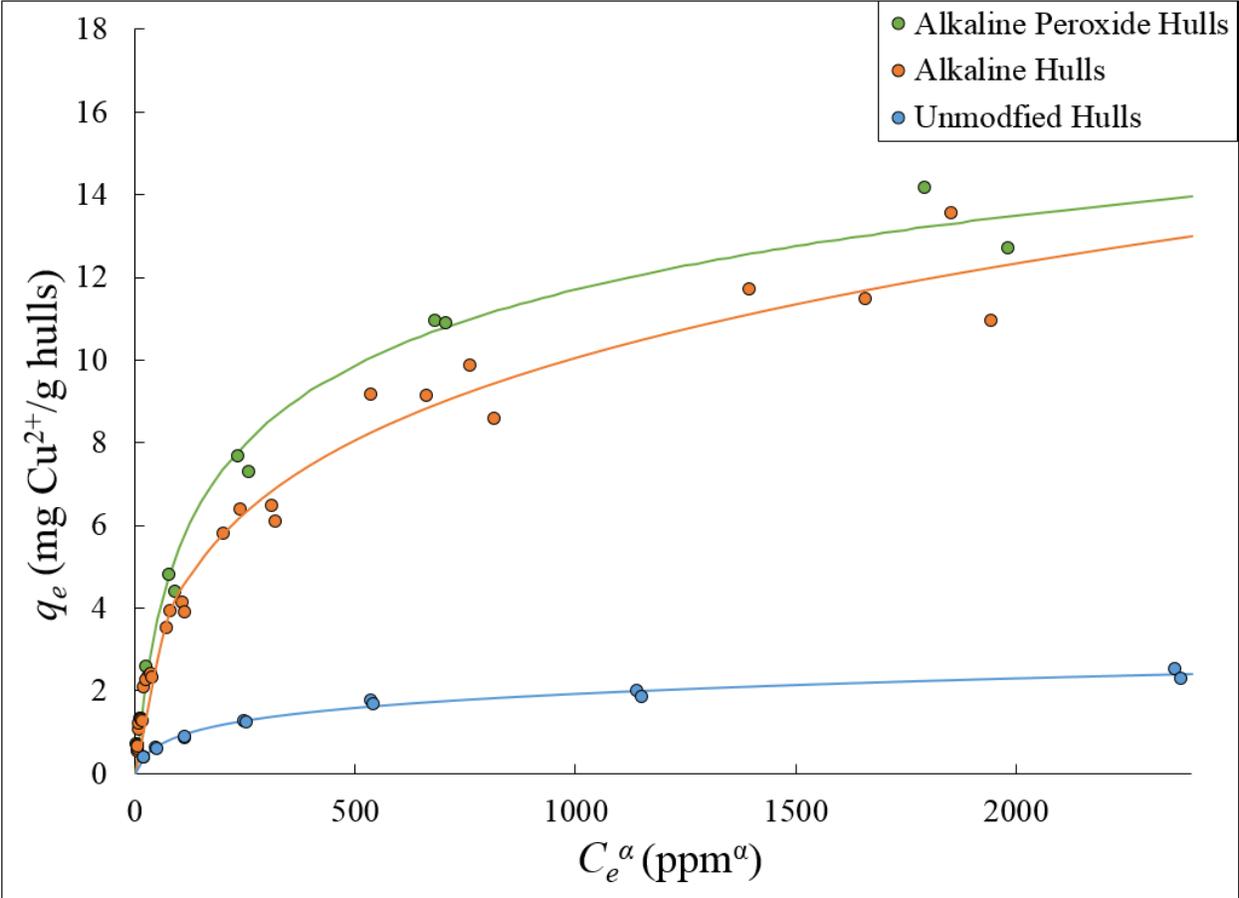


Figure 8. Equilibrium data fit with the Redlich-Peterson nonlinearized equation.

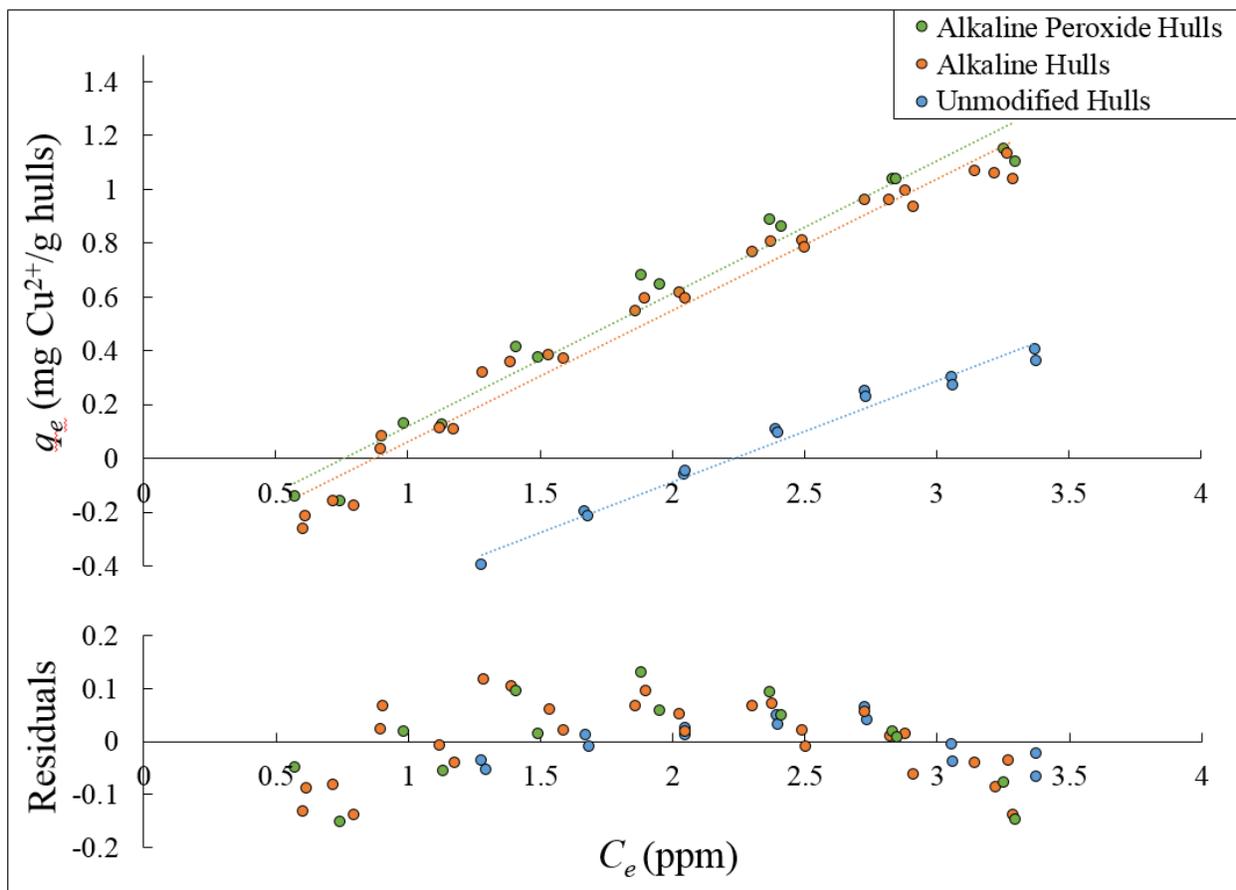


Figure 9. Equilibrium data fit with the Freundlich linearized equation. A residuals plot is shown below the linearized plot.

