ABSTRACT

HESS, BRIANNA JADE. Heavy Metal Remediation of Swine Lagoons Using Waste Biomass (Under the direction of Dr. Praveen Kolar).

The production of swine is a vital contributor to the economy of the Southeastern United States. Many of the hog farms in the Southeast meet criteria defined by the Environmental Protection Agency to be considered Concentrated Animal Feeding Operations (CAFO). Swine CAFOs are required to meet standards set by the Clean Water Act to maintain minimal discharge of pollutants. Nearly all swine CAFOs utilize lagoon waste storage and treatment to comply with federal regulations.

Due to lack of a market for manure in the Southeast, it is necessary for swine waste to be disposed of in geographically-limited areas near the farming operation. Although well-regulated for the responsible disposal of nutritive compounds, land application of wastes creates a concentration of inorganic constituents cumulative over time. As these non-degradable compounds accumulate in the soil, negative environmental impacts will become evident. Hedging off these effects will be important to the sustainability of the Southern hog industry, as hog operations are increasingly concentrated both in production density and location to small geographic regions.

It is the goal of this study was to explore waste biomass adsorption technologies as a component to the remediation of swine lagoons from heavy metal contamination. The individual objectives are as follows: (A) Survey a selection of NC waste biomasses for copper adsorption efficiency. (B) Characterize one NC waste biomass to elucidate copper adsorption mechanisms and evaluate performance in the swine lagoon matrix (C) Test the hypothesis that annealing high metal capacity adsorbents onto the waste biomass will result in a composite adsorbent material possessing a higher adsorption capacity than unmodified material. (D) Test the hypothesis that the presence of co-occurring species (that would be present in swine lagoons) will decrease the copper loading capacity of the adsorbent.

To carry out these objectives, three waste biomasses were selected and the copper loading capacity was measured for each in batch adsorption experiments (Cu 0-80 mg L$^{-1}$, 72 hr, unadjusted pH). The biomass with the highest copper loading capacity was selected for further characterization of its adsorption thermodynamics (20, 30, 50°C), kinetics (0-240 hr at 20, 30,
and 50°C), performance in varying solution pH conditions (controlled pH 2-9, 50% lagoon effluent initial pH 2-9) and surface characterization using scanning election microscopy- energy dispersive x-ray spectroscopy (SEM-EDS) and x-Ray photoelectron spectroscopy (XPS). Various facile surface modifications using iron oxide, manganese oxide, and peanut skin tannin resin amendments were attempted to increase copper loading capacity of the adsorbent. Copper adsorption capacity of the adsorbent was also measured in the presence of species co-occurring in swine lagoons, acetate (0-1000 mg L⁻¹), ammonia (0-1000 mg L⁻¹), and zinc (0-100 mg L⁻¹).

The outcome of this study was the development of a low-cost adsorbent material for the passive removal of environmental pollutants. The intellectual merit of the proposed study was:

(1) proposal of a copper adsorption mechanism onto eggshells that has not been previously suggested in literature

(2) the elucidation of eggshell adsorbent efficiency and mechanisms in mixed systems containing organic species. Adsorption performance of waste biomass derived adsorbents in the presence of organic species have received very little attention as to date.

The broader impact of the research will be the development of adsorbents to mitigate the environmental impact of waste effluent from animal husbandry, agriculture, and chemical industries. This will reduce hazardous pollution and allow from the sustainable expansion of waste-effluent producing industries.
Heavy Metal Remediation of Swine Lagoons Using Waste Biomass

by
Brianna Jade Hess

A dissertation submitted to the Graduate Faculty of
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in partial fulfillment of the
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DEDICATION

I would like to dedicate my dissertation to my husband, Richard Channing Hess, who suffered equally through my graduate studies. I love you a latte.
BIOGRAPHY

Brianna Jade Hess (née Massie) was born August 29th, 1990 and grew up in the Appalachian Mountains of Southwest Virginia. She received her Bachelors of Science in Chemistry from Radford University in 2012. She then received her Masters of Science from the department of Food, Bioprocessing, and Nutrition Sciences at North Carolina State University in 2014 under the direction of Dr. Lisa Dean in the USDA-ARS Market Quality and Handling Research Unit. Following her Master’s degree, she enrolled in a Ph.D. program at NCSU in the Biological and Agricultural Engineering department to continue her work on developing waste biomass adsorbents under the direction of Dr. Praveen Kolar.
ACKNOWLEDGMENTS

I would like to thank my graduate mentor, Dr. Praveen Kolar, as well as the members of my committee: Dr. Detlef Knappe, Dr. Jay Cheng, and Dr. John Classen.
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CHAPTER ONE: BACKGROUND & LITERATURE REVIEW OF SWINE LAGOONS AND POTENTIAL OF ADSORPTION TECHNOLOGY FOR USE IN SWINE LAGOONS

1.1 Introduction

The production and processing of swine is a vital contributor to the economy of the Southeastern United States with over 9000 productive farms. Production is most heavily concentrated in North Carolina which produces 80% of the region’s output with an estimated total of 2800 farms housing eight million hogs (USDA-NASS 2009; USDA-NASS 2014). Many of the hog farms in the Southeast meet criteria defined by the Environmental Protection Agency to be considered Concentrated Animal Feeding Operations (CAFO):

(1) confinement of animals for periods longer than 45 days during the growing season
(2) there is no vegetation growing within the confinement area
(3) total number of housed animals meets certain size criteria. Swine farms are divided into three classes for regulatory purposes: small (<750), medium (750-2499), and large (>2500) sizes (EPA 2014).

Medium and large swine CAFOs are considered point-source polluters in the same category as factories or municipal sanitation plants (Williams 2006; EPA 2014). Swine CAFOs are required to meet standards set by the Clean Water Act to maintain minimal discharge of pathogens, volatile organic compounds, and nutritive compounds such as nitrates and phosphorus (Williams 2006). Nearly all swine CAFOs utilize lagoon waste storage and treatment to comply with federal regulations.

Regulations and operational practices, however, lag behind the emerging deleterious effects of swine CAFO operations which threaten to harm hog farm operators, soil fertility, and the environment. Due to lack of a market for manure in the Southeast, it is necessary for swine waste to be disposed of in geographically-limited areas near the farming operation. Although well-regulated for the responsible disposal of nutritive compounds, land application of wastes create a concentration of its inorganic constituents cumulative over time. As these non-degradable compounds accumulate in the soil, negative environmental impacts will become evident over time. Hedging off these effects will be important to the
sustainability of the Southern hog industry, as hog operations are increasingly concentrated both in production density and location to small geographic regions.

As with most of the agricultural industry, narrow profit margins leave little opportunity or incentive for hog farm operators to invest in superior treatment technology. Adoption of superior technologies are hindered by four key financial factors: prior investment in lagoon construction; cost of lagoon closure or conversion; construction of new technology will require large capital investment and finally new strategies have higher operational costs. Solutions, therefore, must be low-cost and designed to work within the confines of current lagoon systems. The scale and chemical complexity of swine waste adds further constraints to the selection of appropriate metal remediation technology. Therefore, significant effort should be invested in developing pollutant mitigation strategies that work within the confines of current lagoon systems and have minimal additional operation costs. The rapidly growing field of study utilizing waste biomass for adsorption is a promising technology for addressing metal remediation in swine and other agricultural wastewaters.

1.2 Swine Farms

1.2.1 Operation and Management of Swine Lagoons

Swine CAFOs in the Southeast differ from those located in the Midwest in that manure is processed as waste rather than as fertilizer. A typical swine CAFO in the region is constructed so that waste from several swine house buildings are conveyed to a shared pond structure called a lagoon. The primary functions of lagoons are the storage and treatment of swine waste to reduce overall volume and pathogenic load. Swine manure is composed of large insoluble compounds such as carbohydrates, fats, and proteins that pass through the animal undigested. Bacteria in the lagoon decompose solids into smaller soluble compounds and eventually into gasses and organic acids (Barker 1996). There are three lagoon types that each utilize the different types of bacteria present in the manure; 1) aerobic 2) anaerobic and 3) facultative.

Aerobic is the least odorous of the three lagoon types but is infeasible for most applications. Aerobic bacteria require sufficient dissolved oxygen throughout the lagoon water which necessitates that the lagoon be designed with a large surface area to volume ratio to allow natural aeration to occur. An aerobic lagoon can require as much as twenty-five times more land than an anaerobic lagoon (Barker 1996). The required ratio can be reduced
by adding oxygen mechanically but requires a sizable energy input. For these reasons, aerobic lagoons are virtually nonexistent (Chastain and Henry 2003; Barker 1996).

Nearly all manure lagoons are of the more efficient anaerobic type. Anaerobic lagoons are built with a small volume to surface area ratio to limit oxygen diffusion. Vigorous anaerobic decomposition results in the formation of odorous volatile organic compounds. The lagoon must be properly managed to balance efficiency of decomposition with odor emissions. One way to achieve this balance is designing the lagoon structure to facilitate the growth of facultative bacteria. Facultative lagoons are constructed with the depth of an anaerobic lagoon but a larger surface area to allow aerobic or facultative bacteria to grow in the first few feet of the lagoon surface. This layer serves as a cap to slow the release of volatile organic compounds produced by the productive anaerobic bottom layer (Chastain and Henry 2003).

Waste is conveyed from the swine buildings into the lagoon by one of two methods: flush or pit-recharge. In both systems, swine buildings are constructed with slotted floors through which manure falls onto a concrete sub-floor or pit sloped towards a collection gutter at the far end of the building (Chastain and Henry 2003). Manure that has been washed from the swine house enters the lagoon as a slurry with solid contents approximately 4-12% (Barker 1996).

The lagoon pond may be dug into the earth or constructed partially above grade with earthen walls. The lagoon bottom and sloped walls are lined with clay, concrete, or a synthetic liner to prevent seepage. The lagoon structure must be carefully designed to maintain an optimum operating level. There are five distinct volumes which must be considered in the design and maintenance of the lagoon:

1. sludge storage
2. anaerobic treatment
3. manure and water storage
4. net rainfall for 180 days including a 25-year 24-hour (5-9”) rainfall event
5. an additional foot of freeboard for safety.

Furthermore, minimum operating, design treatment and maximum operating levels are defined and marked for maintenance of the lagoon (Chastain and Henry 2003; Barker 1996). The component volumes of a typical lagoon are illustrated in Figure 1.1.
The overall size of the lagoon to maintain the required volumes is dependent on the number and weight of animals housed on the swine CAFO. Table 1.1 shows the waste output of swine per production unit and the required lagoon volume to accommodate.

Figure 1.1. Design Volumes of a Swine Lagoon (not drawn to scale)

<table>
<thead>
<tr>
<th>Swine Farm Model</th>
<th>Production Unit</th>
<th>Average Animal Live Weight (lbs)</th>
<th>Lagoon Accumulation</th>
<th>Lagoon Liquid Capacity (ft³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Liquid (gals yr⁻¹)</td>
<td>Solid sludge (ft³ yr⁻¹)</td>
</tr>
<tr>
<td>Weanling-to-feeder</td>
<td>Per head</td>
<td>30</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>Feeder-to-finish</td>
<td>Per head</td>
<td>135</td>
<td>2.7</td>
<td>10</td>
</tr>
<tr>
<td>Farrow-to-weanling</td>
<td>Per sow</td>
<td>433</td>
<td>8.8</td>
<td>23</td>
</tr>
<tr>
<td>Farrow-to-feeder</td>
<td>Per sow</td>
<td>522</td>
<td>10.6</td>
<td>28</td>
</tr>
<tr>
<td>Farrow-to-finish</td>
<td>Per sow</td>
<td>1417</td>
<td>28.7</td>
<td>115</td>
</tr>
</tbody>
</table>
A well-designed and functioning lagoon should be maintained at the design operating depth and should not fall below the minimum operating level to ensure optimal anaerobic digestion. An active anaerobic lagoon should be a pH of 7-8 and brown or pink in color (Barker 1996). Lagoon levels must be actively monitored and supernatant liquid removed in anticipation to weather events so that levels never exceed the maximum operating level to prevent lagoon spillage (Chastain and Henry 2003).

To maintain operating levels, the supernatant liquid is removed from the lagoon and applied onto nearby crops, wood lots, or grass fields. Periodically, accumulated solid sludge will also be dredged from the lagoon for application onto fields. Waste which is rich in nutrients must be applied to fields at controlled agronomic levels such that the amount of nutritive compounds applied does not exceed what the crop is able to uptake and utilize for growth. Agronomic application of waste reduces groundwater and surface water contamination from field runoff (Camberato 2003).

