KINETIC STUDIES OF BIOSORPTION OF COPPER FROM AQUEOUS SOLUTION USING GROUND PEANUT HULLS

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By

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“O for a thousand tongues to sing, my great redeemer praise, the glories of my God and king, the triumphs of his grace”

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LISTS OF ABBREVIATIONS

A	Frequency factor
C	Concentration
C_0	Initial concentration
C_t	Concentration at time t
E_a	Activation energy
EDTA	Ethylenediaminetetraacetic acid
f	Fraction of adsorption capacity
FAAS	Flame Atomic Absorption Spectroscopy
HD	High density
HDM	High density modified
HDU	High density unmodified
k	Rate Constant
k'	Rate constant for pseudo kinetic model
k'_1	Rate constant for pseudo first order kinetics model
k'_2	Rate constant for pseudo second order kinetics model
k_B	Boltzmann constant
LD	Low density
LDM	Low density unmodified
LDU	Low density unmodified
M^{2+}	Divalent metal ion
m_{hull}	Mass of hulls
m_{sol}	Mass of Cu^{2+} solution
MX_2	Metal ion - substrate complex
NPA	Normalized percent adsorbed
NPA_{max}	Biosorption capacity
PFO	Pseudo first order
PSO	Pseudo second order
q_e	Surface coverage at equilibrium
q_t	Surface coverage at time t
R^2	Correlation coefficient
RMSE	Root mean square error
T	Temperature
t	Time
X	Substrate

ABSTRACT

KINETIC STUDIES OF BIOSORPTION OF COPPER FROM AQUEOUS SOLUTION USING GROUND PEANUT HULLS

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Water contamination by heavy metals from industrial wastewater discharge is a serious global environmental concern. For a heavy metal like copper, accumulation beyond the tolerant limit would constitute a serious environmental and public health problem. Biosorption of copper to bio-sorbents like peanut hulls has proven to be a considerably good method for wastewater remediation, but the parameters for industrial application are yet to be fully studied. The purpose of this research is to study the kinetics of biosorption of copper from aqueous solutions using ground peanut hulls. There are two types of ground hulls, low density hulls which float and high density hulls which sink in water. Each hull type was studied in its unmodified form and compared to hulls that had been modified via an alkaline peroxide solution. Most of the biosorption takes place in the first 2 h of biosorption process. The initial rate of the biosorption process was faster for modified hulls have than for unmodified hulls, and the rate was faster for low density hulls than high density hulls. This trend is likely due to the higher concentration of binding sites in the low density and modified hulls. The process fits best to the pseudo second order kinetic model, which is typical of biosorption processes. The modified hulls had roughly the same rate constant while the low density unmodified hulls had a much higher rate constant.

This result may be due to a higher collision frequency factor or reduced transition energy state. The high density unmodified hulls had a lower rate constant, possibly because of the materials responsible for the high density.

CHAPTER ONE: INTRODUCTION

Motivation

Water contamination by heavy metals from the discharge of industrial wastewaters is a serious global environmental problem. Heavy metals include copper, lead, cadmium, mercury, chromium etc. These metals are toxic, and can cause problems such as renal kidney disease, nervous system damages, cancer, and mental retardation.[1] They are also non-degradable and therefore persistent in the environment, and can enter the food chain through the water channels. Some industries responsible for the discharge of wastewaters containing metals are mining and mineral processing, pigment manufacture, painting, and photographic industries, metal-working and finishing processes.[2] Since metals are non-biodegradable, and may bio-accumulate in living tissues, their removal from wastewaters is nowadays legally imposed.[2]

Copper has been reported as one of the most widely used heavy metals in electrical and electroplating industries.[3] When humans are exposed to excess copper, it accumulates in the liver, brain, skin, pancreas, and myocardium.[3] Acute copper poisoning after ingestion may show systemic effects such as hemolysis, liver and kidney damage, and fever with influenza syndrome. Local effects include irritation of upper respiratory tract, gastrointestinal disturbance with vomiting and diarrhea and a form of contact dermatitis. Therefore, treatment of copper containing wastewaters before they are discharged into water streams is necessary.[4]

Current treatment technologies for removal of metal ions in wastewater include flocculation, precipitation, membrane separation and biological methods.[5] Adsorption is another remediation technique in which metal ions are adsorbed to the surface of a solid substrate, which is then removed from the water, taking the contaminants with it.[5] Adsorption has been widely used in the removal of metal ions from aqueous media.[6] However, the development of convenient, low-cost, highly efficient, and practical adsorbents for metal ions in aqueous media is still a challenge.[6] Agricultural materials used in this process of adsorption are generally called biosorbent.[2]

Many researchers consider biosorption as a type of adsorption, where the sorbent is a biological matrix.[7] Biosorbents could be obtained free of charge since they are agricultural waste products. They are cheaper than ion exchange resins and activated carbon because the only costs to be considered are those of transport and grinding. Several biosorbents from vegetable source have been tested for the removal of heavy metals, mainly agricultural wastes.[2] Biosorbents like maize cob and husk, hard wood sawdust,[8] sunflower stalks,[9] sago waste,[10] cassava waste,[11] banana pith,[12] peanut skin,[13] *medicago sativa* (Alfalfa),[14] sphagnum moss peat,[15] and so on, have been used to adsorb metal ions such as lead, copper, zinc, cadmium in aqueous solutions. Generally, biosorbents contain abundant alcoholic hydroxyl, phenolic hydroxyl, and carboxyl groups. These polar groups can act as metal binding sites or be chemically modified to form new compounds with changed properties to improve adsorption capacity.[3]

Peanut hulls, one of the most abundant food industry waste products, are a natural low-cost material able to fix metal ions.[2] Peanut hulls have been investigated as a low-cost adsorbent to remove heavy metals such as copper ions, nickel ions, and chromium ions from aqueous solutions.[4] Research revealed that different modification techniques, such as the use of alkaline peroxide [16] or acidic solutions like EDTA,[3] nitric acid[17] or mercapto acetic acid[6] or the addition of dyes like C.I. Reactive Orange 13[16] improved the adsorption capacity of different biomass.[6]

Adsorption kinetics is an important characteristic in defining the efficiency of sorption. The data obtained from the study of adsorption dynamics are necessary to understand the variables that affect the sorption of solutes, and the rate of sorption observed can also be used to develop predictive models for column experiments.[18] Sorption mechanisms can be further understood by choosing a mathematical model which not only fits the data with satisfactory accuracy but also complies with a reasonable sorption mechanism.[18] The purpose of this research is to study the kinetics of the biosorption of copper to ground peanut hulls.