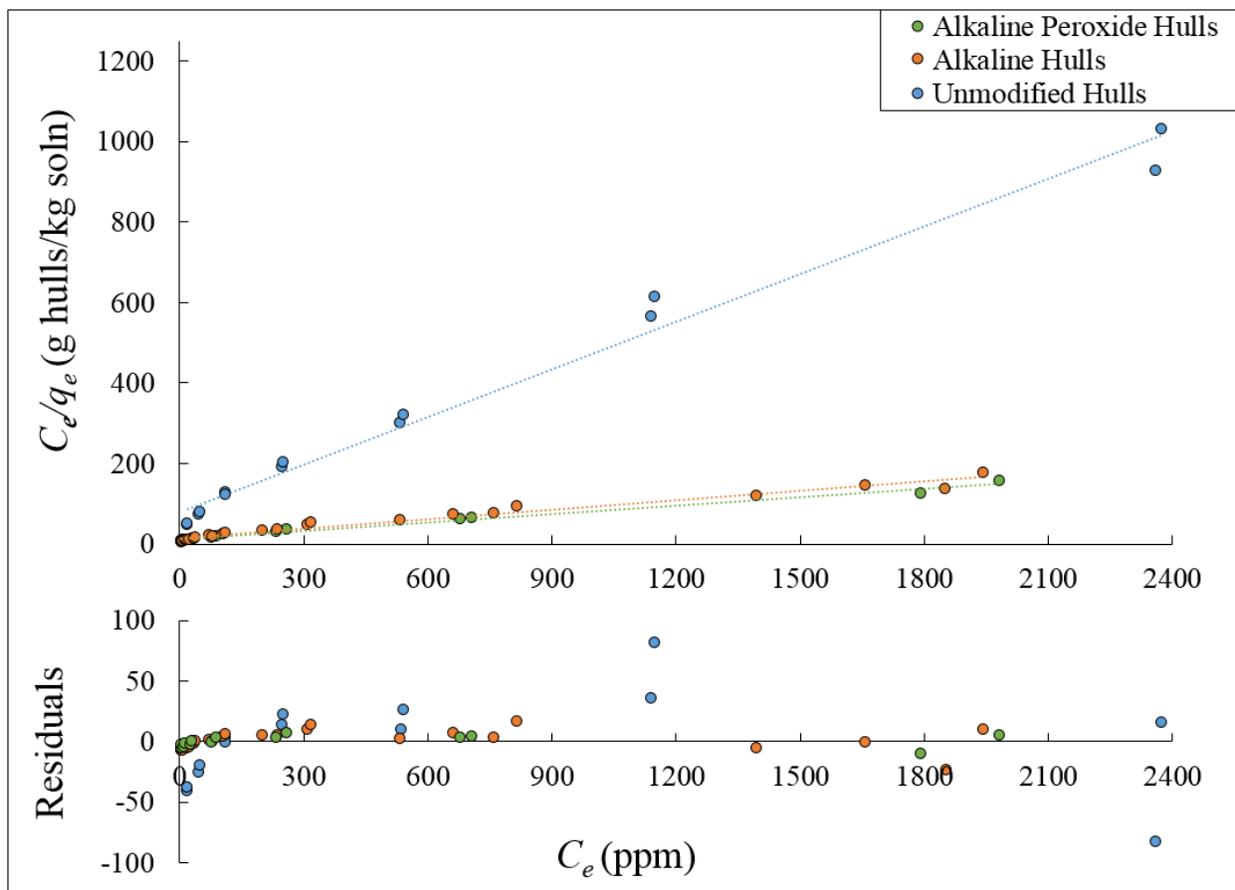


Figure 10. Equilibrium data fit with the Langmuir linearized equation. A residuals plot is shown below the linearized plot.

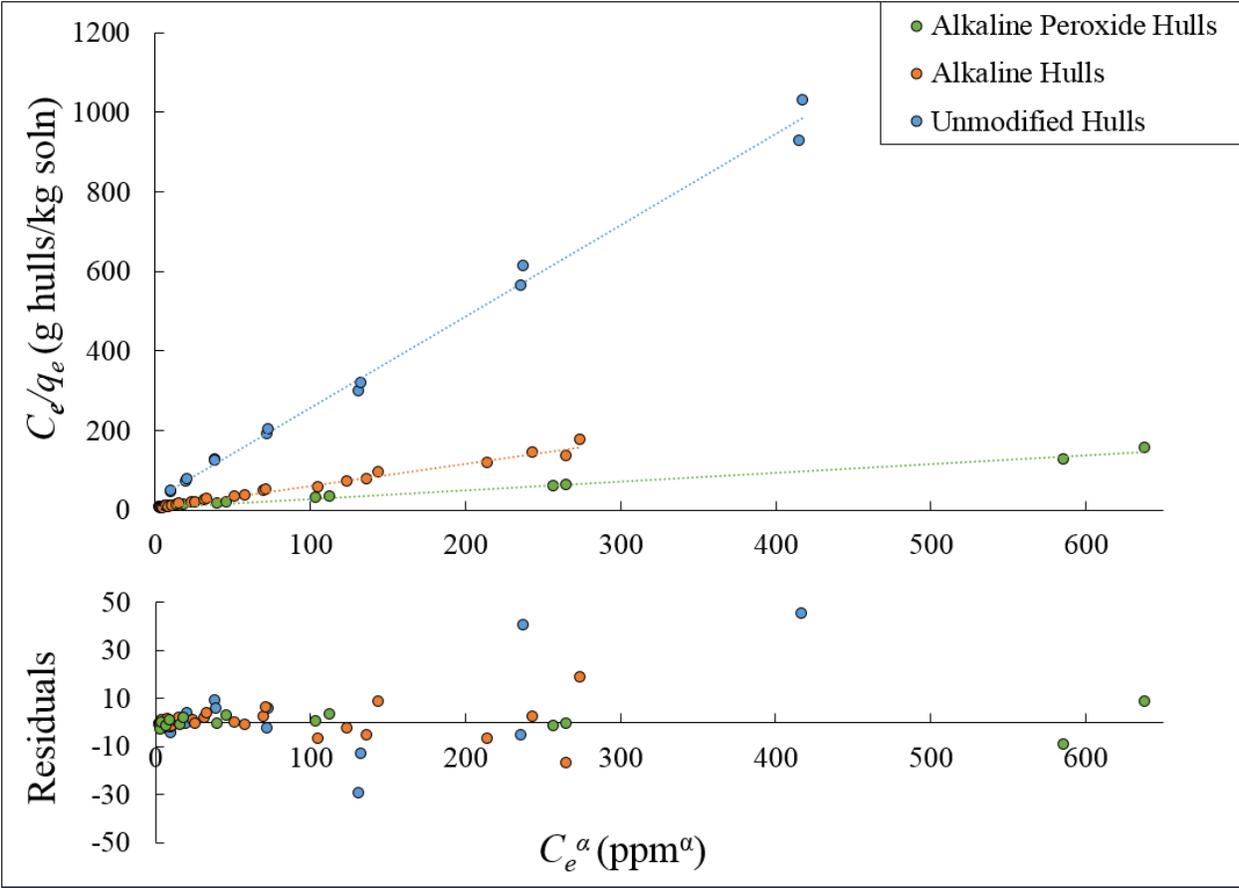


Figure 11. Equilibrium data fit with the Redlich-Peterson linearized equation. A residuals plot is shown below the linearized plot.

adsorption of Cu^{2+} onto peanut hulls very well. The Freundlich isotherm describes multilayer adsorption in which there is not a definite amount of binding sites on the surface of the hulls. As the model describes multilayer adsorption, the Freundlich model does not approach an asymptote and adsorption capacity cannot be calculated. This model having the poorest fit suggests that multilayer adsorption is not occurring, and the Freundlich model is not accurate in describing the mechanism for Cu^{2+} adsorption to peanut hulls.