1.2.2 Heavy Metals in Swine Lagoons

Heavy metals concentrations gradually accumulate within swine lagoons over time as the waste organic matter is decomposed and lower solubility inorganic compounds are left behind (Barker 1996). Those of highest levels of concern are metals intentionally introduced as supplements into the animal feed (Nicholson 1999). Cobalt, iron, manganese, and selenium are required for proper metabolic function within the animal. Other added metals are not nutrients but serve to prevent diseases and improve feed conversion into mass (Bolan 2004a; Nicholson 1999). Copper sulfate (≤200 mg kg⁻¹ feed) and copper hydroxide are added to pig feeds to suppress enteropathogenic bacterial growth and to maximize feed conversion (Bolan 2004a; Nicholson 1999). Organoaarsenical compounds such as roxarsone and p-arsanilic acid, are added to pig feed to control dysentery, respiratory infections, and promote swine growth as well (Makris 2008). These therapeutic metals are not essential to swine metabolism and are not well absorbed by the animal. Therefore, therapeutic metals must be added at much higher levels and thus are largely excreted (Bolan 2004; Kornegay 1976).

1.2.3 Negative Outcomes of Land Application

Heavy metals introduced to the soil may induce plant phytotoxicity and contribute to non-point source pollution of ground and surface waters (Bolan 2004). Depending on the
soil, application method and period of repeated application, copper from swine waste could have deleterious effects on plant growth. Copper from municipal sewage was found to have an inhibitory effect on the growth of model organisms, duckweed and radish seeds. Copper toxicity on duckweed had a lowest observed effect concentration of 3200 mg Cu/kg dry weight material (Fjallburg 2003). Another research study tested copper toxicity from wood ash on sunflowers and acid-tolerant wheat species, finding root growth suppression at 250mg kg\(^{-1}\) soil (Jones 2004). Soybean seedlings grown in a media with as little as 3mg L\(^{-1}\) copper exhibited a marked decrease in growth and root biomass (Kulikova 2015). In comparison, lagoon surface water is estimated to have a copper concentration of 640 mg kg\(^{-1}\) dry weight or 2.4 mg L\(^{-1}\) (Chastain 2003). The toxic effect on plant growth is not only a matter of crop yield but also decreased nitrogen and phosphorous uptake; necessitating the use of more land or risking downstream eutrophication due to excess nutrient runoff. The EPA caps land application of municipal biosolids to a lifetime limit of 1340lb Cu per acre (US EPA 1993). This limit, which is based on non-conservative plant uptake coefficients and an acceptance of up to 50% plant death, is considered extremely lenient by other parties who recommend a lifetime limit of around ten times lower (Harrison 1999).

Assuming a conservative approach that negative effects on plant growth at the very least become evident at a cumulative loading of 134lb Cu per acre, one can calculate years of swine waste application to reach this limit. In a hypothetical scenario, assuming broadcast application of swine effluent (0.12lb Cu per 1000gal) onto corn grown in Lynchburg fine sandy loam. When swine lagoon effluent is applied at agronomic rates for nutrients (nitrogen and phosphorous), one can expect plant toxicity to occur within 50-60 years. Nearly thirty years into the advent of industrialized swine production, only one more generation of farmers may see unhindered crop growth on spray fields.

Copper leached from the spray field finds its way into surrounding watersheds where it has further deleterious effects. Once washed into freshwater environments, copper partitions between particulate, soluble, and sediment-associated forms depending on the unique conditions of the aquatic environment (Hall 1998). Excessive copper concentrations are extremely disruptive to aquatic biomes as it has algaecidal effects. Small crustaceans are also vulnerable to copper-induced mortality (DeForest and Meyer 2015). Copper is less toxic to fish but may still cause significant damage to gills, kidneys, blood cells, and nerve tissues.
Exposure to copper also causes reduced egg production and abnormalities in fish fry (Hall 1998).

**1.3 Mitigation of Heavy Metals**

Several conventional technologies exist for the treatment of excess copper in drinking water and wastewater treatment. Outlined in Table 1.2, these technologies are described along with their incongruity with swine lagoons.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Description</th>
<th>Disadvantages for Swine Lagoon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulation/Flocculation</td>
<td>Addition of metal salt to destabilize suspensions causing settleable particles to form and/or aggregate</td>
<td>High chemical costs; forms large volume of sludge</td>
</tr>
<tr>
<td>Ion Exchange</td>
<td>Polymeric resins/minerals exchange ions with target metal ions in solution</td>
<td>Not feasible in high levels of total dissolved solids</td>
</tr>
<tr>
<td>Lime Soda Softening</td>
<td>Addition of Ca(OH) to precipitate calcium and magnesium; removes other metal ions via co-precipitation</td>
<td>Forms fine colloidal precipitate in solution.</td>
</tr>
<tr>
<td>Reverse Osmosis/Membrane</td>
<td>Solution is driven under pressure through a semi-permeable membrane to exclude particles</td>
<td>Excessive cost to build and operate</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>Charged current used to separate metals</td>
<td>High investment and operation costs</td>
</tr>
<tr>
<td>Distillation</td>
<td>The solution is boiled and condensed to leave behind insoluble constituents.</td>
<td>Very large energy input</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Adhesion of metal ions onto a solid surface</td>
<td>---</td>
</tr>
</tbody>
</table>

**1.4 Adsorption Theory**

Adsorption is a physicochemical process occurring at the surface interface of a solid material submerged in a gas or liquid. Compounds dissolved in the fluid adhere to the surface
of the adsorbent (Engel and Reid 2010) via either physical van der Waal forces or a chemical reaction between the dissolved compound and adsorbent surface or both. The solid material is referred to as the adsorbent while the dissolved contaminant is referred to as the adsorbate. The process is widely utilized in several environmental applications to remove contaminants from a fluid including; treatment of drinking water, industrial waste remediation, air fresheners, and aquarium maintenance although it has not yet been applied to swine waste management (Worch 2012).

Adsorption has several advantages. It is a passive and low-cost process in which adsorbent materials could be added directly to lagoon waters. Submerged adsorbent would have minimal maintenance while in place; requiring only periodic changing of spent material. Considering the typical layout of a swine facility, adsorption technology lends itself to the removal of dissolved contaminants in swine lagoons.

Several theoretical and empirical interpretations of observed adsorption processes emerged in the early 20th century from which, numerous mathematical equations have been derived to describe and predict adsorption behavior (Toth 2001). Some of the most widely employed models are presented below:

### 1.4.1 Langmuir Model

The Langmuir equation was derived by Irving Langmuir in 1916 using kinetic principles assuming the adsorbent surface is homogenous with a finite number of independent binding sites which adsorb one solute particle per site. At equilibrium, the adsorption may be expressed as

\[
Q_{eq} = Q_{max} \frac{bC_{eq}}{1+bC_{eq}}
\]

where \(Q_{max}\) is the maximum absorbable amount of the monolayer (mg g\(^{-1}\)), \(C_{eq}\) is the equilibrate concentration of adsorbate in bulk solution (mg l\(^{-1}\)), \(b\) is a constant (function of enthalpy of adsorption and temperature) with the unit of L mg\(^{-1}\).

Although widely applied to a variety of adsorption systems with great success, the Langmuir equation suffers limitations arising from its basic assumptions of monolayer coverage and an energetically homogeneous adsorbent surface. In situations where these assumptions are violated, the Freundlich equation is often used as a substitute (Worch 2012).
1.4.2 Freundlich Equation

The Freundlich model was empirically derived to describe adsorption of gaseous adsorbates onto an adsorbent surface. It is frequently used to describe adsorption processes in water treatment especially onto activated carbon materials.

\[ Q_{eq} = K_F C_{eq}^n \]  

(1.2)

The adsorbed solute per adsorbent mass \( Q_e \) is dependent upon the adsorption parameters \( K_F \) and \( n \). The adsorption coefficient \( K_F \) represents the strength of adsorption where increasing value of \( K_F \) corresponds to increasing maximum adsorption. The exponent affinity term \( (n) \) describes the curve of the adsorption isotherm resulting from the energetic heterogeneity of the adsorbent surface. Smaller \( n \) values (<1) represent concave curves showing high adsorption at low concentrations. As \( n \) value increases, the adsorption isotherm tends towards exponential curvature (Worch 2012). The Freundlich equation is best applied to low and intermediate concentrations due to the limits of the exponential term (Liu and Liu 2008).

Several reactions and diffusion-based kinetic models have been proposed to mathematically describe the speed of adsorption. Some of the reaction-based kinetics models are described as under:

1.4.3 Lagergren Pseudo-first-order Reaction Model

The simplest of the reaction-based kinetic model, the pseudo-first-order describes a linear relation between the available rate of adsorption and the available active sites on the surface of the adsorbent and can be expressed as (Ho 2000):

\[ \frac{dQ_{eq}}{dt} = k_1 (Q_{eq} - Q_t) \]  

(1.3)

Where \( k_1 \) is the adsorption reaction rate constant \( (\text{min}^{-1}) \), \( Q_{eq} \) and \( Q_t \) are adsorption capacities at equilibrium \( (\text{mg g}^{-1}) \) and at any given time, \( t \). After integrating equation 1 and applying boundary conditions \( (Q_t = 0 \text{ at } t = 0; \text{ and } Q_t = Q_t \text{ at } t = t) \), we obtain the linearized form as shown below (Ajmal 2003):

\[ \log(Q_{eq} - Q_t) = \log(Q_{eq}) - \frac{k_1}{2.303} t \]  

(1.4)
The values of $k_1$ and $q_e$ can be determined from plot between $\log (q_e-q_t)$ versus time.

### 1.4.4 Pseudo-second-order Reaction Model

The pseudo-second order model assumes that adsorption occurs on two surface sites (Kumar 2006) and is expressed as below:

\[
\frac{dQ_{eq}}{dt} = k_2 (Q_{eq} - Q_t)^2
\]  

(1.5)

Where $k_2$ is the adsorption reaction rate constant (min$^{-1}$), $Q_{eq}$ and $Q_t$ are adsorption capacities at equilibrium (mg.g$^{-1}$) and at any given time, t. After integration and rearranging the linearized form of the equation is written as below (Ho 2000)

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_{eq}^2} + \frac{1}{Q_{eq}}
\]  

(1.6)

The kinetic parameters, $Q_{eq}$ and $k_2$ may be obtained from the plot between $t/Q_t$ versus t. Due to the applicability of this model for a wide range of concentrations, pseudo-second-order reaction model gained popularity to describe the kinetics of adsorption data. Additionally, several researchers suggested that conformity of data to pseudo-second-order reaction model indicates a possibility of chemisorption on the adsorbent surface (Ho and Mckay 1999).

### 1.4.5 Diffusion Based Models

As per Allen (1987), Choy (2004) and Ho (2000) adsorption of solutes on the surface of an adsorbent involves multiple consecutive steps including, (1) transport of the solute from the bulk of the solution to the boundary layer surrounding the adsorbent particle, (2) diffusion of the solute across the boundary later to reach the external surface of the adsorbent (external mass transport or film diffusion), (3) diffusion of the solute within the pores of the adsorbent to reach the internal surface area of the adsorbent (pore diffusion or intra-particle diffusion), and finally (4) adsorption of the solute on the surface of the adsorbent. As suggested by Ho (2000), adsorption may be controlled by any of the aforementioned steps. However, in a typical adsorption system, movement of solute from bulk to the boundary layer and adsorption on the surface are considered to occur very fast (Sarkar 2003). As a result, most of the modeling of adsorption processes were focused on film and internal diffusion.
1.4.5.1 Film Diffusion Model

The film-diffusion model is based on the assumption that the transport of the solute across the boundary layer is assumed to be the rate-limiting. Mathematically, the model is expressed as

\[ \ln(1 - F) = -k_{film}t \] \hspace{1cm} (1.7)

where F is the fraction of \( Q_t/Q_{eq} \) and \( k_{film} \) is the film diffusional rate constant (min\(^{-1}\)). A linear plot of the \( \ln(1-F) \) versus t usually verifies that the adsorption process is limited by diffusion through the liquid film.

1.4.5.2 Intra-particle Diffusion Model

Originally proposed by Weber and Morris, the model is based on the assumption that diffusion of adsorbate into the inner pores of the adsorbent is rate-limiting (Mohd Din 2009). The complete derivation of the model was covered comprehensively by Cooney (1998) in their excellent review. After simplification, the model is mathematically expressed as eqn (10).

\[ Q_t = k_i t^{0.5} \] \hspace{1cm} (1.8)

where the \( k_i \) is the reaction rate constant (mg m\(^{-1}\)t\(^{-0.5}\)). Application of this model includes plotting of \( Q_t \) versus \( t^{0.5} \) and a linear plot between \( Q_t \) versus \( t^{0.5} \) suggests an internal pore-transport diffusional limitation. Owing to its simplicity, this model has been widely used diffusion models by several researchers to determine the rate-limiting step in the overall adsorption processes.