Research Goals

This research involves biosorption of copper ions using different types of hulls based on separation and surface treatment methods. Previous research had shown that a modification using a mixture of hydrogen peroxide and sodium hydroxide oxidizes the hydroxyl groups of cellulose present in jute fibers to carboxyl groups, thus creating a weak cationic ion-exchanger, which increases the uptake of copper ion.[16] Unmodified jute fiber showed an adsorption capacity of 4.23 mg/g of copper compared to 8.4 mg/g for dye loaded jute fiber and 7.73 mg/g for oxidized jute fiber.[16] An earlier study of ground peanut hulls modification in our laboratory showed similar improvement in adsorption capacity going from 2.54 mg/g hull to 14.2 mg/g hull upon alkaline peroxide modification.[19] Other research has also shown that ground peanut hulls can be separated into two types based on their density and ground hulls with lower density have a greater adsorption capacity for methylene blue (0.22 mmol/g) than high density hulls (0.1 mmol/g).[20] The research from this group on adsorption to ground peanut hulls to date has focused on equilibrium adsorption studies, but the study presented in this thesis is one of the first studies to explore the kinetics of the process of biosorption of Cu ions to ground peanut hulls. Also, this research is the only study (to our knowledge) that investigates adsorption to ground hulls that have been separated by density combined with the effect of an alkaline peroxide modification.

The goals of this research are to study the kinetics of the biosorption of copper onto unmodified and modified, low and high density ground peanut hulls. Specifically, the study will determine

(i) the initial rate of biosorption,
(ii) whether the biosorption process follows pseudo first order or pseudo second order kinetic models, and
(iii) the rate constant for biosorption.

Background

Biosorption onto Peanut Hulls

Biosorption has been used by different researchers using a living or dead biomass for the uptake of pollutants from the solution.[21] The prefix "bio" indicates involvement of biological material, while sorption is a term used either for adsorption or absorption. The term sorption has been used to describe any system where a sorbate (an atom, molecule, ion in aqueous solution) is attached to a sorbent (solid surface) resulting in an accumulation at the sorbate–sorbent interface.[21]

The Langmuir adsorption model describes the amount of sorbate taken up by an adsorbent as a function the sorbate concentration in solution.[22,23] This model has been applied to adsorption of metals onto biomass, and it assumes the sorbate is adsorbed to definite sites on the sorbent surface and that all the adsorption sites are equivalent.[24]

Biosorption is a mass transfer process where solutes in solution are transferred to the solid adsorbents. This process can occur in three stages:[25]

1. External diffusion: This is a process where metal ions in solution moves such that it breaks the barrier between solid-solution interface to be in contact with the solid substrate. The concentration gradient causes a movement from a region of high

concentration in the bulk solution to a region of low concentration solid-solution interface.

2. Internal diffusion: This is the movement from the surface of the solid substrate into the pores. This process may not be as fast as the external diffusion.
3. Adsorption onto active site: This occurs when the metal ions have the appropriate orientation such that they get attached to the active sites on the solid substrate.

Generally, biosorbents contain abundant alcoholic hydroxyl, phenolic hydroxyl, and carboxyl groups. These polar functional groups containing a partial negatively charged oxygen atom act as binding sites because they have a high affinity for positively charged species like metal cations in solution.[26]

Peanut hulls are composed mainly of cellulose (35.7%), hemicellulose (18.7%) and lignin (30.2%).[13,27] Lignin is a polymer having phenyl propene-like structures with methoxy ($-OCH_3$), hydroxyl (−OH) and aldehyde -CHO) functional groups.[13,28] Cellulose is a polymer of glucose units, which contain primary and secondary alcohols, joined together by ester linkages.[29] The oxygen atom present in carbonyl and hydroxyl group of the functional group present in lignin and cellulose can be considered strong Lewis bases with pairs of electrons ready for binding with metals that are positively charged, forming a complex coordination compound.[2] Researchers have shown a correlation between lignin content and their ability to bind with metals form aqueous solution.[2]

Also, cellulosic surfaces are negatively charged when dipped in water, exhibiting columbic attraction for cationic metals and high binding abilities of the metals.[2,30] In an aqueous solution of above a pH of 3.5, the functional groups of the peanut hulls acquire negative charges and are able to adsorb cationic species through electrostatic attraction.[13,31,32]

Peanut hulls have been proven to be a good adsorbent material in a variety of applications due to their macroporous nature and resistance to temperature, mechanical stress and prolonged submersion in water.[13,33] Many researchers have shown that peanut hulls exhibit good biosorption efficiency for heavy metal ions at a reasonable cost.[5,29,32,34] Under optimal conditions, peanut hulls have exhibited a metal loading capacity of 23.7–46 mg/g hull.[13,33] Research revealed alkaline modification process improved the adsorption capacity of peanut hull.[6]

Biosorption Kinetic Models

Chemical kinetics is an aspect of chemistry that describes the rates with which chemical reactions proceed and the experimental conditions that affect or influence the speed of a chemical reaction or process.[35] Generally**,** rate is determined experimentally by measuring concentration of the reactants, over time (t).[35]

The rate of reaction is proportional to the concentration of the reactant(s) raised to a power.[35] This relationship is called the rate law, and the power is the order of the reaction with respect to each reactant. The reaction is first order if the rate depends on only one reactant with a power of one; second order if it depends on two reactants with each having a power of one or one reactant with a power of two; and third order when the sum of the power is two.[35] Kinetics of a sorption process describes the rate of adsorbate uptake.

Consider the chemical equation below used to describe the biosorption of metal ion (M) onto available binding sites of a substrate (X) to form an ion-substrate complex, MX.

$$\mathrm{M\ (aq) + X\ (s) \rightleftharpoons MX\ (s)} \tag{1}$$

Here, the rate of reaction is defined as the change in concentration (C) of reactants or products over time and the rate law can be written as

$$Rate = \frac{dC}{dt} = k[X]^n[\mathrm{M}]^m \quad (2)$$

where k is the rate constant and n and m are the orders of the reaction with respect to available binding sites and metal ion, respectively. If expressed with respect to the concentration of the product, MX, one would instead monitor surface coverage (q), which is the amount of solute adsorbed per unit mass of substrate. The concentration of available binding sites, [X], then becomes

$$[\mathrm{X}] = q_e - q_t \quad (3)$$

where q_e is the maximum surface coverage, which is achieved at equilibrium, and q_t is the surface coverage at some time, t, during the adsorption process. The difference between these two values is the number of available sites per unit mass of hulls that remain. Using this definition in Equation 2 yields

$$Rate = \frac{dq}{dt} = k(q_e - q_t)^n[\mathrm{M}]^m \quad (4)$$

When the metal ion concentration in the solution [M] is assumed to be much greater than the concentration of available binding sites on the adsorbent, then any change in metal ion concentration is negligible. So, [M] can be considered constant to give

$$Rate = \frac{dq}{dt} = k'(q_e - q_t)^n \quad (5)$$

where $k' = k[\mathrm{M}]$. Here, the rate only depends on the surface coverage and not the concentration of the aqueous solution.[36] When $n = 1$, the model is considered pseudo first order (PFO) kinetics, and

$$\frac{dq}{dt} = k_1'(q_e - q_t) \quad (6)$$

where k'_1 is the PFO rate constant. Integrating Equation 6 gives a non-linear equation[25]