Figure 10 shows the plot of C_e/q_e vs. C_e fit with the linear Langmuir equation (Equation 7). The Langmuir model is a better fitting isotherm with R^2 values of 0.985, 0.972 and 0.989 for unmodified, alkaline modified, and alkaline peroxide modified hulls, respectively. The plot of the residuals in Figure 10 shows that the residuals are more random and smaller, especially for the modified hulls, indicating that the Langmuir model is a better model for describing this particular system. The Langmuir model describes a system with monolayer adsorption, a finite amount of binding sites, and no interaction of Cu^{2+} ions at the binding sites. Since this model assumes monolayer adsorption, the fit approaches an asymptote. This model provides a fairly good fit and suggests that the adsorption mechanism is likely closer to the monolayer Langmuir adsorption mechanism rather than the multilayer Freundlich adsorption mechanism.

Figure 11 shows the plot of C_e/q_e vs. C_e^α fit with the linear Redlich-Peterson equation (Equation 9). The Redlich-Peterson model is the best fitting isotherm with R^2 values of 0.994, 0.985 and 0.993 for unmodified, alkaline modified, and alkaline peroxide modified hulls, respectively. The plot of the residuals in Figure 11 shows that the Redlich-Peterson model is a much better fitting model than the previously mentioned models. The residuals are small at low concentrations and more random throughout the data. However, at larger concentrations the residuals increase, indicating that there is a larger uncertainty in surface coverage at large concentrations. The Redlich-Peterson model incorporates a blend of both the Freundlich model and the Langmuir model into a three parameter system that can

describe both multilayer and monolayer adsorption. An α value of 1 describes Langmuir (monolayer) adsorption and an α value of 0 describes Freundlich (multilayer) adsorption. For each type of hull the α values range from 0.74 – 0.85. The large value suggests more monolayer, Langmuir type adsorption. The alkaline modified hulls have the lowest value for α , indicating they have the most Freundlich character of the three types of hulls tested.

Despite the good fit for the Redlich-Peterson model, this model (and the Freundlich model) have one major short coming. The variable that relates to the adsorption capacity (Q_o for Redlich-Peterson and K_F for Freundlich) has unusual units which stems from the equilibrium concentration (C_e) being raised to a power. The Freundlich units for K_F are $\text{mg Cu}^{2+}/\text{g hulls ppm}^{1/n}$ and the Redlich-Peterson units for Q_o are $\text{mg Cu}^{2+}\text{ppm}^{\alpha-1}/\text{g hulls}$. These units make the values of the adsorption capacity difficult to interpret. While their relative values cannot be compared to values obtained by other models, the Redlich-Peterson value can be compared for the different types of hulls. These units also make it difficult to apply this constant to other calculations, as the units for adsorption capacity should be in units of $\text{mg Cu}^{2+}/\text{g hulls}$ like the Langmuir adsorption capacity value. Visual inspection of the Langmuir isotherms for alkaline peroxide modified hulls in Figure 5, the expected value for Q_o is approximately $14 \text{ mg Cu}^{2+}/\text{g hulls}$. The value calculated for the alkaline peroxide modified hulls with the Langmuir isotherm is $14.2 \pm 0.4 \text{ mg Cu}^{2+}/\text{g hulls}$. The Langmuir isotherm not only has a good fit with the data, but also is able to accurately quantify the adsorption capacity with meaningful units.

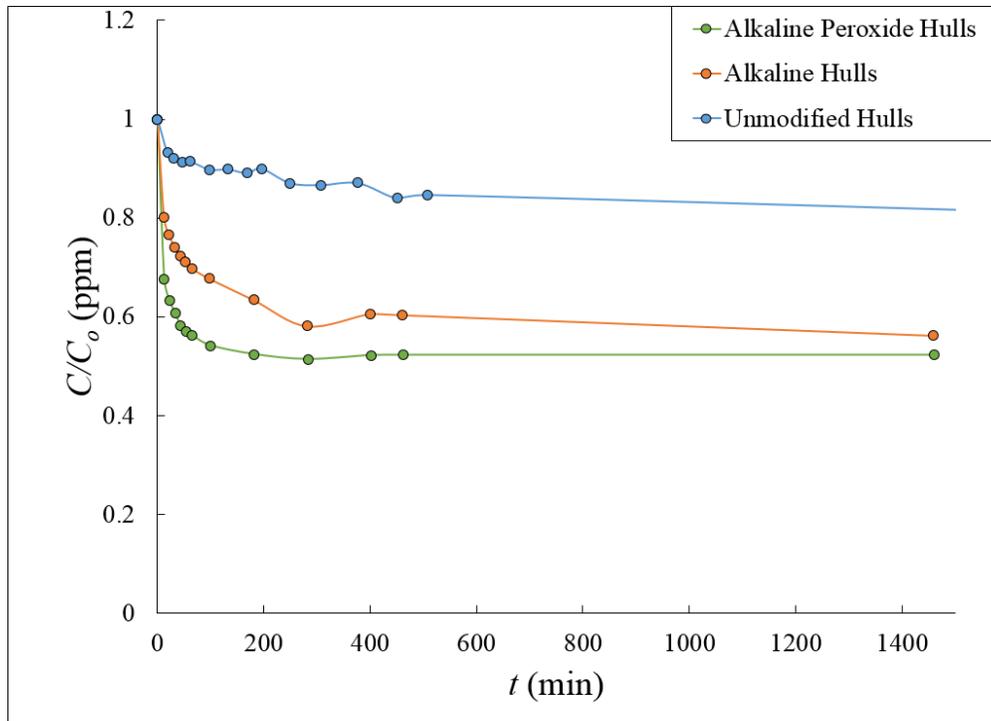
3.2 Kinetics of Adsorption

Figure 12 shows data from kinetics studies of adsorption of Cu^{2+} to unmodified, alkaline modified, and alkaline peroxide modified hulls. Figure 12a represents one trial of data for each type of hull. The concentration of the samples was normalized to the stock solution concentration since the stock solution varied from experiment to experiment. The initial