1.4.6 Adsorption Thermodynamics

More basic parameters can be gleaned from the application of thermodynamics. It can be applied through the repetition of kinetic experiments at different temperatures. The Arrhenius equation is shown in Eqn (9).

\[ \ln k = \ln A - \frac{E_a}{RT} \] \hspace{1cm} (1.9)

By plotting \( \ln(k) \) versus the reciprocal of the absolute temperature in Kelvin, the activation energy (Ea) can be determined from the slope. From the same data, the Eyring
equation (Eqn 10) may also be applied to calculate the activation entropy (ΔS) and enthalpy (ΔH).

\[ \ln \left( \frac{k}{T} \right) = \ln \left( \frac{k_B}{R} \right) + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  \hspace{1cm} (1.10)

The same parameters can be calculated from the repetition of isotherm adsorption capacity studies at several different temperatures using Eqn (11) where \( b \) is the Langmuir rate constant (Zhu 2009).

\[ \ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  \hspace{1cm} (1.11)

1.5 Adsorbent Materials

1.5.1 Commercial Adsorbents

Traditionally, activated carbon has been used almost exclusively as an adsorbent for water treatment. Activated carbon may be prepared by two methods; physical or chemical activation. Carbon-rich material such as coconut shell, coal, or wood is physically activated by first pyrolyzing at 600-900°C under an inert nitrogen purge. The char is then heated again in the presence of oxygen or steam at a higher temperature, 600-1200°C. The same material may be chemically activated by impregnation with an oxidizing chemical, such as \( \text{H}_3\text{PO}_4 \), KOH, or NaOH, before heating under an inert atmosphere at 450-900°C. The final engineered product has a very large surface area available for adsorption but also a correspondingly high cost (Gupta 2009). Due to the large-scale of the swine lagoon but low investment potential, activated carbon must be ruled out and alternative materials requiring less strenuous preparation investigated.

1.5.2 Waste Biomass

Many alternative materials have been studied for their adsorbent properties including nonliving microbial and algae cells, extracted biological polymers, processing waste such as rubber scraps, and lignocellulosic materials from agricultural waste (Kratochvil and Volesky 1998, Wan Ngah 2011, Rowley 1984, Demirbas 2008). Biomass adsorbents are considerably less efficient than commercially available adsorbent materials in terms of adsorbate capacity to mass ratio. The overall cost of adsorbate removal is much lower, however, making biomass an attractive alternative to standard water treatment options. To maximize economy
of usage, the biomass adsorbent for an application must be geographically convenient to their application point to reduce additional transportation costs.

1.5.2.1 Agricultural Crop Waste

Agricultural waste biomasses are abundant, inexpensive, renewable, and require minimal additional processing for use as adsorbents (Sud 2008). The adsorbent properties of plant-type agricultural wastes are largely due to the polar functional groups present in plant structural fibers: cellulose, hemicellulose, and lignin (Sud 2008). Cellulose and hemicellulose are polysaccharides which contain many hydroxyl groups available for complexation with metal ions. Lignin is a complex three-dimensional polymer of various aromatic compounds which contain a variety of hydroxyl, methoxyl, and carbonyl functional groups. When submerged water permeates through the plant fibers exposing a large surface area where metals can bind to the charged functional groups (Demirbas 2008).

Various examples of agricultural wastes that have been evaluated for adsorption are tree bark, grain husks, fruit peels, corn cobs, and waste crop stalks (Suksabye 2008; Shin 2007; Man 2012; Feng 2009; Vafakhah 2014). These wastes exhibit different adsorption properties due to the differences in composition and arrangement of the plant structural polymers. The presence of additional functional groups from proteins, polyphenols, and other starch polymers also contribute to different adsorption efficiencies (Sud 2008). Major regional crops include but are not limited to corn, cotton, peanuts, soybeans, and tobacco. Copper adsorption studies using wastes from these crops are presented in Table 1.3.
Table 1.3. Copper Adsorption Studies of Agricultural Wastes

<table>
<thead>
<tr>
<th>Study</th>
<th>pH</th>
<th>Adsorption Model</th>
<th>Loading Capacity (mg g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Kinetic Model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Peanut Hulls</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brown 2000</td>
<td>7.0</td>
<td>Langmuir</td>
<td>8.0</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9835</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Johnson 2002</td>
<td>7.0</td>
<td>Langmuir</td>
<td>9.0</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9991</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oliveira 2009</td>
<td>4.0</td>
<td>Langmuir</td>
<td>13.0</td>
<td>Pseudo-second</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.882</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zhu 2009</td>
<td>5.5</td>
<td>Langmuir</td>
<td>12.0</td>
<td>Pseudo-second</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9991</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Corn Crop Residue</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wartelle 2000</td>
<td>4.8</td>
<td>Langmuir</td>
<td>11.4</td>
<td>---</td>
</tr>
<tr>
<td>Sciban 2008</td>
<td>Unadjusted</td>
<td>Langmuir</td>
<td>3.74</td>
<td>---</td>
</tr>
<tr>
<td>Vafakhah 2014</td>
<td>4.5</td>
<td>Freundlich</td>
<td>1.27</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.999</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tobacco Stalk</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Demirbas 2008</td>
<td>5.5</td>
<td>Langmuir</td>
<td>10.5</td>
<td>---</td>
</tr>
<tr>
<td><strong>Cotton</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ozsoy 2006</td>
<td>5.0</td>
<td>Langmuir</td>
<td>11.4</td>
<td>Pseudo-second</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9934</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Soybean Crop Residue</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wartelle 2000</td>
<td>4.8</td>
<td>Langmuir</td>
<td>35.0</td>
<td>---</td>
</tr>
<tr>
<td>Sciban 2008</td>
<td>Unadjusted</td>
<td>Langmuir</td>
<td>5.40</td>
<td>---</td>
</tr>
<tr>
<td>Zhu 2008</td>
<td>6.0</td>
<td>Freundlich</td>
<td>32.0</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9245</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.4.2.2 Animal Product Waste

Adsorbents derived from animal sources such as eggshells, crustacean shells, bones, and feathers (Table 1.4) are less extensively covered in adsorption research. However, there are some advantages versus lignocellulose materials; (1) more mechanically stable (2) degrade slower and (3) many contain calcium carbonate. Stability will be a critical advantage
if adsorbent materials require long contact times as adsorbents will be subjected to the microbial action of the lagoon. Similarly, greater stability will mean slower leaching if spent material is placed in landfills. Finally, calcium carbonate acts not only as an adsorbent but also promotes removal of metals via sweep coagulation (Papadopoulos 1989; Zhizhaev and Merkulova 2014).
Table 1.4. Copper Adsorption Studies of Animal Husbandry Waste

<table>
<thead>
<tr>
<th>Study</th>
<th>pH</th>
<th>Adsorption Model + R²</th>
<th>Loading Capacity (mg g⁻¹)</th>
<th>Kinetic Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eggshell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ahmad 2012</td>
<td>5.5</td>
<td>Langmuir R² = 0.999</td>
<td>2.05</td>
<td>---</td>
</tr>
<tr>
<td>Rohaizar 2013</td>
<td>7.0</td>
<td>Freundlich R² = 0.982</td>
<td>14.0</td>
<td>Pseudo-second</td>
</tr>
<tr>
<td>Feather</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Asheh 2002</td>
<td></td>
<td>Unadjusted Freundlich R² = 0.9977</td>
<td>17.4</td>
<td>---</td>
</tr>
<tr>
<td>Al-Asheh 2003</td>
<td></td>
<td>Unadjusted Freundlich</td>
<td>11.8</td>
<td>---</td>
</tr>
<tr>
<td>Yang 2007</td>
<td>11</td>
<td>---</td>
<td>29.0</td>
<td>---</td>
</tr>
<tr>
<td>Bone</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Asheh 1999</td>
<td>5</td>
<td>Freundlich R² = 0.947</td>
<td>20.7</td>
<td>---</td>
</tr>
<tr>
<td>Oyster Shells</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hsu 2009</td>
<td>2</td>
<td>Langmuir R² = 0.949</td>
<td>49.26</td>
<td>Pseudo-second</td>
</tr>
<tr>
<td>Wu 2014</td>
<td>5.5</td>
<td>Langmuir R² = 0.9932</td>
<td>2.01</td>
<td>---</td>
</tr>
</tbody>
</table>

1.6 Adsorption in Swine Lagoons

Application of adsorption for the remediation of swine lagoons presents a series of unknown variables which will require further investigation. Until this point, studies of adsorption have largely been limited to dilute water solutions. Swine lagoons contain organic compounds, salts, and inorganic species. Extensive analytical analysis will be required to ensure that the adsorbent properties of the proposed agricultural waste adsorbents can be tailored and suited to the unique environment of the swine lagoon.

The first consideration is that a working lagoon has a neutral to slightly basic pH. Adsorption capacity is largely dependent on the surface charge of the adsorbent. Adsorbents in solutions above their zero-point charge are negatively charged and attractive to metal ions.
in solution. The chosen adsorbent, therefore, should have a zero-point charge below the normal pH range of the lagoon.

Solution pH also affects speciation and charge of dissolved metals in solution as well. Adsorption has not normally been tested under basic conditions because metals form colloidal hydroxide species. Metal adsorbates must be in their free ion state or exist as weakly bound species to be available for adsorption. Along with basic pH, the complex nature of the swine lagoon adds uncertainty to the speciation of the target metal, copper.

Copper speciation studies in swine lagoons have produced a mix of conclusions over the years. Initially, it was thought that swine fed a copper-enriched diet would excrete nearly all consumed copper as mineralized cupric sulfide, CuS (Robel and Ross 1975; Kornegay 1976). The concern at the time being towards downstream run-off, cupric sulfide would not solubilize in soil and therefore would pose no hazard for use as fertilizer. To confirm this hypothesis, Robel and Ross (1975) sampled fresh manure and pre-digested to remove soluble copper species. Assuming the remaining residue to be entirely cupric sulfide, it was concluded 40-60\% of excreted copper was copper sulfide (Robel and Ross 1975). Miller (1986) revisited this conclusion using a selective nine-step sequential extraction using non-sequential extractions. Analyzing the relative amounts of copper in each fraction, Miller concluded that copper was primarily bound to organic ligands and that copper sulfide was not present in fresh manure.

Analysis of fresh manure, however, was still not adequately reflective of practices. Later research was performed with slurry sampled from waste processing lagoons. L’Herroux (1997) employed another selective sequential extraction to determine metal speciation in lagoon slurry to investigate metal stability upon land application. Slurry samples were treated with selective reagents to solubilize metal into successively more stable fractions. Results are shown in Table 1.5. These results show that metals were primarily present in weak to semi-stable complexes while very little were in a mineralized form.
Table 1.5. Relative percentages of metal species in pig slurry. Adapted from (L'Herroux 1997).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Exchangeable</th>
<th>Carbonates</th>
<th>Oxides</th>
<th>Organic</th>
<th>Residual Minerals</th>
<th>% Unaccounted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>1.8</td>
<td>2.8</td>
<td>28.4</td>
<td>66.5</td>
<td>0.4</td>
<td>5</td>
</tr>
<tr>
<td>Cobalt</td>
<td>&lt; detect</td>
<td>&lt; detect</td>
<td>76.7</td>
<td>23.3</td>
<td>&lt; detect</td>
<td>13</td>
</tr>
<tr>
<td>Iron</td>
<td>5.3</td>
<td>1.7</td>
<td>71.7</td>
<td>7.9</td>
<td>13.4</td>
<td>-4</td>
</tr>
<tr>
<td>Zinc</td>
<td>4.4</td>
<td>26.8</td>
<td>67.2</td>
<td>1.4</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>Manganese</td>
<td>12.9</td>
<td>69.4</td>
<td>16.2</td>
<td>1.3</td>
<td>0.2</td>
<td>8</td>
</tr>
</tbody>
</table>

More recently, Legros (2010) elucidated the copper speciation of swine waste slurry from a French hog farm using a multi-technique approach. Using data obtained from inductively coupled plasma-optical emission spectrophotometry, micro-x-ray fluorescence photometry, and x-ray near edge structure spectroscopy, a Pourbaix diagram of present copper species was developed as shown in Figure 1.2.

Figure 1.2. Pourbaix diagram of Cu in raw pig slurry (pH= 7.67, Eh= -150mV) (Legros 2010)
Legros concluded that on average 4% of copper existed bound to carboxyl groups of organic ligands. Chalcocite (Cu₂S), a mineralized solid of copper, was predicted to be the predominant species. Support for this prediction exists in the detection of metal sulphides in the similar anoxic, highly-reductive conditions of the sludge at the bottom of the Venice Canals (Zaggia and Zonta 1997). Chalcocite is susceptible to dissolution in the presence of oxidizers which may provide an explanation for the disagreement of results between L’Herroux versus the Legros study (Zaggia and Zonta 1997). Treatment of slurry samples with 30% H₂O₂ for analysis of the organic-bound fraction may have resulted in the dissolution of Cu₂S and thus an erroneously high measurement in the L’Herroux study (Miller et al. 1986; Antonijević 2004).

Overall research suggests that metals in swine lagoons probably undergo mineralization but not entirely. In smaller suspended particle size fractions, the percent of free copper may be up to 28% although majority of copper is mineralized in the bottom sludge layer (Legros 2010). This increased mobility in smaller size fractions is likely due to the slightly oxygenated supernatant waters. For best application, adsorbents should be located in the top layer of the lagoon or after some type of forced aeration treatment.