$$q_t = q_e\left(1 - e^{-k_1' t}\right) \quad (7)$$

The pseudo second order (PSO) model is used when *n* = 2 in Equation 5. Equation 5 then becomes

$$\frac{dq}{dt} = k_2'(q_e - q_t)^2 \tag{8}$$

where k'_2 is the rate constant for PSO kinetics. The integrated form of equation 8 becomes the non-linear form of the second order model which is[37]

$$q_t = \frac{q_e^2 k'_2 t}{1 + q_e k'_2 t} \tag{9}$$

The PFO kinetic model aligns with the Langmuir model,[22,23] which is a common classification of biosorption systems,[24,38] when the initial concentration of solute is relatively high. PFO kinetics also models the initial stages of the adsorption process, external and internal diffusion, well. In some cases, these steps are the rate controlling steps of the adsorption process, especially when there are few active sites for binding.[25] The PFO model is generally applicable over the initial 20 to 30 minutes of the biosorption process, and does not fit well for longer times.[39] This has been observed for adsorption of hydrophilic compounds onto hydrophobic adsorbents, in which diffusion was determined to be the rate determining step.[25]

The PSO kinetic model aligns with the Langmuir model when the initial concentration of the solute is relatively low. It also has been used successfully to model the final stages of the adsorption process, binding to the active sites. PSO kinetics also fits well when there is an abundance of active sites available for adsorption. If the rate of sorption follows a PSO model, chemisorption is assumed to be the rate determining step. The process likely involves the sharing or exchange of electrons between the heavy metal ions and the adsorbent.[40,41] Other models like Elovich and Ritchie,[25] also exists but they are not discussed in this research.

CHAPTER TWO: EXPERIMENTAL METHODS

Materials

Laura Lynn brand of roasted, unsalted, peanuts in the shell were purchased from Ingles, a grocery store in Sylva, North Carolina. Ultrapure water from a Barnstead filter system having resistivity of 18.2 mΩ cm was used in preparation of all the solutions required for the research. Laboratory grade copper (II) chloride dihydrate, sodium hydroxide, nitric acid (70%), and hydrogen peroxide (30-35%), were supplied by Fisher Scientific, Waltham, MA, USA, and pH 4 buffer capsules (potassium biphthalate) by Micro Essential Laboratory, Brooklyn, NY, USA, were used to prepare buffered solutions according to package directions. A flame atomic absorption spectrometer (FAAS, Perkin Elmer PinAAcle 900F) was the instrument used for the analysis of copper ion concentration in solution. A sieve shaker (model: SS-15-7598) produced by Gilson Company Inc., was used to separate the hulls by size.

Peanut Hull Preparation

The purchased peanuts were manually shelled to separate the nuts, and seed coats from the hulls. The hulls were then ground using a Hamilton Beach 305365, custom grind hand-free coffee grinder, and were separated by size using various sieves in a sieve shaker. Only ground hulls that passed through the 1mm mesh sieve but were retained by a sieve with 500 µm mesh were used for the study.

Approximately 1700 mL of ultrapure water was heated to a temperature of about 60 – 70 □. Then about 600 g of hulls were poured into the warm water, stirred for three minutes, and allowed to stand for another three minutes. Some of the hulls sank to the bottom of the mixture, while some float to the top. The hulls that float, dubbed “low density hulls,” were separated from the hulls that sink, dubbed “high density hulls,” by decantation. Each set of hulls was removed from the water by vacuum filtration. The hulls were then oven dried at a temperature of 70 □ for 24 h and allowed to cool for 30 min before being stored in a polymeric bag for future study.

A portion of low density and high density hulls were chemically modified. A mass of 7.6 g of NaOH pellets was added to a 1000 mL water jacketed beaker, which was connected to a Thermo Scientific Iso-temp cold water bath regulator set at 20 □. Then, 200 mL of cold H_2O_2 was added to the NaOH and continuously stirred using a magnetic stirrer. Four (4) g of either low or high density hulls were added to the system and the temperature of the system was regulated at 20 □. After 6 h, the water bath temperature regulator was disengaged, and the reaction continued for another 18 h. The hulls were separated from the mixture using vacuum filtration and rinsed with water until the pH of the rinse water was 6.5 – 7.5 using a universal indicator, pH paper. Finally, the hulls were oven dried for 24 h at 78 □. The LDM hulls were re-grinded to separate the hulls from the whitish flaky substance that held them together.

Biosorption Kinetics

A solution of 1000 ppm Cu^{2+} was prepared by dissolving 0.0671 g of $CuCl_2 \cdot 2H_2O$ in 25 g of ultrapure water. Then, 1 g of hulls was mixed with the copper ion solution. The mixture was manually shaken for the first 5 minutes, and subsequently placed on tube revolver and mixed for 24 h. Throughout the experiment, 100 µg aliquots were taken from the mixture at specific time intervals. Each aliquot was diluted to approximately 10 g with 5% HNO_3 and passed through a syringe containing a 0.45 µm micro-filter. Flame atomic absorption spectroscopy (FAAS) was used to determine the concentration of the filtered samples. The biosorption process was then performed twice for each of the four types of hulls: high density unmodified hulls, high density modified hulls, low density unmodified hulls, and low density modified hulls.

CHAPTER THREE: RESULTS AND DISCUSSION

Ground Peanut Hulls Preparation and Separation

Figure 1a shows the separation process using ultrapure water. The ground hulls with density less than the density of water float, and they are referred to as low density (LD) hulls. The ground hulls with density greater than the density of water sink to the bottom of the beaker, and these are referred to as high density (HD) hulls. Previous porosity studies have shown that HD hulls have less open space within the hull particle than LD hulls, which would account for the difference in density.[20] After drying in the oven, the percentage of LD hulls is 13.7% by mass, while the percentage of HD hulls is 86.3% The relative quantity of dry LD and HD are as shown in Figure 1b. The LD hulls are lighter in color than the HD hulls. This observation is consistent with previous findings.[42]

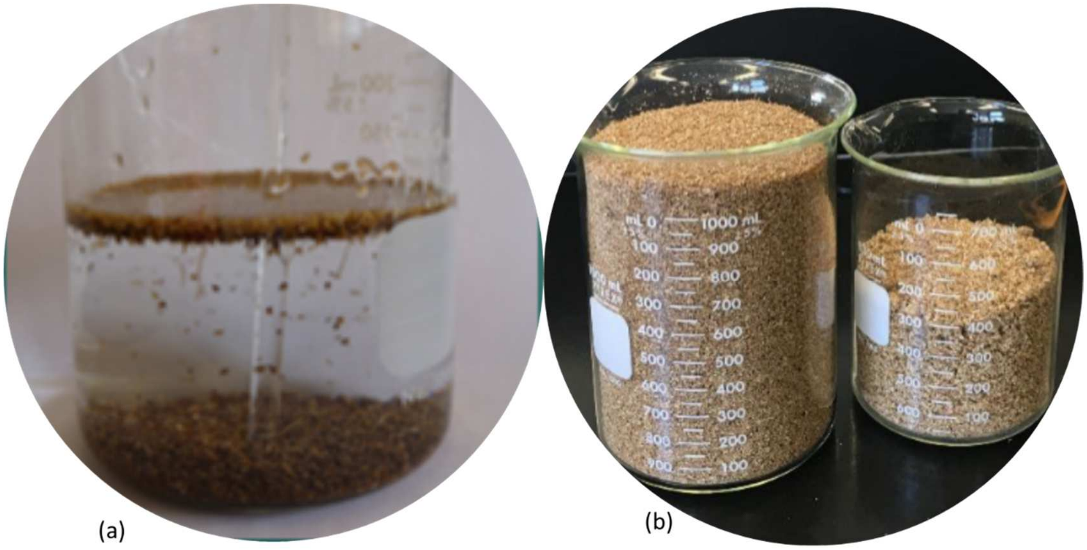

Figure 1. Images of (a) ground hulls in ultrapure water and (b) HD (left) and LD (right) hulls after drying.