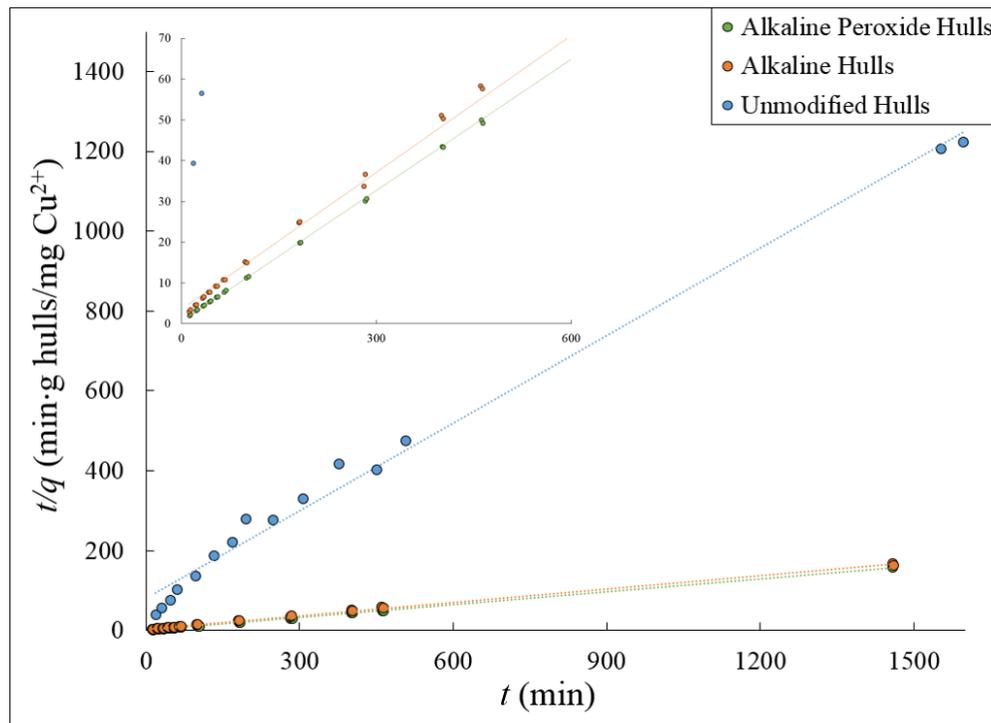
stock solution used for the unmodified hull experiment had a Cu^{2+} concentration (500 ppm) much lower than the modified hull studies (1000 ppm) since the unmodified hulls have a lower adsorption capacity than modified hulls. For each type of hull, the Cu^{2+} concentration in solution initially drops quickly as the Cu^{2+} ions are adsorbed to the hulls. The concentration then levels off as the system reaches equilibrium. The leveling off occurs as the hulls' binding sites become saturated and can no longer accept more ions. The rate is related to how fast the Cu^{2+} concentration decreases to reach equilibrium. Visually this is difficult to distinguish. However, it has been shown previously that the adsorption of Cu^{2+} to peanut hulls is modeled particularly well by pseudo-second order kinetics.¹¹ With the application of a pseudo-second order kinetics model, the rate constant (k_2) and the surface coverage (q_e) can be quantified.

The data was linearized by plotting C/q vs. t and fit with a pseudo-second order kinetics model. Figure 12b shows the linearized data from the kinetics studies by plotting t/q vs. t . The inset more clearly shows the distinction observed for the modified hulls. The line of best fit was determined by the LINEST function in Microsoft Excel. The parameters from fitting with Equation 12 are in Table 4. At least two trials were used for the parameter calculations. The R^2 , greater than 0.99 for each of the fits, shows great correlation. As expected, the surface coverage (q_e) for these samples follows the same trend as was observed with the equilibrium adsorption data results. The surface coverage for unmodified, alkaline modified, and alkaline peroxide modified hulls are 1.37 ± 0.04 , 8.93 ± 0.07 , and 9.28 ± 0.02 mg Cu^{2+} /g hulls, respectively. The alkaline peroxide modified hulls have the highest surface coverage, closely followed by the alkaline modified hulls, and the unmodified hulls have a much lower adsorption capacity.

The higher the rate constant (k_2), the faster the Cu^{2+} binds to the hulls. Fast binding is ideal for wastewater remediation because the adsorbent requires less contact time with the contaminated solution to bind the adsorbate. The rate constants (k_2) for the adsorption to unmodified, alkaline modified, and alkaline peroxide modified hulls are 0.007 ± 0.001 ,



(a) Kinetics data normalized to show comparison of equilibrium concentration.



(b) Linealized kinetics data fit with the pseudo-second order rate law. The inset shows a comparison of the data for the alkaline modified and alkaline peroxide modified hulls.

Figure 12. Pseudo-second order rate law applied to unmodified, alkaline modified, and alkaline peroxide modified hulls.

Table 4. Pseudo-second order kinetics fitting parameters for the adsorption of Cu^{2+} to unmodified, alkaline modified, and alkaline peroxide modified hulls. Uncertainties were calculated with error propagation.

Kinetics Data	Unmodified Hulls	Alkaline Modified Hulls	Alkaline Peroxide Modified Hulls
k_2 (g hulls/(mg Cu^{2+} min))	0.007 ± 0.001	0.0036 ± 0.0004	0.028 ± 0.008
q_e (mg Cu^{2+} /g hulls)	1.37 ± 0.04	8.93 ± 0.07	9.28 ± 0.02
R^2	0.991	0.999	1.000

0.0036 ± 0.0004 , and 0.028 ± 0.008 g hulls per mg Cu^{2+} min, respectively. The k_2 results show that the alkaline peroxide modified hulls are an order of magnitude faster at pulling Cu^{2+} out of solution than the other hulls. This is likely due to the presence of carboxylate binding sites and suggests a different, faster binding mechanism for these hulls than the cellulose-containing hulls, which have alkoxide binding sites. The alkaline modified hulls show a slight decrease in rate constant compared to the unmodified hulls. This suggests that the removal of lignin, which makes the binding sites more accessible, has only a small effect on the rate constant.

3.3 Continuous Flow, Fixed-Bed Column Adsorption

Figure 13 shows the data from the continuous flow, fixed-bed breakthrough curves for adsorption of Cu^{2+} onto unmodified, alkaline modified and alkaline peroxide modified hulls. The copper and sodium concentrations were plotted on separate y-axes to show the simultaneous concentrations of copper and sodium in the effluent. The unmodified hulls have no sodium data as they do not contain a sodium counterion. The effluent Cu^{2+} concentration starts around zero because at time $t = 0$, all the Cu^{2+} ions being introduced to the system are being adsorbed by the hulls. As the hulls' binding sites become occupied with Cu^{2+} , some Cu^{2+} passes through the adsorbent bed without being bound and is observed in the effluent. Once the hulls are saturated, the effluent Cu^{2+} concentration levels out at around

the same concentration as the stock solution introduced in the column (C_o).

The unmodified hulls were the quickest to have Cu^{2+} contaminant breakthrough followed by the alkaline modified and alkaline peroxide modified hulls. The unmodified hulls showed immediate breakthrough of Cu^{2+} in the effluent at time zero. The alkaline modified and alkaline peroxide modified hulls both had very little Cu^{2+} breakthrough in their first sample but quickly showed breakthrough in subsequent samples. The breakthrough points (τ) were determined by interpolating between data points closest to the breakthrough point. The breakthrough points for unmodified, alkaline modified and alkaline peroxide modified hulls are 7.1, 17.5, and 27.5 min, respectively. The alkaline peroxide modified hulls showed the best ability to retain Cu^{2+} ions in a continuous flow setup. This trend was expected since unmodified hulls had the lowest adsorption capacity and the alkaline peroxide modified hulls had the highest adsorption capacity as well as the fastest rate of adsorption.

The alkaline and alkaline peroxide modified hulls both showed an initial release of sodium in the effluent. Since the modified hulls were rinsed extensively before being used in any studies, the source of the Na^+ ions are likely bound Na^+ ion at the surface binding sites on the hulls. As the hulls were subjected to a Cu^{2+} solution, sodium was immediately released from the hulls' binding sites confirming an ion exchange mechanism. The sodium concentration at time zero is quite large due to a large amount of Cu^{2+} displacing the sodium bound to the surface of the hulls. As the hulls become saturated, no more Na^+ is released and the Na^+ concentration approaches zero. The ratio of Na^+ to Cu^{2+} of alkaline modified and alkaline peroxide modified hulls are 4.30:1 and 2.37:1, respectively. According to Equations 18 and 19 the expected ratio for these particular systems was a 2:1 ratio, where one Cu^{2+} ion would be bound to the surface of the hulls displacing two Na^+ ions. Both the alkaline modified and alkaline peroxide modified hulls are considered a weak acid cation exchanger because of their weakly acidic alkoxide and carboxylate binding sites, respectively. Ion exchange systems preferentially bind certain ions over others replacing the weaker associated counterions with