The third hurdle is the unknown effect of competitive species present within the swine lagoon. Adsorbent functional groups are available for complexation with metal ions but also other positively charged species. Concentrations of metal ions in lagoons can vary considerably by farm location and diet of the swine (Chastain 2003). Concentrations are also correlated to the percent solids of the sampled effluent or equivalent layer of depth. Upper supernatant waters contain lower concentrations as noted by Lovanh (2009). In order of relevant abundance; potassium, sodium, calcium, magnesium, iron, zinc, and copper are present in the supernatant waters of swine lagoons along with other elements in trace amounts. Metals present in higher concentration will be adsorbed more readily than the primary target, copper if equally favored for adsorption. There is some value to removing these less toxic metals from the waste effluent but would ultimately require larger volumes of adsorbent media. Other positively charged species of concern are ammonium (NH₄⁺) as well as its dipolar analog, nitrate (NO₃⁻). Nitrate despite having a net negative charge may bind to anionic species due to the spatial positioning of its dipole moment. The possibility of
ammonium adsorption onto waste biomasses has not been extensively researched but could be a significant limiting factor to metal adsorption.

1.7 Conclusions

Waste biomass could be a powerful multi-purpose tool in the search for new methods for swine lagoon remediation. Biomass has a promising body of research supporting their efficacy in metal removal from wastewater effluents. It will be important to investigate the various unknowns unique to swine lagoons to use agricultural wastes to their best advantage as remediation agents. Utilization of biomass adsorbents to mitigate the environmental impact of waste effluent from swine lagoons will reduce hazardous persistent pollution and allow for the sustainable expansion of the swine industry.

The goal of this research is to employ adsorption to mitigate heavy metals from swine lagoons via agricultural wastes. Specifically, this goal is defined by the following objectives:

(A) Survey a selection of NC waste biomasses for copper adsorption efficiency.
(B) Characterize one NC waste biomass to elucidate copper adsorption mechanisms and evaluate performance in the swine lagoon matrix
(C) Test the hypothesis that annealing high metal capacity adsorbents onto the waste biomass will result in a composite adsorbent material possessing a higher adsorption capacity than unmodified material.
(D) Test the hypothesis that the presence of co-occurring species (that would be present in swine lagoons) will decrease the copper loading capacity of the adsorbent.
REFERENCES


2.1 Literature Review of Selected Adsorbents

Many alternative materials have been studied for their adsorbent properties. Biomass adsorbents are considerably less efficient than commercially available adsorbent materials in terms of adsorbate capacity to mass ratio. The overall cost of adsorbate removal is much lower, however, making biomass an attractive alternative to standard water treatment options. For application in swine lagoon remediation, agricultural wastes were selected for evaluation of loading capacity based on the following criteria:

1. An agricultural waste produced in the state of North Carolina or its directly neighboring states
2. Produced at a central processing facility
3. Inexpensive with few alternative uses

2.1.1 Peanut Hulls

By the criteria, peanut hulls are a viable option for the remediation of North Carolina swine lagoons. North Carolina is the third largest producer of peanuts in the United States with 284.4 million pounds harvested in 2013 (Brown 2014). Hulls, a significant percentage of this yield, are generally removed in processing. There are few uses for this by-product: burned for energy or transported to landfills for disposal (Charmarthy 2001). Hulls could be obtained for little more than their transportation costs. Further support for use of hulls is the successful body of the literature supporting their use as adsorbents of metals from industrial waste water and run-off.

Some the earliest investigations of peanut by-products as an adsorbent began in the 1970s. Waiss (1973) was an early proponent for the use of waste biomass materials to adsorb metal ions from industrial effluents. Waiss investigated peanut skins and hulls as well as other high-tannin agricultural by-products for use as adsorbents. The study found that hulls adsorbed $220 \text{mg g}^{-1}$ from a 0.1M mercury solution. Peanut skins which contain more tannins were four times as effective and were further investigated for column application in the study. Results were extremely promising with adsorption capacities of peanut skins rivaling ion exchange resins available at that time even in the presence of excess competing metal
ions. However, it was noted that peanut skins have very poor mechanical properties and disintegrate when soaked in water. Waiss suggested that future studies should investigate the use of formaldehyde to polymerize skin tannins to improve stability. However, the more sturdy hulls which contain similar although less tannins were more prevalently investigated in subsequent studies.

For the next nearly three decades, progress on the study of peanut hull adsorption was limited to short communications even as prevalence of biomass adsorbents steadily increased. Henderson (1977) investigated the adsorptive properties of hulls for use as an inexpensive adsorbent for municipal waste treatment. One gram of hull was introduced into a solution of metals commonly found in municipal wastes: mercury, copper, nickel, cadmium, and zinc. The study can only be considered the roughest of preliminary studies of peanut hull adsorption properties but was the first to show success adsorption of multiple metals in solution. Azab and Peterson (1989) briefly surveyed a variety of biological materials for adsorption of cadmium and found peanut hulls to be comparable in performance to activated charcoal. After an unspecified alkaline treatment, Azab and Peterson reported an increase in cadmium adsorption in nearly all tested biomasses. Okieimen (1991) modified the peanut hull surface by amending it with ethylenediaminetetra-acetic acid (EDTA). It was found that EDTA-modified hulls had a Langmuir loading capacity of 24 mg g$^{-1}$ copper and 39 mg g$^{-1}$ lead. Unmodified hull loading capacity values were not reported so the magnitude of modification effect is unknown.

Wafwoyo (1999) continued the work reported by Azab and Peterson by testing acid-modified peanut hull adsorption of copper, nickel, zinc, cadmium, and lead. Hulls were washed in either deionized water, dilute NaOH solution, or left unwashed. Following wash treatment, hulls were heated with citric or phosphoric acid. The author proposed that citric acid treatment modified the hull surface by increasing the number of carboxyl groups and thereby the number of binding sites available to cation adsorbates. Phosphoric acid treatment increased the surface charge of the peanut hull by reacting with hydroxyl groups to form phosphate esters. Effect of treatment was tested in both single and mixed metal systems. Phosphoric acid modified hulls regardless of wash treatment performed the best on a percent adsorbed per gram hulls basis followed by base-washed citric acid modified hulls. It was noted that in both treatments there was a preference for copper adsorption. From the same
laboratory group, Chamarthy (2001) published an extension of the previous work. Chamarthy tested acid-modified hulls under the same conditions to determine the Langmuir adsorption capacities of the previously tested metals in addition to lead. Results were compared to commercial resins for reference. Results are recreated for the most successful treatments in Table 2.1.

Table 2.1. Langmuir adsorption capacities of acid-modified peanuts for selected metals. Adapted from (Chamarthy 2001).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Metal ion adsorption capacities (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd(II)</td>
</tr>
<tr>
<td>Water-washed citric acid hull</td>
<td>36</td>
</tr>
<tr>
<td>Base-washed citric acid hull</td>
<td>51</td>
</tr>
<tr>
<td>Unwashed phosphoric acid hull</td>
<td>42</td>
</tr>
<tr>
<td>Base-washed phosphoric acid hull</td>
<td>83</td>
</tr>
<tr>
<td>Duolite GT-73</td>
<td>106</td>
</tr>
<tr>
<td>Amberlite IRC-718</td>
<td>254</td>
</tr>
<tr>
<td>Amberlite 200</td>
<td>223</td>
</tr>
</tbody>
</table>

At the same time, collaboration between the University of Alabama and Mississippi State University produced two papers which investigated the use of peanut hull pellets for remediation of dilute waste streams. Pelleting increases bulk density and mechanical stability of hulls for full-scale application. Brown (2000) determined the adsorption capacity of peanut hulls and pellets versus commercial resin TP-207 for copper, cadmium, zinc, and lead. Pelletization did not appreciably affect the adsorption capacity of the hulls. Hulls tested in batch equilibrium experiments had loading capacities; Pb 30mg g⁻¹, Cu 9mg g⁻¹, Cd 6mg g⁻¹, Zn 9 mg g⁻¹. Adsorption isotherms were fit to the Langmuir model ($R^2=0.98$) and Freundlich model ($R^2=0.79$). Contact time experiments were also used to determine the kinetic order of adsorption for each metal. It was found that 85% of uptake occurred within
10 minutes and reached equilibrium within 40 minutes. Pelleted hull adsorption was only slightly slower. Johnson (2002) added to work on pelleted hulls by finding optimum pH of copper (II) adsorption at 6.5-7.5 pH and establishing efficacy of column application. Brown and Johnson calculated the removal of metal per dollar cost of media to underline the efficiency of hulls as adsorbent material. Commercial resin removed less than 10g of metal per dollar. Hulls removed >200g metal per dollar at base price of $16 per ton. For use in agricultural waste management, high efficiency per cost will be an essential component of success.

In more recent years, research has extended to further elucidate the mechanisms of adsorption. Zhu (2009) published a comprehensive study of copper (II) onto unmodified peanut hulls. Various adsorption parameters were studied; metal concentration, pH, contact time, and reaction temperature to determine the most likely adsorption mechanism. Similar to Brown (2000) and Johnson (2002), a loading capacity of 12 mg g\(^{-1}\) occurred at an optimal pH of 5.5-6.5 with uptake occurring primarily in the first 30 minutes of contact time. Experimental data was then fit to various adsorption isotherm and kinetic models to tease out the most likely mechanism of adsorption. In comparison of Langmuir (\(R^2=0.998\)) to Freundlich (\(R^2=0.874\)) isotherms, it was determined that the Langmuir model provided the best fit suggesting monolayer adsorption behavior. The Dubinin-Radushkevich (\(R^2=0.909\)) isotherm was then subsequently fit to the experimental data to distinguish between physical versus chemical biosorption. The free energy of the reaction was determined to be >14kJ mol\(^{-1}\) indicating a chemical ion-exchange mechanism. Adsorption measured as a function of solution temperature determined it to be an endothermic reaction with positive entropy, meaning adsorption proceeded spontaneously. Modeling of loading capacity as a function of contact time found adsorption followed pseudo-second-order kinetics with diffusion from the bulk liquid phase to the adsorbent surface as the primary limiting factor.

Oliveira (2009), a Portuguese researcher also choose copper along with lead as the adsorbates of interest. In agreement with Zhu (2009), Oliveira determined adsorption kinetics best fit a pseudo-second order kinetic model. Adsorption was tested in low pH solutions under the reasoning that adjusting the pH of large volumes of effluent would be unfeasible in actual application. In a pH range of 3.0-4.5, adsorption loading capacities were found to be 2-13mg g\(^{-1}\) for copper and 8-37mg g\(^{-1}\) for lead with capacities increasing with pH. In a bi-
component system, copper and lead adsorption was found to be competitive with their additive loading capacities equal to that achieved in a single-component system. This result supports the Langmuir model of adsorption which postulates that there is a finite number of binding sites to which an adsorbate can fill.

Most recently, a paper coming from Pakistan analyzed arsenic, chromium, and iron adsorption from textile, ceramic and paper industry waste effluents (Husaini 2011). Focus of this study was given to the effect of solution acidity. Similar to previous studies, optimal pH for adsorption was found to be in the range of pH of 5-6 for the selected metals. To investigate the mechanistic effects of pH, Husaini (2011) compared the efficiency of metal adsorption when mineral acids of equal concentration but varying dissociation constants were present in solution. Acids that released more protons into solution decreased adsorption of metals. Hydrogen ions were competitive to binding. Furthermore, metal solutions to which hull adsorbent was added increased in pH as metals were adsorbed suggesting that the peanut hull surface acts as an acidic ion exchanger. Therefore, adsorption proceeds as a condensation reaction between the hydrated metal ions in solution and the hydrogen-bearing functional groups of the hull. This supports the earlier Zhu (2009) adsorption isotherm model suggesting a chemical ion-exchange mechanism.

In summary of available research, peanut hulls are efficient adsorbents of divalent metals with a total metal loading capacity in the range of 30-40mg g\(^{-1}\). Adsorption occurs best at slightly acidic to neutral conditions. Adsorption proceeds spontaneously and reaches equilibrium quickly following pseudo-second-order kinetics. The primary mechanism of adsorption is the exchange of hydrogen ions from the hull surface functional groups with metal ions in solution. A thorough understanding of the adsorption properties and mechanisms of peanut hulls will play a pivotal role in its application to the remediation of swine lagoons.

2.1.2 Feathers

Waste from the poultry industry, feathers, although less researched show burgeoning promise as adsorbents. Most excitingly, one study found maximum loading capacities of 50-60mg g\(^{-1}\) copper and zinc ions after a simple surface modification with tannic acid (Yang 2007). Such promising results show a need for at least a cursory examination of poultry
feathers adsorptive characteristics even if only as a carrier for more potent complexing agents.

2.1.3 Eggshells

Eggshells are the final option selected for evaluation. The North Carolina Egg Association estimates that within the state hens lay around 7.5 million eggs a day. Many of these whole eggs are sold to households and food service businesses but another portion are sent to centralized processing facilities. At these processing facilities, eggs are broken and used to make egg products or more commonly as an ingredient in another food product. Eggshells produced at these locations are largely sent to landfills and could be obtained for little more than their transportation costs. Eggshells are prime for development in new uses such as adsorption.