Alkaline Peroxide Modification

For the first 30 min of the modification process, the temperature increases a few degrees despite the presence of the water bath aimed at keeping the temperature constant. This behavior is consistent with the previous result that showed the uncontrolled reaction to be exothermic.[29] The reaction was accompanied by a copious amount of foam. For HD hulls, the foamy contents later disappeared. However, the foamy substance that formed at the beginning of LD hulls modification process does not disappear at any time of the reaction process, even when the hulls are rinsed with water. After oven drying the LD hulls, the foamy content becomes a whitish substance which sticks to the modified hulls causing them to aggregate as shown in Figure 2. This observation agrees with the previous findings of the alkaline peroxide modification process.[42] This whitish substance partially dissolved when subjected to mixing in a pH 4 buffer solution. The aggregated LD hulls were separated from the whitish substance by grinding lightly with mortar and pestle and then sieved before use in the biosorption process. For both hull types, the alkaline peroxide solution mixture turned yellowish in color. The color of both types of hulls were brighter and lighter after modification, suggesting dark, alkaline soluble component of the hulls is removed via dissolution. This hypothesis is supported by previous findings that indicate the modified hulls are more porous than unmodified hulls.[20]

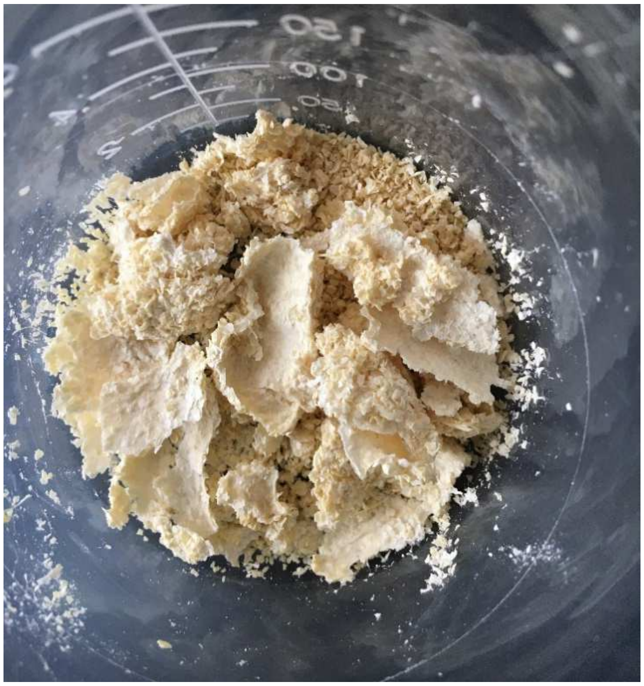

Figure 2. Whitish substance which causes modified LD hulls to aggregate.

Biosorption Equilibrium

The concentration of copper ion was monitored over a 24 h period as a prepared solution was in contact with high density unmodified (HDU), low density unmodified (LDU), high density modified (HDM), and low density modified (LDM) hulls for at least two trials. There were a few outliers in the data, as determined by statistical tools like t-test, difference in fits, and Cook's distance test.[43] Three of the points that were beyond the threshold of the tolerable points by the statistical tools were ignored.

Figure 3 shows the plot of solution concentration against the biosorption time for the first 300 min. The figure shows a rapid decrease in concentration of the aqueous solution in the first few minutes of the biosorption process, and then the decrease in concentration slows down until the concentration remains relatively constant for the remainder of the experiment. The concentration of copper ions decreased the least for the unmodified hulls, and the most for the modified hulls. For the unmodified hulls, more copper was adsorbed by the low density hulls than for the high density hulls.

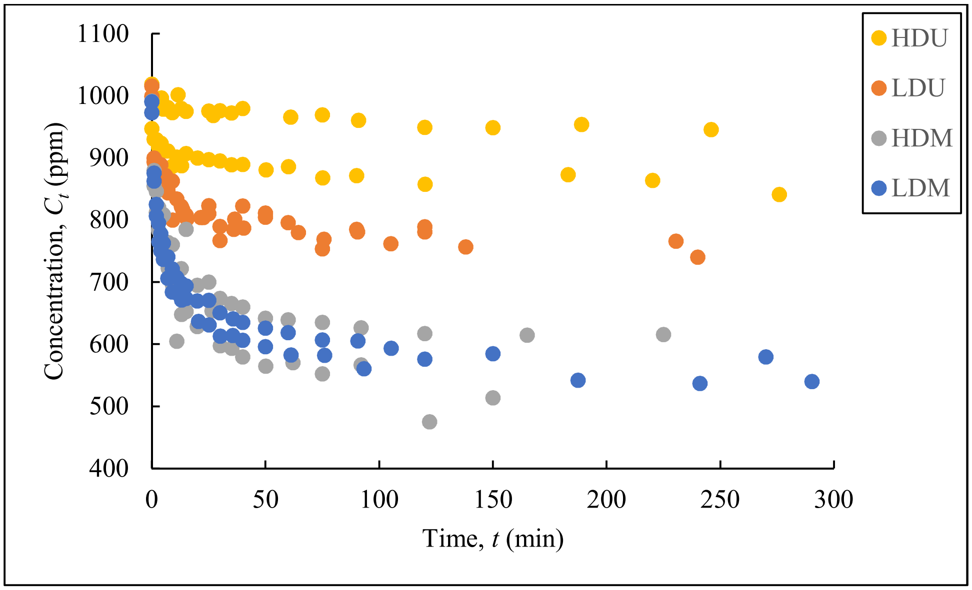

Figure 3. Concentration of copper ions in aqueous solution versus time. The data set for each type of the hulls represent 2 trials.