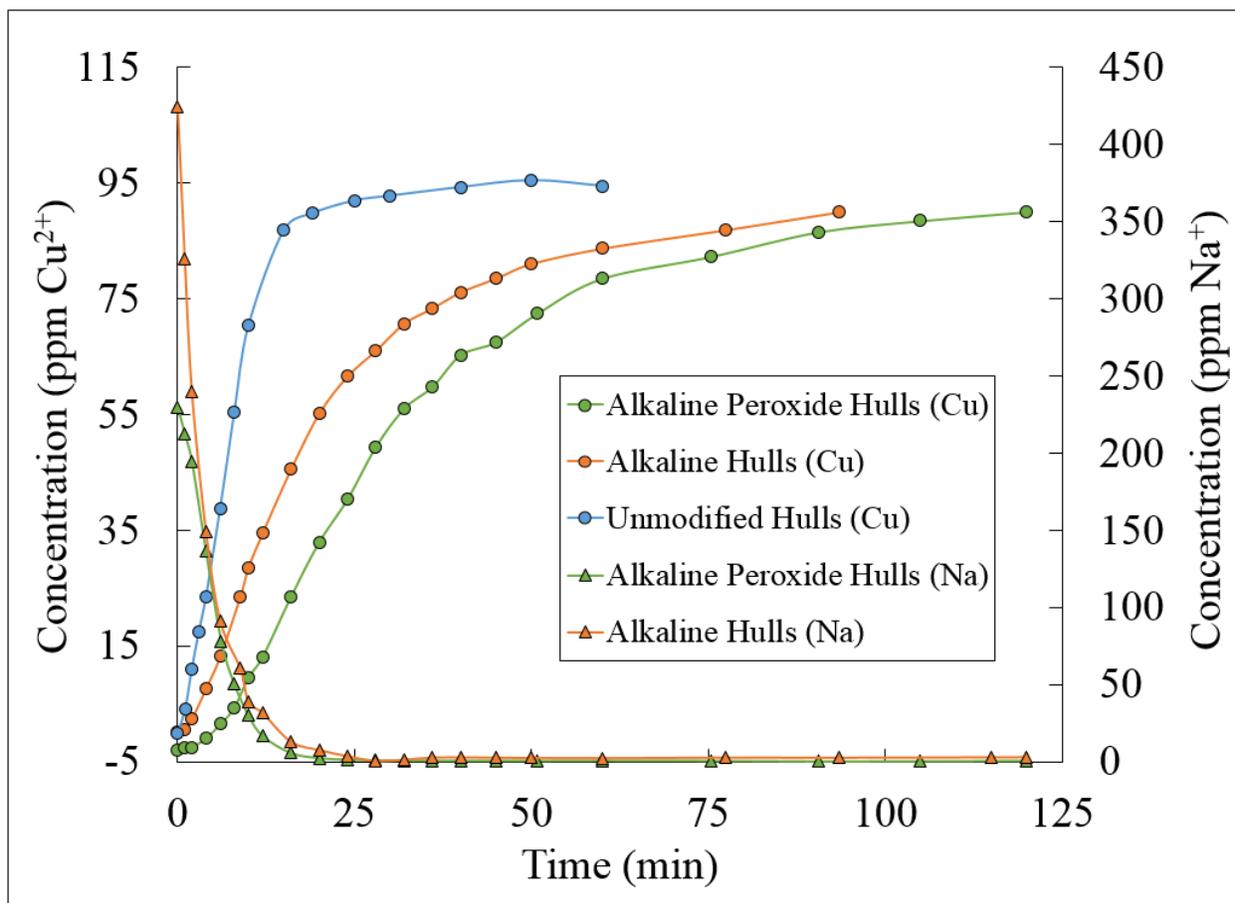
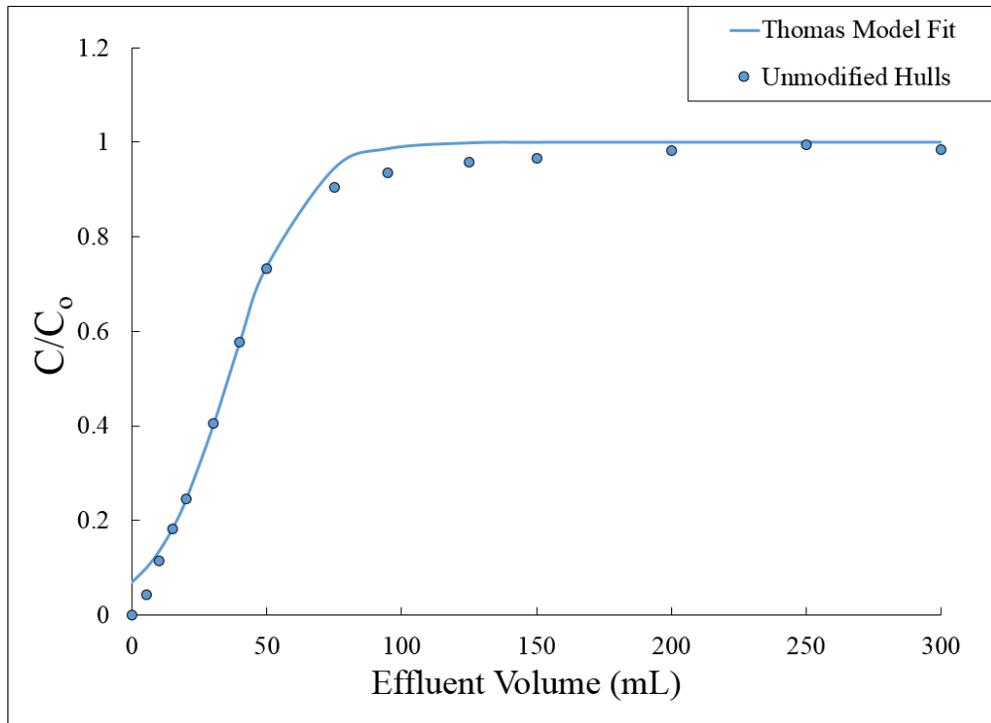


Figure 13. Breakthrough curves for unmodified, alkaline modified, and alkaline peroxide modified hulls.