Eggshells are composed of 2% water, 5% protein, and 93% minerals. The majority is calcium carbonate with smaller amounts of phosphorous and magnesium (Hassan, 2015). Natural calcite crystal may be considered analogous to eggshell in composition but the interlaced protein matrix of the egg creates a unique crystal morphology. The eggshell structure is made up of four layers: an inner protein membrane, a mammillary (100 μm) layer of randomly oriented calcium carbonate crystals followed by the thickest (200 μm) palisade layer of crystals perpendicular to the shell surface and finally a thin (8 μm) vertical crystal layer. Some researchers believe that these layers of CaCO$_3$ allows metal ions to penetrate and adsorb at each interface. This increased area available for adsorption leads to higher adsorption capacities than calcite mineral (Zhou 2017). The eggshell is also studded with round micro-pores ranging in size from 200-400 nm which serve to exchange oxygen for the developing fetus in nature but may impart greater adsorption efficiency in application (Guru and Dash, 2014).

One of the first papers analyzing eggshells as a potential adsorbent came out of Poland in 2005 as result of increased restrictions on metal discharge in the European Union and the related growing interest in low-cost adsorbents (Chojnacka 2005). The paper focused on trivalent chromium as its target adsorbate. It was found that eggshells adsorbed a maximum capacity of 70mg g$^{-1}$ at a pH of 5. The authors proposed that this adsorption was the result of ion-exchange of calcium for chromium. Several years later in 2012, a South Korean paper investigated eggshells for the adsorption of cadmium, copper, and lead finding
maximum loading capacities of 0.5, 2.05, and 4.74 mg g\(^{-1}\) respectively. Adsorption was found to follow the Langmuir model. Molar selectivity for the metals were Cd > Cu > Pb following trends for increasing ionic radius (thus decreasing hydrated radius) and decreasing electronegativity. FTIR analysis found that calcium was exchanged for free ions in solution which then underwent complexation with the carbonyl group (Ahmad 2012).

Granados-Correa (2013) evaluated eggshells for the recovery of lanthanides from nuclear plant waste streams. Like other researchers, Granados-Correa found that eggshells followed pseudo-second order kinetics with spontaneous endothermic adsorption. They, however, fit their adsorption isotherm data to the Langmuir-Freundlich combination model which had not been used in previous studies. The combination model is based on a heterogeneous adsorbent surface and minimal interaction between adsorbed particles. Granados-Correa then concluded that adsorption followed a physical process citing thermodynamic data.

Researchers also working in Mexico at the same time as Granados-Correa studied the adsorption of cadmium onto raw eggshell waste (Flores-Cano 2013). Preliminary analysis found that the point of zero charge (ZPC) was 11.4. It was then understood that the eggshell surface is positively charged below pH 11.4 due to the protonation of calcite surface complexes (\(=\text{CaOH}_2^+\)). Against this assumption, Flores-Cano found a maximum removal of positively-charged cadmium at a pH of 6 with a loading capacity of 3.82 mg g\(^{-1}\). Therefore, it seems that surface charge may not be an accurate predictor of metal removal for eggshells. Flores-Cano explains this deviation by concluding through thermodynamic evidence that the adsorption mechanism occurs by chemical reaction. Further evidence was derived from desorption data that 32% of cadmium adsorption was via reversible ion-exchange while 68% due to non-reversible chemisorption/precipitation. Energy dispersive x-ray spectrometry microanalysis confirmed the exchange of calcium for cadmium cations. XRD pattern shifting was used to validate the formation of a cadmium precipitate on the eggshell surface (Flores-Cano 2013). Interestingly, Flores-Cano fit adsorption data to Langmuir and Freundlich models at different initial solution pH. As pH increased, both Langmuir and Freundlich adsorption models fit with increasingly more discrepancy which perhaps suggests a shift towards another removal mechanism such as precipitation of copper out of solution.
The multi-type adsorption supported by Flores-Cano (2013) is the most pragmatic interpretation of the likely mechanisms of metal adsorption by eggshells. Final judgements of adsorption type, best-fit kinetic model, and their associated mechanism are often made through minor differences in regression analyses. Table 2.2 exemplifies this in the lack of consensus among the many various eggshell adsorption studies.

<table>
<thead>
<tr>
<th>Study</th>
<th>Adsorbate</th>
<th>pH</th>
<th>Determined Model + ( R^2 )</th>
<th>Rejected Model + ( R^2 )</th>
<th>Kinetic</th>
<th>Adsorption Mechanism as stated in article</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tonk 2017</td>
<td>Cd(II)</td>
<td>n/a</td>
<td>Langmuir ( R^2=0.996 )</td>
<td>Freundlich ( R^2=0.985 )</td>
<td>Pseudo-second</td>
<td>Physical</td>
</tr>
<tr>
<td>Chen 2016</td>
<td>Cr(VI)</td>
<td>3.0</td>
<td>Freundlich-Langmuir ( R^2=0.996 )</td>
<td>Redlich-Peterson ( R^2=0.995 )</td>
<td>Second-order</td>
<td>Multiple</td>
</tr>
<tr>
<td>Elabbas 2015</td>
<td>Cr(III)</td>
<td>3.8</td>
<td>Langmuir ( R^2=0.995 )</td>
<td>Freundlich ( R^2=0.722 )</td>
<td>Pseudo-second</td>
<td>N/A</td>
</tr>
<tr>
<td>Vijayaraghavan and Joshi 2013</td>
<td>Pb</td>
<td>5.0</td>
<td>Toth ( R^2=0.889 )</td>
<td>Langmuir ( R^2=0.886 )</td>
<td>Pseudo-first</td>
<td>Precipitation</td>
</tr>
<tr>
<td>Ahmad 2012</td>
<td>Pb, Cd, Cu</td>
<td>5.5</td>
<td>Langmuir ( R^2=0.98 )</td>
<td>Freundlich ( R^2=0.32 )</td>
<td>N/A</td>
<td>Ion Exchange</td>
</tr>
<tr>
<td>Flores-Cano 2013</td>
<td>Cd</td>
<td>6.0</td>
<td>Langmuir ( R^2=0.877 )</td>
<td>Freundlich ( R^2=0.751 )</td>
<td>N/A</td>
<td>Multiple</td>
</tr>
<tr>
<td>Granados-Correa 2013</td>
<td>Eu(III)</td>
<td>6.0</td>
<td>Freundlich-Langmuir ( R^2=0.993 )</td>
<td>Freundlich ( R^2=0.95 )</td>
<td>Pseudo-second</td>
<td>Precipitation</td>
</tr>
<tr>
<td>Yedou 2007</td>
<td>Fe(III)</td>
<td>6.0</td>
<td>Langmuir ( R^2=0.997 )</td>
<td>Freundlich ( R^2=0.946 )</td>
<td>Pseudo-second</td>
<td>Physical</td>
</tr>
<tr>
<td>Balaz 2015</td>
<td>Cd</td>
<td>7.0</td>
<td>Langmuir ( R^2=1.0 )</td>
<td>D-R ( R^2=0.933 )</td>
<td>Pseudo-second</td>
<td>Precipitation</td>
</tr>
<tr>
<td>Rohaizar 2013</td>
<td>Cu</td>
<td>7.0</td>
<td>Freundlich ( R^2=0.982 )</td>
<td>Langmuir ( R^2=0.736 )</td>
<td>Pseudo-second</td>
<td>Chemisorption</td>
</tr>
<tr>
<td>Oke 2008</td>
<td>As</td>
<td>7.2</td>
<td>Activated Sludge ( R^2=0.988 )</td>
<td>Freundlich ( R^2=0.978 )</td>
<td>Pseudo-second</td>
<td>Precipitation</td>
</tr>
</tbody>
</table>
There have been several studies showing eggshells or similar materials (calcite, limestone) used successfully for metal removal in pilot-scale water treatment technologies from which more mechanistic information can be interpolated. Thalagan (2015) showed the efficacy of calcium carbonate for the removal of copper from the industrial waste water in a column adsorption filter. Researchers from the University of Calabria used eggshells when suggesting replacement technologies for activated sludge treatment of wastewater. They tested the use of membrane biological reactors using a pre-treatment of powdered eggshells as a fluidized adsorption media followed by sedimentation. Testing in synthetic wastewater, they measured the removal of aluminum (III), iron(II), and zinc (II). They found that eggshell was effective in the removal of all metals as well as reducing the chemical oxygen demand, an indirect measure of organic compounds in the water. Removal mechanisms were not discussed in the paper but the increase of system efficacy when a sedimentation basin followed eggshell treatment suggests both adsorption and precipitation of dissolved compounds (Pettinato 2015).

More insight from successful pilot-scale applications come from Turkey. Erguler (2015) investigated the use of eggshells as a remediation technique for acidic mine drainage. Target adsorbate metals included copper, iron, lead, and zinc. Eggshells were selected for its acid-neutralizing potential (19 H+ mol kg⁻¹). Researchers, however, investigated the chemical composition of the eggshell after treatment when they noted color change of the eggshell from white to orange. They found that energy dispersive x-ray spectrometry microanalysis was not able to detect certain elements in the initial eggshells that were found after treatment: aluminum, iron, and zinc. They hypothesized that these metals precipitated onto the surface of the eggshells.

Other studies have focused on eggshells’ ability to capture metal ions in the soil. Removal being technically cumbersome, research is primarily focused on immobilization. Lee (2013) chose eggshells for their ability to increase acidic soil pH and facilitate overall precipitation of metals as well as increasing overall negative charge of soil particles. Soil spiked with various metal contaminants were mixed with eggshell and then subjected to conditions that simulated rainfall. Soil drainage was examined to determine metal leaching. Lee found that a 5% eggshell inclusion rate into the soil reduced leaching of cadmium and
lead even when washed with acidic rain. Ashrafi (2015) departed from previous studies that used amendments to raise acidic soil pH. Ashrafi used eggshell as a fixing agent in already alkaline soils. Treated soil was then subjected to sequential extraction to determine metal fractionation. The experiment revealed that eggshell addition decreased metal leaching by converting exchangeable fractions to more stable species. Carbonate species increased as well as the fraction of stable mineralized metals.

Data on the performance of eggshells in basic conditions is important for developing their use in swine lagoons which range between pH 7-8. Research on calcite (CaCO3) may be used as an analog for eggshells due to their high calcium carbonate content (>90%). A mechanistic study revealed characteristics of copper and zinc deposition onto pure calcite in basic conditions. The study found an adsorption limit of 0.038 -0.08 mg g⁻¹ for copper at a pH of 8.2. Copper hydroxide precipitated out of solution more quickly than surface adsorption could occur. This was because copper hydroxide solids are more stable than carbonate species. When tested on natural Upper Chalk limestone (96% CaCO3), adsorption occurred up to 0.19 mg g⁻¹ followed by precipitation as malachite, Cu₂(OH)₂CO₃. The increased loading capacity was attributed to a larger surface area of the natural mineral. Similar to copper, zinc precipitated out of solution as Zn₅(OH)₆(CO₃)₂ before the surface of the calcite was effectively covered. Adsorption completed up to 0.03 mg/g onto pure calcite and 0.12mg g⁻¹ onto Upper Chalk before precipitation (Papadopoulos 1989). The Papadopoulos study showed the competition of adsorption versus precipitation. This will be of special concern in the swine lagoon where metal ions already show a marked tendency to precipitate. Research shows that around only 4% of total copper in lagoons exists weakly-bound to organic ligands. In smaller suspended particle size fractions, this percent may be up to 28%. It appears likely that a mix of more mobile copper species exist the slightly oxygenated supernatant waters (Legros 2010). Addition of eggshell to surface water could shift more of the overall the mass of copper to the bottom sludge layer of the lagoon.

Many available eggshell studies also do not investigate multi-component solutions like the complex chemical composition of the swine lagoon. Swine lagoons are saturated in organic compounds, salts, and inorganic species. Zhizhaev and Merkulova (2013) studied the effect of sulfates, which are abundant in lagoons, on the sorption of metal ions onto calcite (CaCO₃). In these conditions, Zhizhaev found that copper and zinc precipitation is actually
more complex. Calcite must first partially dissolve and re-precipitate as gypsum (CaSO₄·2H₂O) before copper deposits on the surface as posnjakite, Cu₄SO₄(OH)₆. Zinc partially co-precipitates with the initial deposition of copper but is dissolved due to the acidification of the solution as hydroxide ions are bound. Zinc then re-precipitates over the posnjakite layer as namuvite, (Zn,Cu)₄SO₄(OH)₆·4H₂O. Thus in the absence of the original adsorbent substrate, it may be less practical to model metal removal in the presence of additional components using typical adsorption models.