For both HD hull experiments, the trials shown in Figure 3 do not perfectly overlap, which is likely because the initial concentrations of the aqueous solution had slight variation from trial to trial. To account for these differences, as well as slight differences in the mass of hulls used in each experiment, the data for all experiments was normalized and expressed as the normalized percent adsorbed (*NPA*). The *NPA* is calculated by subtracting the ratio of the solution concentration at time t (C_t) to initial concentration (C_0) from one. The value is then divided by the mass of the hulls (m_{hull}) and converted to a percentage by multiplying by 100%.

$$NPA = \left[\frac{\left(1-\frac{C_t}{C_0}\right)}{m_{hull}}\right] \times\ 100\% \qquad (10)$$

Figure 4 shows a comparison of the *NPA* by each type of hull over 300 min. The overlap in the data for each of the two trials for each hull type is much better than in Figure 3. This is particularly true for the high density hulls. The difference in the biosorption profile of LDM and HDM hull is small; the datapoints almost completely overlap.

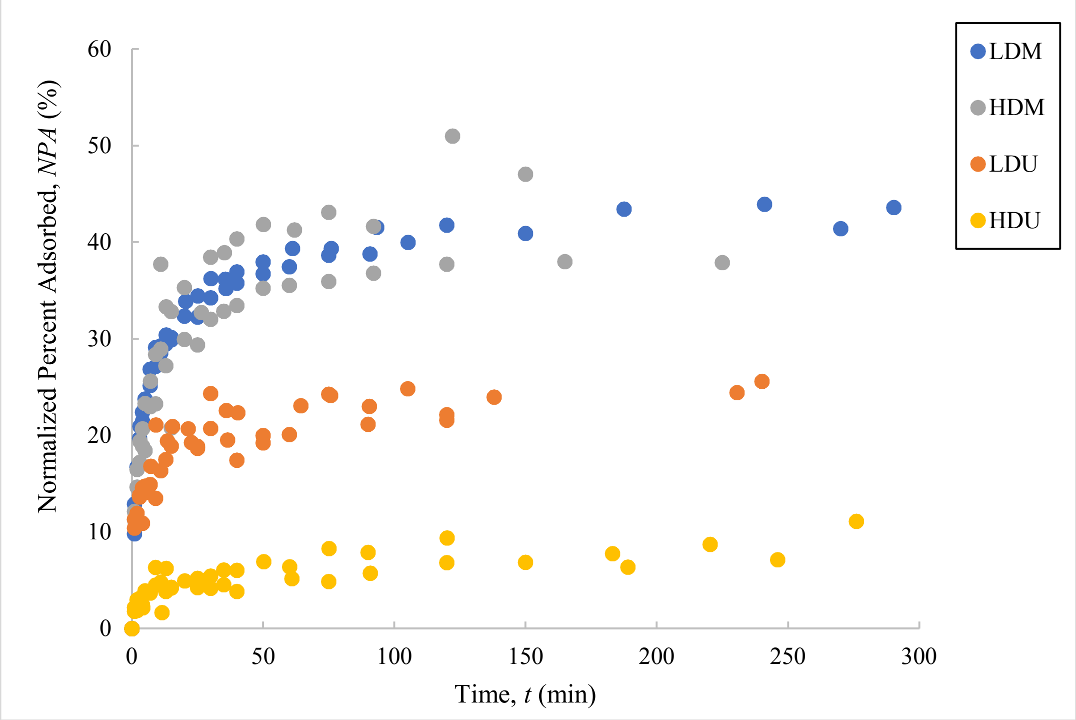

Figure 4. Normalized percent adsorbed (*NPA*) from aqueous copper solution versus time. The data set for each type of the hulls represents two trials.

Adsorption capacity (NPA_{max}) is defined as the maximum percent of ions adsorbed to the hulls. Previous research[2] has shown that equilibrium is reached within the first 2 h, so for these experiments, the adsorption capacity for each hull type was calculated in terms of *NPA* by averaging the *NPA* values from 120 min to the end of the experiment which is 4 - 5 data points for each trial.

The adsorption capacities for each hull type are listed in Table 1. The HDU hulls have the lowest adsorption capacity, while LDU hulls adsorbed more than HDU hulls but not as much as LDM and HDM hulls. This observation is consistent with the previous findings.[20,42] The difference in the adsorption capacity of low density and high density hulls may be due to the difference in their porosity. Low density hulls have higher porosity, which means the hulls have a greater surface area. The increased surface area leads to a greater number of binding sites (per mass of hull) and a greater adsorption capacity. Alkaline peroxide modification of the hulls also results in a greater adsorption capacity. Previous research showed an increase in porosity upon modification which might be the cause for this increase.[20] Also, surfaces becomes partially charged when immersed in basic solution,[2] and the amount of such negative charge may be increased by ion exchange during the alkaline peroxide modification process, where cellulosic alcohol groups are converted to alkoxide groups with a sodium counterion.[2,30] This substitution should increase binding strength between the copper ions and the binding sites. Assuming no change in entropic contributions, the adsorption capacity would increase proportionally.

Table 1. Adsorption capacities for LDM, HDM, LDU, and HDU hulls. Reported uncertainties reflect the standard deviation in the average.

Hull Type	NPA_{max} (%)
LDM	42 ± 1
HDM	41 ± 5
LDU	24 ± 2
HDU	9 ± 2

Biosorption Kinetics

Each hull type has a different biosorption capacity, NPA_{max} (see Table 1), and because of this, the data in Figure 4 is not on the same scale. To easily compare the early progression of the biosorption processes for different hull types, the *NPA* for each biosorption profile from Figure 4 was converted to the fraction (f) of the adsorption capacity by dividing the *NPA* by NPA_{max}.

$$f = \frac{NPA}{NPA_{max}} \tag{11}$$

So, at the beginning of the biosorption process, $f = 0$, and at the conclusion, $f = 1$ for each hull type, making them on the same scale.

The fraction of the adsorption capacity as a function of time for each hull type is shown in Figure 5. Each of the hulls was estimated to attain equilibrium around 2 h based on the value of *f* being approximately 1. The exception is for the HDU hulls, which have an estimated equilibrium at around 4.5 h. However, this perceived lag may be due to noise in the data rather than an actual slower adsorption rate.