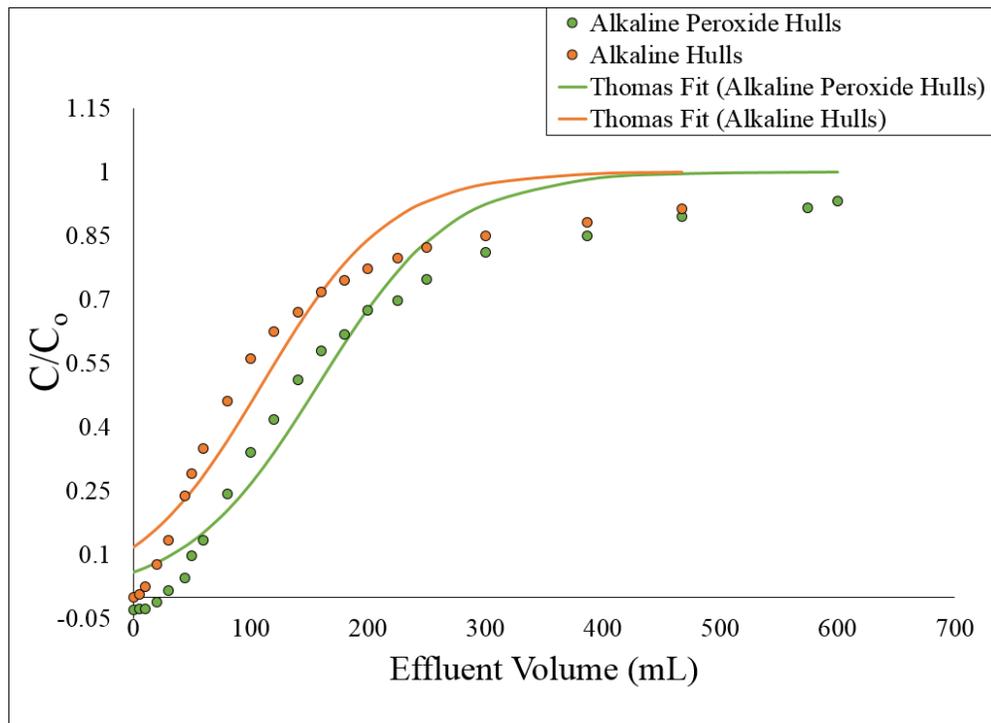
the stronger associating ions. The order usually found for weak acid exchangers is $H^+ > Cu^{2+} > Na^+ > K^+$.⁶ The alkaline modified hulls have approximately double the amount of Na^+ being released than expected. More Na^+ may be released as the H^+ in the buffer may be occupying the binding sites preferentially over Cu^{2+} . This would displace more Na^+ from the binding sites of the hulls than if Cu^{2+} was the only ion being exchanged. The alkaline peroxide modified hulls have a carboxylate functional groups which are more strongly acidic than the alkaline modified alkoxide binding sites, which could account for the more appropriate ratio of Na^+ to Cu^{2+} observed for these hulls. As the acid strength of the adsorbent increases, the affinity for H^+ decreases, which explains why the ratio is lower for carboxylate functionalized alkaline peroxide modified hulls. This would allow the Cu^{2+} more opportunity to bind to the surface of the hulls rather than the H^+ in the buffer and result in ratio of Na^+ to Cu^{2+} that is closer to 2:1.

The dynamic sorption models used to fit the continuous flow, fixed-bed breakthrough curves for unmodified, alkaline modified, and alkaline peroxide modified hulls were the Thomas, three parameter Clark, and four parameter Clark models. Figures 14, 15, and 16 show the dynamic sorption fits of the continuous flow, fixed-bed breakthrough curve using the Thomas model (Equation 14), the three parameter Clark model (Equation 15), and the four parameter Clark model (Equation 16), respectively. The fitting parameters for each model are provided in Table 5. The quality of the fits was compared using the sum of the squared residuals (SSR). A smaller SSR value indicates a better fit of the data to the model.

Figure 14 shows the breakthrough curves for the adsorption capacity of Cu^{2+} to unmodified, alkaline modified, and alkaline peroxide modified hulls fit with the Thomas model (Equation 14). The main advantages that the Thomas model has over the three and four parameter Clark models is the presence of physically meaningful parameters. The parameters for the Thomas model are shown in Table 5 (Equation 14). The Thomas model takes into account parameters from the experiment like the mass of adsorbent (m_{sorb}) and flow

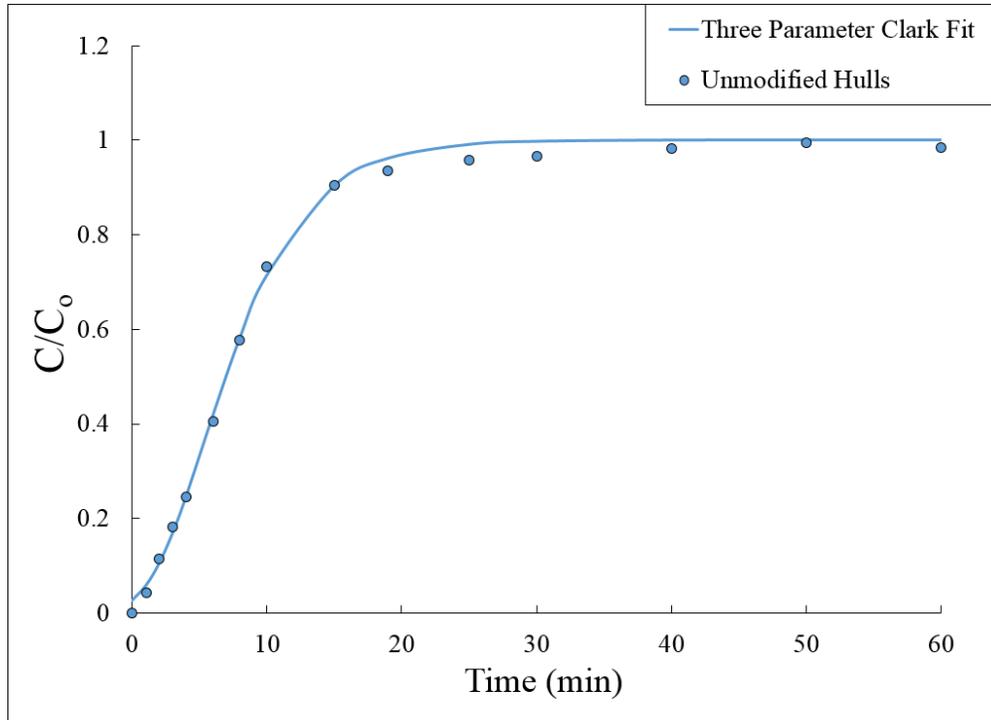


(a) Unmodified hulls fit with the Thomas model.

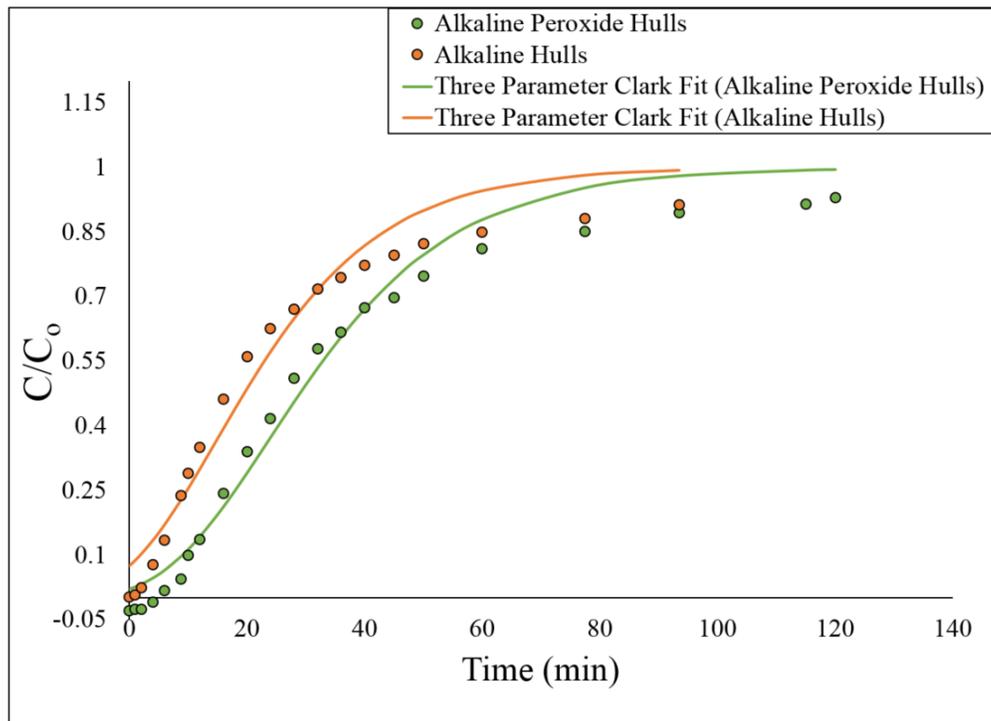


(b) Alkaline modified and alkaline peroxide modified hulls fit with the Thomas model.