From available eggshell adsorption studies, pilot-scale applications, and using research on analog materials, it seems more likely that removal of dissolved metal ions by eggshells follows a mix of mechanisms; a partial adsorption onto the eggshell surface via (1) ion-exchange (2) incorporation into the CaCO₃ crystal lattice (3) micro-precipitation onto the adsorbent surface as dependent on pH and (4) precipitation of metal ions in solution as floc. These steps may occur simultaneously or sequentially.

2.2 Materials and Methods
2.2.1 Adsorbent Material Preparation

Selected adsorbent material (peanut hull and eggshells) were ground to a uniform size with laboratory mill fitted with a 1mm screen. Feathers were manually cut with scissors into small pieces. The final particles were then triplicate washed in deionized water to remove fine dust and stray contaminants. Washed particles were dried at 50°C for 24 hours and stored until use in a desiccator.

2.2.3 Determination of Loading Capacity in Deionized Water

Adsorption experiments were conducted under isothermal conditions at ambient room temperature. A series of six Erlenmeyer flasks were prepared containing copper solutions with varying concentrations (0-80mg L⁻¹). An accurately measured 1.0g portion of selected adsorbent material was added to each flask. Flasks were capped, placed on a stir plate at 350rpm and allowed to equilibrate for 72 hours (as determined by preliminary testing and equilibrium times cited in literature). A 10mL aliquot was then pulled from each flask and stored in a labelled conical tube after being preserved with a 0.2mL addition of concentrated nitric acid. Final equilibrium concentrations of copper were measured by flame atomic absorption spectrophotometry according to ASTM standard method D1688 (1995). Adsorption
experiments for each adsorbent material were carried out in triplicate and the results averaged for analysis.

### 2.2.4 Determination of Loading Capacity in Swine Lagoon Effluent

Swine lagoon supernatant effluent was collected from the Lake Wheeler Swine Research Unit facility on North Carolina State University campus. Lagoon effluent was filtered twice to remove solid particulate matter. Dosed copper solutions (0-100mg L\(^{-1}\)) were prepared in a 50% lagoon effluent: 50% deionized water matrix. Adsorption experiments were conducted under isothermal conditions at ambient room temperature. A series of six 50mL conical tubes were prepared containing copper solutions with varying concentrations (0-100mg L\(^{-1}\)). An accurately measured portion of selected adsorbent material was added to each tube; 1.0g eggshell, 0.5g peanut hull, 0.10g feather. Flasks were capped, placed on a stir plate at 350rpm and allowed to equilibrate for 72 hours. As outlined by ASTM standard method D1688 (1995), each sample was filtered and acid digested prior to analysis by flame atomic absorption spectrophotometry. Adsorption experiments for each adsorbent material were carried out in triplicate and the results averaged for analysis.

### 2.2.5 Analysis

Averaged experimental results for each adsorbent material were analyzed using the Langmuir and Freundlich models of adsorption. Fitting of experimental data to adsorption models determines loading capacities, relative strengths of adsorption and give clues to the responsible mechanisms.

\[
Q_{eq} = Q_{max} \frac{bC_{eq}}{1+bC_{eq}}
\]

\[
Q_{eq} = K_F C_{eq}^n
\]

Experimental results of each adsorbent material were fit to both adsorption models to determine the best model as judged by the coefficient of determination (R\(^2\)) value. The loading capacity of each material as determined by the best fitting adsorption model was used to select the highest loading material to pursue in future research.

### 2.3 Results & Discussion

Experimental results of each adsorbent material were fit to the Langmuir and Freundlich models of adsorption. The Langmuir model provided the best fit for the selected
adsorbents and was used to compare the adsorbents’ performance. Results of both loading capacity studies are shown below in Table 2.3. Eggshells were shown to have the highest loading capacity of the three tested materials. Feathers were the least successful adsorbent of copper. A possible reason for this is the hydrophobic nature of the feathers which float in water thus reducing contact with the solution and repelling hydrophilic metal ions. Peanut hulls also had a lower adsorption efficiency than anticipated which is cited as 8-12mg g⁻¹ in literature.

It was noted that swine lagoon effluent increased the calculated loading capacity of the adsorbents but resulted in decreased fit to the Langmuir model. It was hypothesized that although both copper dosed matrices had an initial pH ≤ 2.0 that the higher buffering capacity of the swine lagoon effluent (normally strongly buffered at a pH of 7.0-8.0) resulted in an increased pH through the duration of the contact time. The increased pH of the lagoon effluent matrix may have acted in two ways to increase metal removal: (1) pH conditions relative to adsorbent zero-point-charge were more favorable or (2) higher pH caused copper precipitation out of solution.

<table>
<thead>
<tr>
<th></th>
<th>Deionized Water</th>
<th>Swine Lagoon Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Langmuir</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>Qₘₐₓ</td>
</tr>
<tr>
<td>Eggshell</td>
<td>0.390</td>
<td>2.60</td>
</tr>
<tr>
<td>Peanut Hull</td>
<td>0.805</td>
<td>0.60</td>
</tr>
<tr>
<td>Feather</td>
<td>--</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kₚ</td>
<td>n</td>
</tr>
<tr>
<td>Eggshell</td>
<td>0.097</td>
<td>0.219</td>
</tr>
<tr>
<td>Peanut Hull</td>
<td>0.270</td>
<td>0.288</td>
</tr>
<tr>
<td>Feather</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

2.4 Conclusions

In the initial evaluation of the three possible adsorbents, eggshells performed better than peanut hulls and feathers in both deionized water and 50% swine lagoon effluent
matrices. In addition to higher loading capacity, eggshells are also more mechanically stable and resistant to microbial action than peanut hulls. For these reasons, eggshells were chosen for further in-depth characterization of its copper adsorption properties.
REFERENCES


CHAPTER THREE: EVALUATION OF WASTE EGGSHELLS FOR ADSORPTION OF COPPER FROM SYNTHETIC AND SWINE WASTEWATER.*

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ABSTRACT

Biomass-derived adsorbents are an attractive alternative to conventional water treatment methods. This study evaluated eggshells produced by the liquid egg and food processing industry for the adsorption of copper from aqueous systems. Research objectives were to determine (1) copper adsorption mechanisms and (2) evaluate copper adsorption by eggshells for the treatment of wastewater. Batch experiments were performed by contacting eggshells with copper solutions to obtain equilibrium, kinetic, and thermodynamic data to determine removal mechanisms and maximum adsorption capacity. Results suggested the adsorption of copper followed a second-order kinetic model with a maximum adsorption capacity of 4.3 mg g⁻¹ (20°C). In addition, eggshell adsorption was found to be a favorable process with an activation energy of approximately 27 to 29 kJ mol⁻¹ and followed similar mechanisms as its calcite analog. Data indicated that slightly acidic (pH=6) to near neutral pH conditions...
enhanced adsorption of copper. Additional experiments were performed using swine lagoon wastewater to evaluate the efficacy of eggshells to treat copper from lagoon wastewater. The data suggested that unmodified eggshells were effective for application in swine lagoon systems only under acidic conditions (pH = 4). Further research is needed to modify eggshells that can adsorb copper in lagoon wastewater at neutral and alkaline pH.

**Keywords.** Adsorption, copper, eggshell, swine lagoon, Water.

**INTRODUCTION**

The study of biomass-derived adsorbents is a rapidly growing field of science focused on two goals: (1) discovering new uses for waste products and (2) developing less expensive options to conventional water treatment. Many waste materials have been studied for their adsorbent properties including but not limited to non-living microbial and algae cells, extracted biological polymers, processing waste such as rubber scraps, and lignocellulosic materials from agricultural waste (Rowley et. al., 1984; Kratochvil and Volesky, 1998; Demirbas et. al., 2008; Wan Ngah et. al., 2011). The overall cost of agricultural waste-derived adsorbents is much lower than conventional adsorbents such as activated carbons or resins. Economic efficiency is especially valued for the treatment of waste effluents in marginalized industries and developing nations (Garg et al., 2007). This is strongly reflected in the global proliferation of interest in biomass adsorbents for the adsorption of dyes, phenols, and heavy metals originating from textile, tannery, electroplating and other industrial activities (Sud et. al, 2008). Biomass adsorbents, however, are less efficient than commercial adsorbents and require larger quantities to treat the same waste stream. Therefore, development of potential biomass should be focused on materials produced in sufficient quantity to ensure a steady supply. Ideally, a potential adsorbent could also be collected at a central facility to ease procurement logistics and be geographically convenient to its end use.

One such potential adsorbent is waste eggshells. Waste eggshells are produced during grading, liquid egg product processing, and at food production facilities where eggs are used as an ingredient in other food products. In the United States alone, 70.4 million dozen eggs are broken into egg products which generate about 5300 metric tons of waste shells (American Egg Board, 2012). Eggshells produced during these processes are largely sent to landfills and
could be obtained for little more than their transportation costs. The quantity of production at centralized facilities make eggshells a prime candidate for further development as an adsorbent material.

Eggshells are well-suited for metal sequestration due to their primarily mineral composition (93%), alkalinity, strong mechanical properties, and resistance to degradation (Guru and Dash 2014). Eggshells are composed of 2% water, 5% protein, and 93% minerals. The majority is calcium carbonate with smaller amounts of phosphorous and magnesium (Hassan, 2015). Natural calcite crystal may be considered analogous to eggshell in composition but the interlaced protein matrix of the egg creates a unique crystal morphology. The eggshell structure is made up of several layers: an inner double-layered protein membrane, a mammillary (100 μm) layer of randomly oriented calcium carbonate crystals followed by the thickest (200 μm) palisade layer of crystals perpendicular to the shell surface and finally a thin (8 μm) vertical crystal layer. The eggshell is studded with round micropores ranging in size from 200-400 nm which serve to exchange oxygen for the developing fetus in nature but may impart greater adsorption efficiency in application (Chai et al., 2012; Guru and Dash, 2014).

As a result, eggshell membranes and eggshells have been investigated as adsorbents. Liu and Huang (2011) studied polyethyleneimine-modified eggshell membranes for mitigation of chromium(IV) from the water. Further, Wang et al (2012) employed eggshell membrane as a precursor to synthesize solid phase extraction material capable of adsorbing polycyclic aromatics from an aqueous sample. Similarly, eggshells were studied for their adsorption capacity of metals including arsenic, cadmium, chromium, copper, iron, lead, and even europium from the nuclear industry (Yeddou and Bensmaili, 2007; Oke et. al., 2008; Ahmad et. al, 2012; Granados-Correa et. al, 2013). Some other scattered studies have investigated eggshells for adsorption of dyes, humic acid, phenol, and phosphate (Tsai et. al, 2006; Zulfikar et. al, 2013; Daraei et. al, 2013; Carvalho et. al., 2015; Chen et. al, 2016). However, mechanistic evaluations of the adsorption process are contradictory and lag behind. Hence, the current study is an attempt to address this gap by applying thermodynamic theory to determine energies of activation and examining the overall adsorption reaction to reveal mechanistic insights.
MATERIALS AND METHODS

MATERIALS

Copper (Cu) stock solution (1000 mg L\(^{-1}\)) was prepared by dissolving 99.999% purity elemental copper (Sigma-Aldrich) in nitric acid and diluting with ultra-pure water. All other chemicals and solvents were purchased from Fisher Scientific (Fairlawn, NJ) and met American Chemical Society standards. Commercial eggshells produced in the state of North Carolina were collected from local grocery stores. Inner contents were removed and the eggshell and attached membranes were thoroughly washed in deionized water. Eggshells were dried at 50°C and ground to a uniform size with laboratory mill fitted with a 1-mm screen. The final particles were then washed three times with deionized water to remove fine dust and stray contaminants. Washed particles were dried at 50°C for 24 hrs and stored until use in a desiccator.

CHARACTERIZATION

The eggshells were characterized for their surface elemental composition via a variable pressure scanning electron microscope (Hitachi S3200) equipped with an Oxford energy dispersive X-ray spectrometer (EDS). Typically, the adsorbent samples were placed on adhesive carbon stub and the data was acquired using a beam energy of 0-20 KeV to determine the elemental composition. Additionally, the eggshells were analyzed via X-Ray Photoelectron Spectroscope (SPECS FlexMod) using a PHOIBIS 150 hemispherical analyzer and an Al/Mg X-ray source. Data were collected before and after the eggshells were subjected to adsorption experiments to confirm that adsorption of Cu on the eggshell surface.

BATCH EXPERIMENTS

Adsorption experiments were conducted under isothermal conditions at 20°C, 30°C, and 50°C without pH adjustment (pH=2.2). The effect of initial adsorbate concentration was investigated at varying concentrations (0-80 mg L\(^{-1}\)) respectively. An accurately measured 1.0 g portion of eggshell was added to each 100 mL replicate and allowed to equilibrate for 240 hrs under constant agitation (350 rpm) to facilitate mass transport of metal ions.