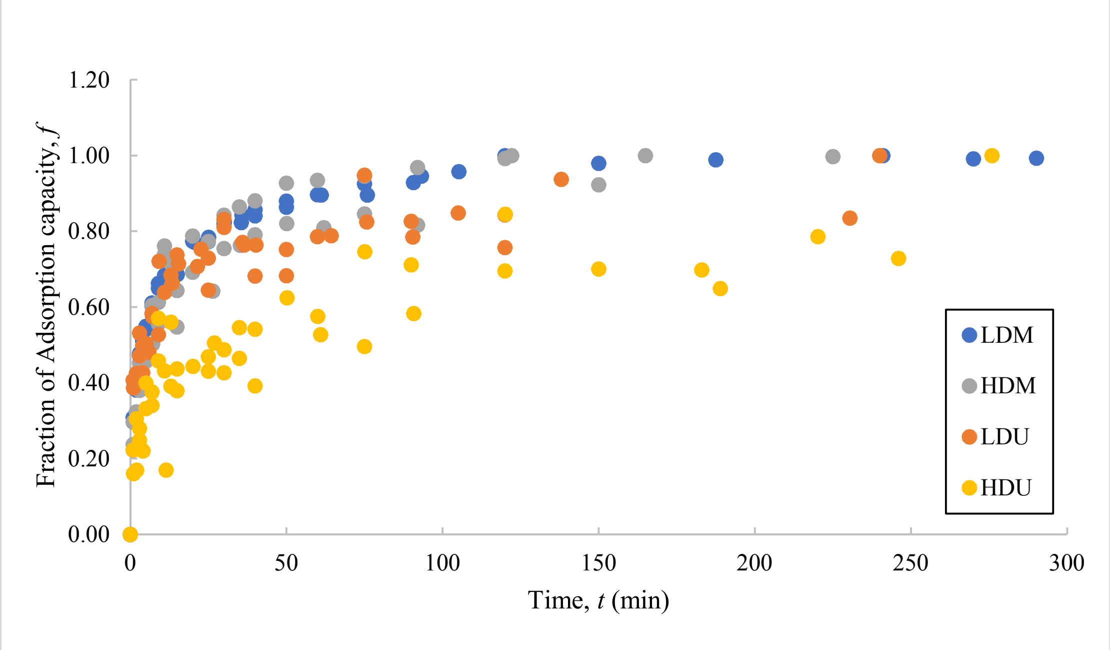

Figure 5. Fraction of adsorption capacity versus time. The data set for each type of the hulls represents two trials.

Figure 6 shows the fraction of the adsorption capacity for just the first 30 min of the adsorption process for the four hull types. The fraction of copper ions taken up by LDM, HDM and LDU hulls follows a similar progression over this time range with a somewhat linear increase that begins to level between 10 and 20 minutes. However, the HDU hulls have more noise in the data and the fraction appears to level off earlier at around 10 min. The pattern observed here may be because the materials that makes the HDU more dense may be blocking the binding sites, affecting the rate at which copper ions are adsorbed.

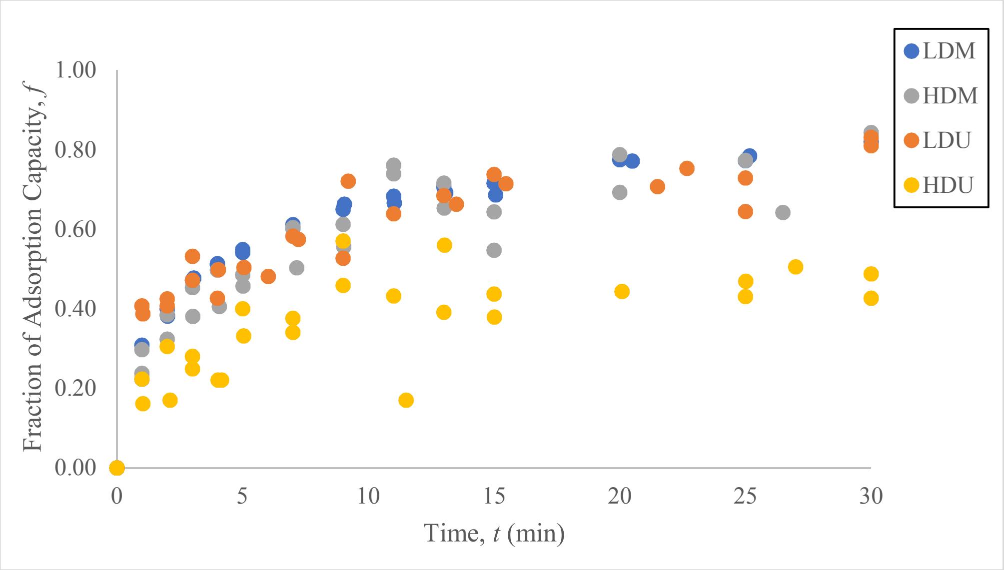

Figure 6. Fraction of adsorption capacity versus time from *t* = 0 to 30 min. The data set for each type of the hulls represents two trials.

The conventional method for modeling the kinetics of biosorption processes is to use surface coverage (q_t), which is the mass of solute that is adsorbed to the surface of a unit mass of sorbent at a given time, *t*. This quantity is calculated by multiplying the difference between the initial concentration (C_0) and the concentration at time *t* (C_t) by the mass of solution (m_{sol}) before measurement, and the dividing by the mass of the hulls (m_{hulls}) as shown in the equation below.[18,44]

$$q_t = \frac{(C_0 - C_t)m_{sol}}{m_{hulls}} \tag{12}$$

Figure 7 shows the plot of surface coverage versus time. The plot shows steep curves at the beginning of the process because ions will bind quickly when there are many available binding sites, and biosorption slows down as sites become occupied.

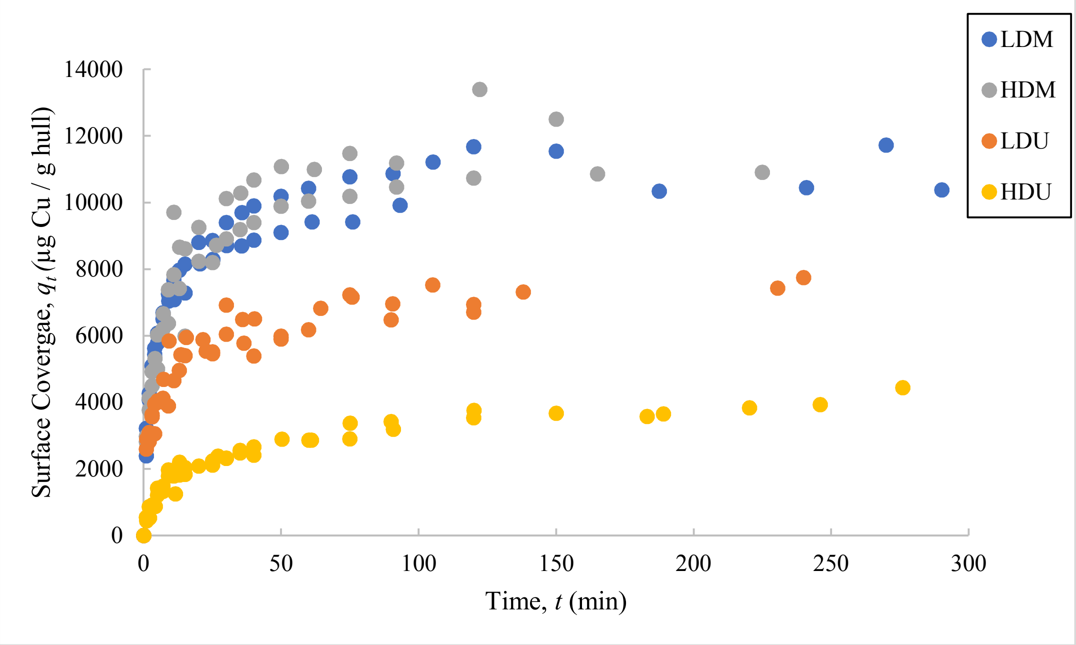

Figure 7. Surface coverage of the adsorbent versus time. The data set for each type of the hulls represent 2 trials.