Figure 14. Breakthrough curves for unmodified, alkaline modified, and alkaline peroxide modified hulls fit with the Thomas model.

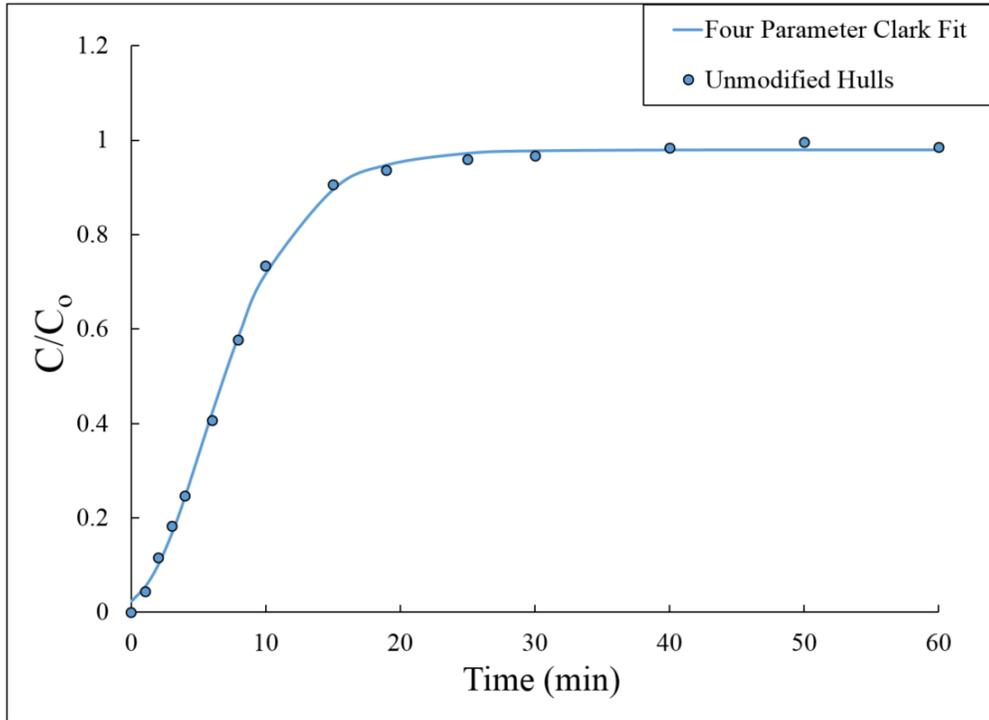


(a) Unmodified hulls fit with the three parameter Clark model.

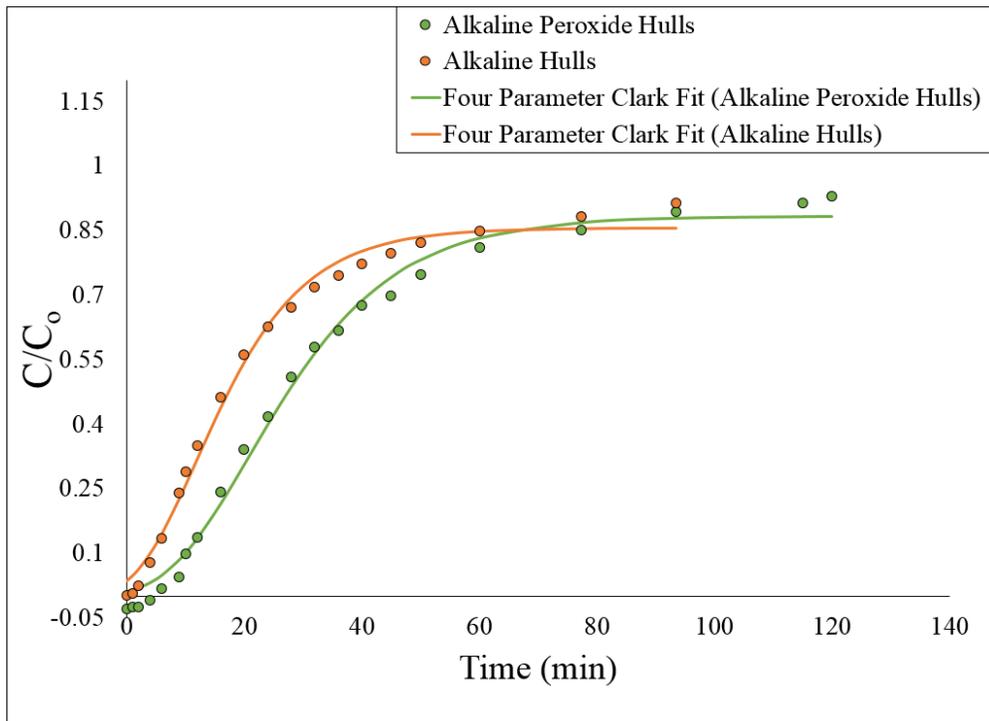


(b) Alkaline modified and alkaline peroxide modified hulls fit with the three parameter Clark model.

Figure 15. Breakthrough curves for unmodified, alkaline modified, and alkaline peroxide modified hulls fit with the three parameter Clark model.



(a) Unmodified hulls fit with the four parameter Clark model.



(b) Alkaline modified and alkaline peroxide modified hulls fit with the four parameter Clark model.

Figure 16. Breakthrough curves for unmodified, alkaline modified, and alkaline peroxide modified hulls fit with the four parameter Clark model.

Table 5. Fitting parameters for the Thomas, three parameter Clark, and four parameter Clark breakthrough curves for unmodified, alkaline modified, alkaline peroxide modified hulls.

Thomas Model	Unmodified Hulls	Alkaline Modified Hulls	Alkaline Peroxide Modified Hulls
k_T (mL soln/mg Cu^{2+} min)	3.93	0.93	0.91
Q_o (mg Cu^{2+} /kg hulls)	993	3080	4351
SSR	0.015	0.145	0.137
Three Parameter Clark Model	Unmodified Hulls	Alkaline Modified Hulls	Alkaline Peroxide Modified Hulls
A	0.0096	0.0017	0.0008
n	1.0025	1.0006	1.0002
r (min^{-1})	0.249	0.064	0.057
SSR	0.005	0.079	0.066
Four Parameter Clark Model	Unmodified Hulls	Alkaline Modified Hulls	Alkaline Peroxide Modified Hulls
A	0.0090	0.0019	0.0098
n	1.0023	1.0006	1.0002
r (min^{-1})	0.249	0.097	0.072
a	0.9793	0.9999	1.0000
SSR	0.003	0.018	0.020

rate (ν) and also predicts the adsorption capacity (Q_o). A good match for Q_o between equilibrium and dynamic flow experiments would allow for the prediction of breakthrough curves from equilibrium results. The Q_o values from the Langmuir isotherms for unmodified, alkaline modified, and alkaline peroxide modified hulls are 2.54 ± 0.09 , 12.6 ± 0.4 , and 14.2 ± 0.4 mg Cu^{2+} /g hulls, respectively (Table 3). The Q_o values from the Thomas model for unmodified, alkaline modified, and alkaline peroxide modified hulls breakthrough curves are 0.993, 3.080, and 4.351 mg Cu^{2+} /g hulls, respectively. Even though the values are on the same order of magnitude, they are not similar enough for the Langmuir Q_o values to be applied as a Thomas model parameter for breakthrough curve predictions.