Aliquots were sampled after the appropriate equilibrium time and preserved with a 0.2 mL addition of concentrated nitric acid (15.8M) until analysis. Final equilibrium concentrations of Cu were measured by flame atomic absorption spectrophotometry via ASTM standard method D1688 (1995). Experiments were carried out in triplicate and the results
averaged for analysis. The amount of Cu adsorbed was determined via equation (1):

\[
Q = \frac{(C_0 - C)V}{M} \tag{1}
\]

where \(Q\) is the adsorption loading capacity (mg g\(^{-1}\)), \(C_0\) is the concentration of Cu at \(t = 0\) (mg L\(^{-1}\)), and \(C\) is the concentration of Cu at equilibrium (mg L\(^{-1}\)), \(V\) is the volume of the solution (L), and \(M\) is the mass of the adsorbent (g). The data collected from the experiments were fit to equilibrium adsorption isotherms listed in Table 1.

### Table 1. Adsorption Isotherm Models Used to Evaluate Data (Zhu et. al., 2009; Worch, 2012)

<table>
<thead>
<tr>
<th>Model</th>
<th>Eqn (#)</th>
<th>Equations</th>
<th>Fitted Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong>[^a^]</td>
<td>(2)</td>
<td>(Q = \frac{Q_{max} bC}{1 + bC})</td>
<td>(b) (L mg(^{-1})) Qmax (mg g(^{-1}))</td>
</tr>
<tr>
<td><strong>Freundlich</strong>[^b^]</td>
<td>(3)</td>
<td>(Q = k_f C^n)</td>
<td>(n) kf (L mg(^{-1}))</td>
</tr>
<tr>
<td><strong>Dubinin-Radushkevich</strong>[^c^]</td>
<td>(4)</td>
<td>(ln(Q) = ln(Q_{max}) - \frac{\beta \varepsilon^2}{2})</td>
<td>Qmax (mmol g(^{-1})) E (kJ mol(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>(5)</td>
<td>(\varepsilon = RT ln(1 + \frac{1}{C}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(6)</td>
<td>(E = \frac{1}{\sqrt{2\beta}})</td>
<td></td>
</tr>
</tbody>
</table>

[^a^] \(Q_{max}\) is the maximum loading capacity (mg g\(^{-1}\)); \(b\) Langmuir rate constant (L mg\(^{-1}\))

[^b^] \(k_f\) is the Freundlich rate constant (L mg\(^{-1}\)); \(n\) is an affinity term

[^c^] \(\varepsilon\) is the Polanyi potential; \(\beta\) mean free energy of biosorption constant (mol\(^2\) kJ\(^{-2}\)); \(R\) ideal gas constant (J K\(^{-1}\) mol\(^{-1}\)); \(E\) free energy of the reaction (kJ mol\(^{-1}\))

### KINETIC STUDIES

One liter aliquots of 40 mg L\(^{-1}\) Cu metal solution (pH 2.2) were prepared to assess the kinetics and activation energy of adsorption. The prepared solutions were decanted into clean reagent storage bottles, stirred at 350 rpm, and allowed to equilibrate at temperatures of 20°C, 30°C, or 50°C. An accurately measured 10.0 g portion of eggshell was then added to the solution. Under constant agitation to facilitate mass transport, 1.0 mL aliquots were pulled from the bulk solution at regular intervals over 240 hrs. Experiments were repeated in duplicate and averaged for analysis. Experimental data were described with the kinetic models described.
in Table 2.

<table>
<thead>
<tr>
<th>Model</th>
<th>Eqn (#)</th>
<th>Equation</th>
<th>Fitted Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-First[a]</td>
<td>(7)</td>
<td>$Q_t = Q_e (1 - e^{-k_1 t})$</td>
<td>$Q_e$ (mg g(^{-1}))  \ $k_1$ (hr(^{-1}))</td>
</tr>
<tr>
<td>Pseudo-Second[a]</td>
<td>(8)</td>
<td>$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t}$</td>
<td>$Q_e$ (mg g(^{-1}))  \ $k_2$ (mg g(^{-1}) hr(^{-1}))</td>
</tr>
<tr>
<td>Liquid Film</td>
<td>(9)</td>
<td>$\ln \left(1 - \frac{Q_t}{Q_e}\right) = -k_L t + C$</td>
<td>$k_L$ (hr(^{-1}))  \ C</td>
</tr>
<tr>
<td>Diffusion[b]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intraparticle</td>
<td>(10)</td>
<td>$Q_t = k_d t^{0.5} + C$</td>
<td>$k_d$ (mg g(^{-1}) hr(^{-0.5}))  \ C (mg g(^{-1}))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[a\] $Q_e$ is the loading capacity measured at equilibrium; $Q_t$, loading capacity measured at any time; $k_1$, $k_2$ the associated rate constants

\[b\] $k_L$, $k_d$ are the respective model rate constants; $C$ is the intercept representing the degree of boundary layer control

**THERMODYNAMIC ANALYSIS**

Repetition of kinetic experiments over various temperatures can reveal mechanistic insight by application of thermodynamic theory (Doke and Khan, 2013). The reaction activation barrier can be gleaned from kinetic data through the use of the Arrhenius equation (Zhu et al., 2009):

$$\ln k = \ln A - \frac{E_a}{RT}$$ \hspace{1cm} (11)

By plotting $\ln(k)$ versus the reciprocal of the absolute temperature ($T$), the activation energy ($E_a$) can be determined from the slope, where $R$ is the ideal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)). The Eyring equation may also be applied to calculate the activation entropy ($\Delta S$) and enthalpy ($\Delta H$), where $k_B$ is the Boltzmann constant (1.381×10\(^{-23}\) J K\(^{-1}\)) and $h$ is the Planck constant (6.6261×10\(^{-34}\) J s\(^{-1}\)) (Zhu et al., 2009):

$$\ln \left(\frac{k}{T}\right) = \ln \left(\frac{k_B}{h}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$ \hspace{1cm} (12)

The Gibb’s free energy ($\Delta G$) can thus be calculated from the equation (13):
\[ \Delta G = \Delta H - T \Delta S \]  

(13)

**EFFECT OF PH**

The effect of pH on adsorbent loading capacity was evaluated to assess the efficacy of eggshells. A series of 500 mL, 80 mg L\(^{-1}\) Cu solutions were prepared at pH of 2 to 9. The pH of the solution was measured by a benchtop pH probe (model: Accumet AB150, manufactured by Fisher Scientific, Hampton, NH, USA) under constant stirring and adjusted with nitric acid or sodium hydroxide as needed. The pH-adjusted solution was divided into triplicate 100 mL aliquots with an additional 100 mL solution reserved as a control for Cu removed via precipitation. An accurately measured 0.50 g portion of eggshells was added to each replicate. Solutions were stirred at 350 rpm and allowed to equilibrate for 240 hrs. Solution pH was kept within ±0.1 of the initial pH by adding nitric acid or sodium hydroxide after the first 2 hrs and every 24 hrs thereafter. Triplicate results were averaged for analysis. A baseline model for Cu precipitation in the presence of calcium carbonate in deionized water was modeled using Visual MINTEQ version 3.1 software (MINTEQ, 2013).

**DESORPTION EXPERIMENTS**

To determine the surface interaction between eggshells and copper ions, desorption studies were performed. A 4.0 g portion of spent eggshells was added to 500 mL of deionized water. Desorption was also performed in calcium solutions equimolar (70 mg L\(^{-1}\) CaCl\(_2\)) and double molar (140 mg L\(^{-1}\) CaCl\(_2\)) to the adsorbed Cu amount. Under constant stirring (350 rpm), the loaded eggshells were allowed to equilibrate at room temperature for more than 30 d. Five-milliliter aliquots were drawn at regular intervals and measured for Cu concentration. Experiments were repeated in duplicate and averaged for analysis.

**RESULTS AND DISCUSSION**

**EQUILIBRIUM LOADING CAPACITY**

Sorption of Cu onto eggshell was studied over an initial concentration range of 0-80 mg L\(^{-1}\) at three temperatures (figure 1). Adsorption capacity increased with increasing equilibrium Cu concentration until about 30 mg L\(^{-1}\) and started to plateau. Adsorption of Cu on the eggshell surface was also corroborated via data collected using EDS (fig 2), in which the EDS detector
clearly identified Cu ions that were accumulated on the surface of the spent eggshell. Similarly, XPS data corroborated the presence of Cu on the eggshell surface after sorption equilibrium (fig 3). Presence of deposited copper on the eggshell surface confirms that removal of copper from solution is a result of adsorption and not precipitation out of the bulk solution. It is important to distinguish these two removal mechanisms in the application as fine precipitants must be captured via subsequent filtration for true removal.

Figure 1. Adsorption isotherm of Cu(II) on eggshell at different temperatures (ES 10g L\(^{-1}\))
Figure 2. EDS spectra of raw eggshell (A) and spent eggshell (B). The spent eggshell surface was found to contain Cu ions due to adsorption.

Figure 3. SEM-XPS spectra of raw eggshell (a) and spent eggshell (b).

Adsorption model constants and respective model fits are shown in Table 3. The Langmuir model ($R^2 > 0.96$) provided only a slightly better fit than the Freundlich equation ($R^2 = 0.92-0.97$).
Table 3. Isotherm constants for the adsorption of Cu(II) onto eggshells at different temperatures.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Dubinin-Radushkevich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b</td>
<td>Q_max</td>
<td>R^2</td>
</tr>
<tr>
<td></td>
<td>(L mg(^{-1}))</td>
<td>(mg g(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.041</td>
<td>4.26</td>
<td>0.960</td>
</tr>
<tr>
<td>30</td>
<td>0.038</td>
<td>4.37</td>
<td>0.978</td>
</tr>
<tr>
<td>50</td>
<td>0.025</td>
<td>5.07</td>
<td>0.989</td>
</tr>
</tbody>
</table>

When no clear distinction between the Langmuir and Freundlich model exists, the DubininRadushkevich (D-R) equation may be applied to suggest a physical or chemical adsorption mechanism. Determining the β constant from multiple temperature isotherms, the mean free energy E (kJ mol\(^{-1}\)) can be calculated via equation (6). The magnitude of the mean free energy corresponds with different adsorption mechanisms: E < 8 kJ mol\(^{-1}\) denotes physical adsorption and 8 < E < 16 kJ mol\(^{-1}\) suggests a chemical ion-exchange mechanism (Zhu et. al., 2009). Eggshell adsorption of Cu for the tested temperature range (20-50°C) determined a mean free energy spread between 3 to 9.5 kJ mol\(^{-1}\) (Table 3), indicating a combination of adsorptive and ion-exchange processes.

Similarly, it is difficult to draw mechanistic conclusions from other studies that employed eggshells for metal adsorption (Table 4) under different experimental conditions as final judgments of adsorption type, best-fit kinetic model, and their associated mechanism was often made through minor differences in regression analyses.
Table 4. Summary of Studies on Eggshell Adsorption of Metal Ions

<table>
<thead>
<tr>
<th>Study</th>
<th>Adsorbate</th>
<th>pH</th>
<th>Loading Capacity (mg g(^{-1}))</th>
<th>Determined Model + R(^2)</th>
<th>Rejected Model + R(^2)</th>
<th>Thermodynamic Parameters (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Study</td>
<td>Cu</td>
<td>2.2</td>
<td>4.3</td>
<td>Langmuir R(^2)= 0.96</td>
<td>Freundlich R(^2)= 0.92</td>
<td>----</td>
</tr>
<tr>
<td>Chen et. al., 2016</td>
<td>Cr(VI)</td>
<td>3.0</td>
<td>11.8</td>
<td>Sips R(^2)=0.996</td>
<td>Redlich-Peterson R(^2)=0.995</td>
<td>----</td>
</tr>
<tr>
<td>Elabbas et. al., 2015</td>
<td>Cr(III)</td>
<td>3.8</td>
<td>200</td>
<td>Langmuir R(^2)=0.995</td>
<td>Freundlich R(^2)=0.722</td>
<td>(\Delta G = -5.66) (\Delta H = +121) (\Delta S = +0.423)</td>
</tr>
<tr>
<td>Vijayaraghavan and Joshi, 2013</td>
<td>Pb</td>
<td>5.0</td>
<td>154</td>
<td>Toth R(^2)=0.889</td>
<td>Langmuir R(^2)=0.886</td>
<td>----</td>
</tr>
<tr>
<td>Ahmad et. al., 2012</td>
<td>Cu</td>
<td>5.5</td>
<td>2.0</td>
<td>Langmuir R(^2)=0.98</td>
<td>Freundlich R(^2)=0.32</td>
<td>----</td>
</tr>
<tr>
<td>Flores-Cano et. al., 2013</td>
<td>Cd</td>
<td>6.0</td>
<td>3.8</td>
<td>Langmuir R(^2)=0.877</td>
<td>Freundlich R(^2)=0.751</td>
<td>----</td>
</tr>
<tr>
<td>Granados-Correa et. al., 2013</td>
<td>Eu(III)</td>
<td>6.0</td>
<td>18.7</td>
<td>Sips R(^2)=0.993</td>
<td>Freundlich R(^2)=0.95</td>
<td>(\Delta G = -14.6) (\Delta H = +28.2) (\Delta S = +0.150)</td>
</tr>
<tr>
<td>Yeddou and Besmaili, 2007</td>
<td>Fe(III)</td>
<td>6.0</td>
<td>8.7</td>
<td>Langmuir R(^2)=0.997</td>
<td>Freundlich R(^2)=0.946</td>
<td>(\Delta G = -1.94) (\Delta H = -19.1) (\Delta S = +0.017)</td>
</tr>
<tr>
<td>Oke et. al., 2008</td>
<td>As</td>
<td>7.2</td>
<td>4.6</td>
<td>Activated Sludge R(^2)=0.988</td>
<td>Freundlich R(^2)=0.978</td>
<td>----</td>
</tr>
</tbody>
</table>