The initial rate at which copper ions bind to the hulls is quantified by the slope of the curves from 1-5 min. The surface coverage from this time range was fit to a linear equation as shown in Figure 8. The slope is equal to the initial rate of biosorption and is given in Table 2 for each hull type. LDM hulls have the fastest sorption rate, followed by HDM, and LDU hulls, while HDU hulls have the slowest sorption rate.

Equation 5 shows that the rate is proportional to the concentration of available binding sites on the hulls. LD hulls have higher porosity, resulting in a greater surface area and by extension more binding sites compared to HD hulls. The alkaline modification increases the porosity, thereby making modified hulls have a greater surface area available for binding than the unmodified hulls. The fastest rate observed in LDM hulls can be attributed to the combined effect of the initially low density and increased porosity from the alkaline modification process. Figure 8 also shows that the surface coverage of LDM, HDM and LDU hulls are similar after the first minute of biosorption, but the HDU hulls have relatively low coverage. The disparity could be because the materials that make the HD hulls more dense may have no characteristic functional groups commonly seen in lignocellulosic materials and therefore have no active binding sites. Further studies would be required to test this idea.

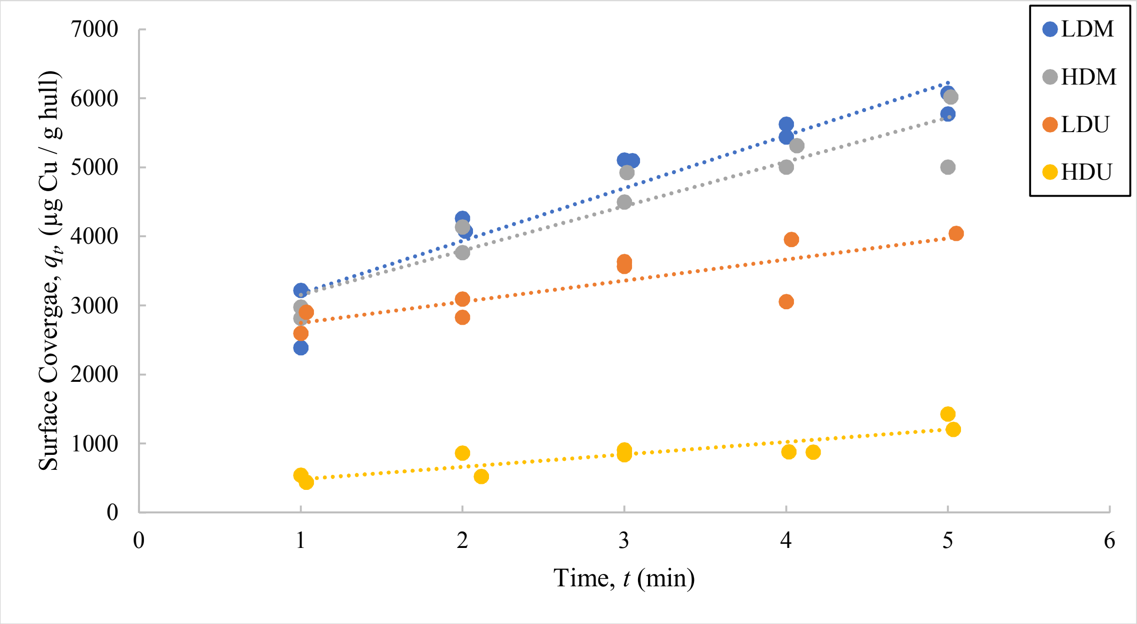

Figure 8. Surface coverage (q_t) versus time (t) between 1 – 5 min. Data was fit to a linear model.

Table 2. Initial rate and R^2 values of surface coverage versus time from 1-5 min.

Hull Type	Initial Rate ($\mu g\ Cu^{2+}/g$ hull/min)	R^2
LDM	760 ± 90	0.90
HDM	640 ± 80	0.88
LDU	310 ± 80	0.69
HDU	180 ± 30	0.79

At $t = 0$, the surface coverage, q_t, is zero because the adsorption process has not begun. No additional data was collected in the first minute. Extrapolating from $q_t = 0$ to the value of q_t at $t = 1$ min gives a much steeper slope than in 1-5 min for LDM, HDM and LDU hulls, suggesting the rate of adsorption in the first minute is much faster than during minutes 1 – 5. The relatively fast rate observed in the first minute of the biosorption process may be because the concentration of the available binding sites on the hulls is at its maximum, and a high percentage of interaction results in fast adsorption. The rate then decreases after the first minute. For the HDU hulls, the rate is fairly constant over the entire first five minutes, which is likely because the hulls have much fewer binding sites for adsorption. Therefore, the rate in the first five minutes is slow but steady.

To determine the order and the rate constants of the biosorption processes, the data was fit to two different models, pseudo first order and pseudo second order models. The nonlinear formula of pseudo first and second order kinetic model are given in Equations 7 and 9. Vernier's LoggerPro software was used for the analysis of the kinetic parameters of this biosorption process. The surface coverage data for both trials was treated as a single data set for each hull type. The coefficients were computed using the iterative, best-fit values approach of the Levenburg-Marquadt method.[45,46] The root mean square error (RMSE) and the correlation coefficient (R^2) were used to determine the quality of the fit of the data to each model. The model with the smallest RMSE and correlation coefficient (R^2) closest to one was determined to be best fit and was then used to determine the rate constant.

The data and the fit to the models is shown in Figure 9 and the fitting parameters are provided in

Table 3. The RMSE is larger, and the R^2 value is smaller for the pseudo first order (PFO) model than that of pseudo second order (PSO) model for all the hull types. This means the PSO model is a better fit when compared to PFO model. Because the time range of the data that was fit to these models incorporates 300 min, most of the datapoints represent binding during the final stages of the adsorption process (mainly adsorption onto the active sites). External and

internal diffusion are likely achieved quickly in the first few minutes of the process, so the data from longer times is likely dominated by the binding to the active sites. The final step of the binding process tends to follow the pseudo second order model, which fits with these results. This fit to the PSO model also suggests there may be an abundance of available binding sites on the ground peanut hulls even though the initial copper ion solution concentration was not very low.