The Thomas model is a symmetric sigmoidal curve, meaning rate of increase in effluent concentration at early time matches the rate at which the effluent concentration levels off as it approaches the stock concentration. The unmodified hulls are fit best with this model (SSR = 0.015), but there is a significant decrease in quality of fit with the alkaline modified and alkaline peroxide modified hulls (SSR = 0.145 and 0.137, respectively). The breakthrough curve for unmodified hulls was fit well with the Thomas model because the data is more symmetric. The alkaline modified and alkaline peroxide modified hulls have a much more asymmetric curve since the effluent concentration approaches the stock concentration more gradually.

Figure 15 shows the breakthrough curves for the adsorption of Cu^{2+} to unmodified, alkaline modified, and alkaline peroxide modified hulls fit with the three parameter Clark model (Equation 15), which is also a symmetrical model. This empirical model is more flexible in fitting a wide variety of curve shapes. The unmodified hulls are fit well (SSR = 0.005), but the modified hulls are not fit well by the three parameter Clark model (SSR = 0.079 and 0.066 for alkaline modified and alkaline peroxide modified hulls, respectively). The SSR values show a significant improvement over the Thomas model SSR values, indicating that the three parameter Clark model is able to fit the breakthrough curves of all types of

hulls better.

The final model tested is a variation of the three parameter Clark model in which a fourth parameter (a) is added to give the model increased flexibility for fitting asymmetric curves. The fourth parameter allows for the fit to be stretched/shortened along the y-axis. As the three parameter Clark model is already empirical, the addition of the fourth parameter only adds more flexibility to the model. Figure 16 shows the breakthrough curves for the adsorption of Cu^{2+} to unmodified, alkaline modified, and alkaline peroxide modified hulls fit with the four parameter Clark model (Equation 16). The addition of the fourth parameter provides a significant increase in fit when compared to the three parameter Clark, and Thomas models, as the SSR values are lower. For the unmodified hulls, the SSR value for the four parameter fit (0.003) is only slightly improved because the previous fits of the three parameter Clark and Thomas model were not poor. The most significant improvement was observed for the alkaline modified (SSR = 0.018) and alkaline peroxide (SSR = 0.020) modified hulls, as the SSR values were improved by an order of magnitude going from the Thomas model to the four parameter Clark model.

The unmodified hulls has the best fit for each model applied. Figures 14a, 15a, and 16a show the breakthrough curves for the adsorption of Cu^{2+} to the unmodified hulls fit with each model. Each model was able to fit the unmodified hulls' breakthrough curve quite well as shown by the SSR values (Table 5), which are the smallest for unmodified hulls, regardless of the model applied. This is possibly due to the unmodified hulls having more uniform binding sites resulting in a constant rate of adsorption. A constant rate of adsorption is associated with homogeneous binding sites and leads to a symmetric breakthrough curve.³⁷ The breakthrough curves for the modified hulls are asymmetric, steeper at the beginning of the breakthrough curve than at the end, which can be associated with a dynamic rate of adsorption. A dynamic rate of adsorption is related to the heterogeneity in the binding sites.³⁷ For the alkaline modified hulls, this variation in diffusion rate could be due to inconsistency in

pore size caused by the delignification that occurs in the modification process. The alkaline peroxide modified hulls, increased heterogeneity could be caused by incomplete oxidation. In both cases, heterogeneity could cause broadening of the mass transfer zone. The most active sites are occupied first while less active sites become occupied with subsequent waves of solution.

CHAPTER FOUR: CONCLUSIONS AND FUTURE DIRECTIONS

The biosorption of Cu^{2+} on unmodified and modified, high density, ground peanut hulls was investigated using equilibrium studies, kinetics studies, and dynamic adsorption studies. Adsorption isotherm models were applied to equilibrium data to determine the adsorption capacity at equilibrium. A pseudo-second order rate law was applied to the kinetics data to determine the rate constant of adsorption. Dynamic sorption models were applied to the breakthrough curves to determine breakthrough point.

The Freundlich, Langmuir, and Redlich-Peterson isotherms were used for the mathematical descriptions of adsorption to unmodified and modified peanut hulls. It was shown that the equilibrium data was best fit by the Redlich-Peterson isotherm, followed closely by the Langmuir isotherm. Even though the Redlich-Peterson isotherm was the best fitting model, the parameters are not physically meaningful. The Langmuir model provided the next best fit with the main advantage being the presence of meaningful parameters. The Freundlich isotherm was the poorest fitting model. The hulls with the highest adsorption capacity were the alkaline peroxide modified hulls, followed closely by the alkaline modified hulls. The unmodified hulls showed much lower adsorption ability than the modified hulls. The hull modifications improved the adsorption capacity by making more active and accessible binding sites for Cu^{2+} .

Pseudo-second order kinetics was applied to the rate study data to determine the rate constant of adsorption. The unmodified and alkaline modified hulls had an order of magnitude lower rate constant of adsorption than the alkaline peroxide modified hulls, indicating that the modification with hydrogen peroxide was the main contributing factor to the increase in the rate of adsorption. The resulting oxidation of binding sites likely changes the adsorption mechanism.

The dynamic adsorption breakthrough curves were acquired, and the breakthrough points

were compared to determine which type of hulls performed best. A high adsorption capacity and fast binding rate (large k_2) should result in a large breakthrough point, which is ideal for continuous flow, wastewater remediation. The trend matched the ranking of adsorption capacities observed in the equilibrium studies. The unmodified hulls were the quickest to reach 50 % saturation followed by the alkaline modified hulls and the alkaline peroxide modified hulls. The dynamic adsorption studies with the modified hulls also confirmed that the mechanism of adsorption is similar to an ion exchange mechanism. As Cu^{2+} was pumped through the column, the Cu^{2+} was adsorbed onto the surface of the hulls, displacing the counterion of sodium.

Dynamic adsorption models were applied to the experimental breakthrough curves of unmodified, alkaline modified, and alkaline peroxide modified hulls. The three models applied were the Thomas model, the three parameter Clark model, and the four parameter Clark model. The best fitting model was the four parameter Clark model, followed by the three parameter Clark and Thomas model. Although the empirical four parameter Clark model resulted in the best fit, the model's parameters are not physically meaningful. The Thomas model was the poorest fitting model. However, its main advantage is that it contains meaningful parameters, like adsorption capacity and adsorption rate constant. Although the Thomas model has this advantage, it was a poor fit to the breakthrough curves for the modified hulls, and the calculated adsorption capacities were not comparable to the values from the equilibrium studies.

The breakthrough curve for the unmodified hulls fit all three models better than the alkaline modified and alkaline peroxide modified hulls' breakthrough curves. This is because the breakthrough curve for the unmodified hulls had a much more symmetric shape, whereas the modified hulls had a much more gradual increase in concentration, taking a much longer time to reach full saturation. This is possibly due to the unmodified hulls' binding sites being more homogeneous, resulting in a constant rate of adsorption and a symmetric breakthrough

curve shape. The modified hulls have an asymmetric breakthrough shape, suggesting a dynamic rate of adsorption and heterogeneous binding sites. This may result from the exposure to an alkaline or an alkaline peroxide modification mixture.

Although the breakthrough data was successfully modeled by the four parameter Clark model, the empirical nature of the model means it is not useful for comparing to equilibrium and kinetics data. It was not possible to apply adsorption and kinetic parameters to the Thomas adsorption model for the prediction of breakthrough curves. There is a need for additional models to be tested and/or developed for these types of systems, as the current models were developed for other types of systems and applied to the biosorption of heavy metals. More specifically, in many recent studies ion exchange models have been developed in an attempt to model these complex systems. These types of models need to be explored for the adsorption of Cu^{2+} onto peanut hulls in a dynamic system. Future studies also include the potential regeneration of the biosorbent and its biodegradability. A continuation of this study would also explore the adsorption of other heavy metals, such as zinc, cadmium, and lead, as well as heavy metal mixtures.

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