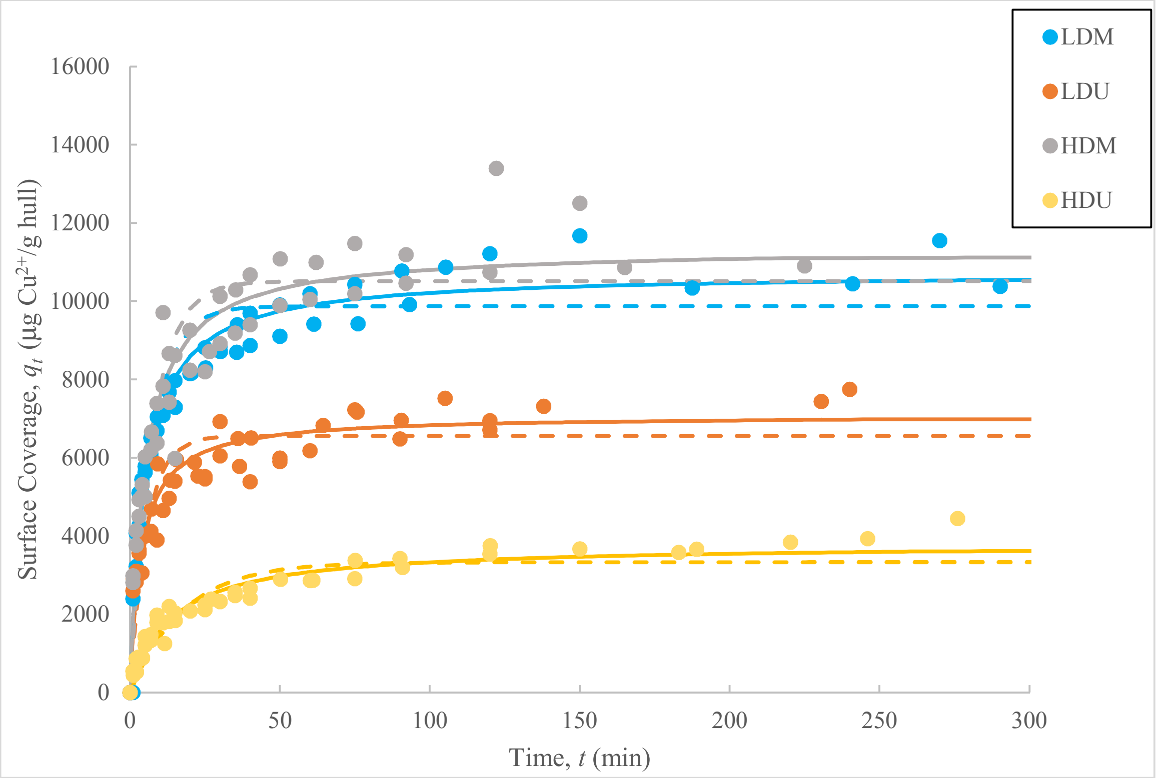

Figure 9. Pseudo first and second order fits of surface coverage of LDM, HDM, LDU, and HDU hulls over time. The data set for each type of the hulls represents two trials which were fit as a single dataset to the pseudo first order model (Equation 7) and shown with a dashed line and also fit to the pseudo second order model (Equation 9) and shown with a solid line.

Table 3. Kinetic parameters for pseudo first order (PFO) and pseudo second order (PSO) models.

Hull Type	PFO R^2	PSO R^2	PFO RMSE	PSO RMSE	PSO q_e (μg Cu/g hull)	PSO k_2' x 10^{-5} (g hull/μg Cu · min)
LDM	0.95	0.98	939	594	10,719 ± 2	1.9 ± 0.1
HDM	0.93	0.96	1144	849	11,343 ± 2	1.77 ± 0.01
LDU	0.90	0.95	829	603	7,084 ± 6	3.7 ± 0.3

HDU	0.94	0.97	440	291	4,140 ± 2	1.4 ± 0.1

One of the fitting parameters for the model is the rate constant. Since the PSO model fit the data the best, only the rate constant for this model, k_2', is reported in Table 3. The LDU hulls have the highest rate constant. The modified hulls show a rate constant that is nearly half that of the LDU hulls, and the HDU hulls have a slightly lower rate constant. This observation may be related to Arrhenius equation[47,48] where the rate constant, k, is related to the number of collisions per minute of ions with proper orientation (also called the frequency factor, A) and the activation energy, E_a:[47,48]

$$k = Ae^{\frac{-E_a}{k_B T}} \tag{13}$$

Here, k_B is the Boltzmann constant and T is temperature.

Metal ions are spherical, so there is no specified orientation for their approach to a binding site. Therefore, the frequency factor is determined by how quickly the ion can get to the active site, the diffusion rate, rather than spatial orientation of the ion. However, if the position of the ion relative to the binding sites requires a specific arrangement for adsorption to occur, this may increase A. For this system, a higher density of sites makes this more probable, which would result in a higher frequency factor and therefore a greater rate constant. So, perhaps the LDU hulls have a greater binding site density.

Alternatively, the transition state energy of the LDU hulls may be lower than that of the other hull types, resulting in a smaller energy of activation. This would also result in a larger rate constant, although it is unclear why the HDU hulls do not have a similarly small activation barrier.

CHAPTER FOUR: CONCLUSIONS AND FUTURE DIRECTIONS

The kinetics of biosorption of copper ions onto modified and unmodified, low and high density ground peanut hulls was studied. Modified hulls have a faster initial rate of adsorption than the unmodified hulls. LDM hulls have the fastest initial rate, followed by HDM hulls, then LDU hulls. HDU hulls have the slowest initial adsorption rate. The trend seen here can be attributed to the effect of density, porosity, and alkaline modification.

Pseudo first and second order kinetic models were used to fit the experimental data. The pseudo second order model fits the data better because most of the data is in the second and third stage of adsorption, internal diffusion, and adsorption onto the active sites. This suggests there are abundance of active sites on peanut hulls.

The rate constant for biosorption process is almost the same for the LDM, HDM, and HDU hulls, but it is much higher for the LDU hulls. This is because rate is a function of frequency factor which is determined by the orientation of both the metal ions in aqueous solution and the number of available binding sites. Hence, LDU hulls might have a greater binding site density. Alternatively, LDU hulls might have lower transition state energy, which results in high rate constant.

The results could be further strengthened by comparing the fitting of the data to other models, particularly mixed models that incorporate both pseudo first *and* pseudo second order models. This would help to determine if early stages of the adsorption process are dominated by pseudo first order kinetics. Also, the surface coverage data was normalized to account for small variations in the mass of the hulls used, but not for differences in the initial concentration of the copper ion solution. Normalization of the data in this way could make the data from the different trials more consistent and eliminate questions of reproducibility.

Future studies could include the kinetics of the adsorption of other hazardous metals like cadmium, and lead to different peanut hull types. The rate for multi-metal system can also be investigated to find out the effect of competitive binding processes on the rate of biosorption using peanut hulls.

Research has shown how temperature affects biosorption of iron and manganese to rice husk, and also of cadmium biosorption by dead *Sargassum* species.[49,50] Therefore, a similar study for adsorption of Copper to peanut hulls could be performed. The maximum temperature tolerable without degradation of the peanut hulls can be determined as well. Such a study would also enhance the picture of the thermodynamics by giving us information about the entropic contributions to the biosorption process and give rise to the Arrhenius parameters.

Finally, computational analysis can also be done to calculate the transition state energy for the formation of the metal-hull complex. This would help in the calculation of the theoretical rate constant and could be compared to with the experimental values.

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