However, the most in-depth analysis came from Flores-Cano et. al. (2013) who studied the adsorption of cadmium and found a maximum removal at a pH of 6 with a loading capacity of 3.82 mg g\(^{-1}\). The authors concluded the Langmuir equation best modeled the experimental data of those evaluated (R\(^2\) = 0.877). The authors’ analyses were based on thermodynamic evidence that the adsorption occurred via two mechanisms; the evidence was derived from desorption data that 32% of cadmium adsorption was via reversible ion-exchange while 68% due to non-reversible chemisorption and/or precipitation. EDS microanalysis confirmed the exchange of calcium for cadmium cations. The formation of a cadmium precipitate on the eggshell surface was also validated using XRD pattern shifting (Flores-Cano et. al., 2013). XPS data obtained for the adsorption of copper also shows loss of calcium, 5.5% to 0.9% surface abundance, corresponding with an uptake of copper ions.
As eggshells are composed primarily of calcium carbonate, mechanistic studies of the interactions of divalent metals with calcite may be consulted to verify conclusions of a mixed adsorption process. For years, geochemists have known that divalent metals ions are incorporated onto calcium carbonate by both adsorption and surface precipitation mechanisms as dependent on metal ion concentration (Papadopoulos and Rowell, 1989; Schosseler et. al., 1999). Adsorption is the primary method of removal at low concentrations but as concentration increases, the rate of precipitation exceeds the rate of adsorption. Furthermore, the relative proportions of each are understood as a function of time and solution pH.

**KINETIC ANALYSIS**

The kinetics of Cu adsorption onto eggshells were evaluated with an initial Cu concentration of 40 mg L\(^{-1}\) over 10 d. Kinetics were observed at three temperatures (20, 30, 50°C). Figure 4 shows the Cu uptake by the adsorbent surface over time for different temperatures tested. Kinetic data were modeled using the Lagergren pseudo-first-order and pseudo-second-order models as shown in Table 5.

![Figure 4. Effect of temperature on eggshell Cu loading capacity (C\(_o\) = 40 mg L\(^{-1}\), eggshell dosage = 10 g L\(^{-1}\)) fit to second-order model.](image-url)
Table 5. Kinetic model rate constants for the adsorption of Cu onto eggshell at different temperatures across 240 hrs.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Experimental Q (mg g⁻¹)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( k_1 ) (hr⁻¹)</td>
<td>( Q_e ) (mg g⁻¹)</td>
<td></td>
<td>( k_2 ) (mg g⁻¹ hr⁻¹)</td>
<td>( Q_e ) (mg g⁻¹)</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>20</td>
<td>2.99</td>
<td>0.037</td>
<td>2.40</td>
<td>0.980</td>
<td>0.015</td>
<td>2.75</td>
<td>0.989</td>
</tr>
<tr>
<td>30</td>
<td>3.53</td>
<td>0.029</td>
<td>3.16</td>
<td>0.995</td>
<td>0.008</td>
<td>3.78</td>
<td>0.996</td>
</tr>
<tr>
<td>50</td>
<td>3.75</td>
<td>0.056</td>
<td>3.68</td>
<td>0.999</td>
<td>0.014</td>
<td>4.12</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Across the three temperature sets, the adsorption occurred relatively quickly within the first 72 hrs followed by a slower uptake period over the following 168 hrs. Two-step adsorption has been described in previous calcite studies. Schosseler et al. (1999) observed a rapid initial adsorption of Cu onto CaCO₃ followed by a dissolution of the carbonate mineral and attached Cu ions. Then as carbonate recrystallized, Cu was reincorporated into the bulk mineral as \( \text{Cu}_x \text{Ca}_{(1-x)} \text{CO}_3 \text{(s)} \). This multi-step adsorption mechanism likely explains why the current and other eggshell adsorption studies (Table 5) favor a pseudo-second-order. The pseudo-second-order kinetic model may encompass multiple factors such as agitation rate, side reactions, complex formations in solution, and ion dissociation prior to exchange by the adsorbent/adsorbate. This broad universality often results in a pseudo-second-order model determination across many different biomass adsorption studies (Gupta and Bhattacharyya, 2011).

Further mechanistic insight may be gleaned by considering that transport of adsorbates from solution onto the adsorbent surface involves multiple consecutive steps (Cheung et al., 2007; Hameed et al., 2007). First, transport from the bulk solution to the boundary layer surrounding the adsorbent particle. This step is considered to occur very fast and can be neglected as long as sufficient agitation is provided. Next, diffusion across the film layer to reach the external surface of the adsorbent and within the pores of the adsorbent. Finally, adsorption of the solute onto the surface of the adsorbent. Evaluation of the liquid film diffusion and intraparticle diffusion models can be used to determine if mass transport is the rate-limiting step of the overall adsorption process. Models were fit over 72 hrs and 240 hrs to reflect the separate...
stages of adsorption that were observed: (1) rapid adsorption followed by (2) slower de/sorption cycled uptake. Calculated model parameters are listed in Table 6.

A linear plot of the liquid film diffusion model in which the intercept is zero denotes that diffusion from the bulk solution to the surface of the adsorbate is the rate-controlling step. The magnitude of the intercept denotes the degree of control exerted by other reactions which may also be occurring simultaneously. Plotting \(-\ln(1-F)\) versus \(t\) over the full 240 hrs yielded linear plots \((R^2 = 0.91-0.97)\). Reducing the model application to the initial 72 hrs, however, resulted in improved correlations \((R^2 = 0.99\), faster rate constants, and intercepts that more closely approached zero, \(C = 0.06-0.10\)). Similar results were noted in application of the intraparticle diffusion model across 72 hrs \((C = 0.04 – 0.35)\) versus 240 hrs \((C = 0.03 – 0.17)\) as depicted in figure 5. Overall, small intercept values suggest that mass diffusion plays an important role throughout the adsorption process. Fits of both transport models, however, display a distinct multi-linearity indicating that two distinct phases of adsorption occur. This agrees with the initial fast adsorption of Cu onto calcite observed by Schosseler et. al. (1999) which was then followed by a multi-step desorption and incorporation reaction. The notable exception being adsorption occurring at 50°C which reached a stable equilibrium after the initial 72 hr period.

For application in wastewater treatment systems, eggshells could be deployed in a long-term contact system such as a storage lagoon or in a batch treatment tank for shorter contact times as more than 70% of loading occurs within the first three days.
Figure 5. Intraparticle diffusion kinetics of Cu onto eggshell at various temperatures. Fit across 72 hrs (solid line) and 240 hrs (dashed line).

Table 6. Comparison of liquid film and intraparticle diffusion models applied across 72 and 240 hrs.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Liquid Film Diffusion</th>
<th>Intraparticle Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_L$ (hr$^{-1}$)</td>
<td>$C$</td>
</tr>
<tr>
<td>20</td>
<td>0.010</td>
<td>0.14</td>
</tr>
<tr>
<td>30</td>
<td>0.024</td>
<td>0.06</td>
</tr>
<tr>
<td>50</td>
<td>0.0463</td>
<td>0.07</td>
</tr>
</tbody>
</table>

**THERMODYNAMIC ANALYSIS**

Reaction activation parameters were calculated from the mass transport kinetics models: liquid film diffusion and intra-particle diffusion models. By measuring the kinetics across several isothermal conditions (20, 30, 50°C), the Arrhenius equation (eq. 11) can be utilized and the value of $E_a$ calculated from the plot slope. The value of $E_a$ for Cu(II) onto eggshells was 27 and 25 kJ mol$^{-1}$ for the liquid film and intraparticle models respectively. The activation
energy corresponds to the magnitude of resistance that must be overcome for the metal ions in solution to move to the adsorbent surface.

Further analysis using the Eyring equation (eq. 12) yielded the activation enthalpy ($\Delta H^\#$) and activation entropy ($\Delta S^\#$) values. The free energy of activation ($\Delta G^\#$) for each model was obtained using the relationship: $\Delta G = \Delta H - T\Delta S$. Results of these calculations are shown in Table 7. Both models yield high $\Delta G^\#$ values that confirm mass transport of the adsorbate to the adsorbed surface requires an energy input. A positive enthalpy value of approximately 25 kJ mol$^{-1}$ denotes that the mass transport reaction is endothermic in nature as evidenced by the increasing rate constant and loading capacity with temperature. Although, the reaction proceeds at ambient temperature (20°C) greater system efficiencies can be achieved. As many copper-bearing industrial effluents are produced at elevated temperatures and must be subsequently cooled for discharge, eggshells may be applied at any point in the process (Chowdhury 2015; Sing 2016). The negative entropy values indicate that the mass transport leads to a more ordered system as free ions concentrate around and attach to the adsorbate surface. Comparison of the magnitude of $\Delta H$ versus $T_{avg}\Delta S$ showed that increasing order in the system contributed more than twice as much resistance than the reaction enthalpy.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Intraparticle Diffusion</th>
<th>Liquid Film Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta G^#$ (kJ mol$^{-1}$)</td>
<td>Constants</td>
</tr>
<tr>
<td>293</td>
<td>92.8</td>
<td>$E_a = 27.5$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>303</td>
<td>95.1</td>
<td>$\Delta H^# = +24.9$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>323</td>
<td>99.8</td>
<td>$\Delta S^# = -232$ J mol$^{-1}$</td>
</tr>
</tbody>
</table>

EFFECT OF PH

The pH of the solution was theorized to be the greatest potential factor affecting adsorption. As a result, experiments were carried out over a pH range of 2 to 9. This pH range is not often evaluated in Cu adsorption studies as Cu begins to precipitate in deionized water above a pH
of 5.5. To differentiate between the two removal mechanisms, an untreated control was used to determine precipitation that occurred during the same time period. Total removal and removal attributed to adsorption by the eggshell material was calculated by mass balance.

As shown in figure 6, adsorption increased when pH is increased from 2 and reached a maximum at a pH of 6. At $5 < \text{pH} < 6$ both mechanisms are present but precipitation dominates as free Cu ion begins to fall out of solution. At pH > 6, adsorption decreases to essentially zero while precipitation becomes the predominant mechanism for removal of Cu. These results are consistent with previous studies (listed in Table 4) on metal adsorption on eggshell that reported best removal results at pH values between 5 to 6. The effect of pH on removal mechanisms suggests significantly faster precipitation kinetics than the rate of adsorption.

![Figure 6. Effect of pH on removal mechanism of Cu by eggshell. Precipitation at infinity model (MINTEQ) for 40mg L$^{-1}$ Cu in deionized water provided as a baseline comparison.](image)

Our results are in accordance with Papadopoulos and Rowell (1989), who reported an adsorption limit of 0.038-0.08 mg Cu per g of pure calcite at a pH of 8.2 while the majority of
Cu in solution was removed via precipitation as fine crystals of Cu(OH)₂. When tested on natural Upper Chalk limestone (96% CaCO₃), adsorption occurred up to 0.19 mg g⁻¹ but was also accompanied by precipitation onto the surface as malachite, Cu₂(OH)₂CO₃. The increased loading capacity was attributed to a larger surface area of the natural mineral sample. Eggshells likely follow a similar mechanism and exhibit a blue-green color upon adsorption consistent with that of azurite or malachite. Cu removal from basic solution, however, can be largely contributed to precipitation as Cu(OH)₂ crystals (90-100%).

DESORPTION EXPERIMENTS

A final consideration for the further employing eggshells as a Cu adsorbent under any application is the fate of adsorbed Cu upon storage. Lability of adsorbed Cu was observed for over 30 days in deionized water and equal and double molar Ca solutions (Figure 7). An initial spike of desorption was observed in the samples over the first three days followed by a cycle of resorption/desorption over the next 7 to 13 days. After 15 days, solution concentrations of Cu were largely stable. No more than 4% of adsorbed Cu leached back into solution at any given time. Results from desorption experiments indicated that increasing solution calcium concentration had no effect on desorption suggesting that adsorption occurring by ion exchange of copper for calcium at the eggshell surface is not a dominant mechanism. This lends further support for a mechanism that incorporates Cu into the CaCO₃ lattice or surface precipitation as a low-solubility precipitant such as malachite. Adsorption onto eggshells could safely be considered as a long-term storage vehicle of metal ions.
Figure 7. Leaching Cu from spent eggshell adsorbent at various ionic strengths.

**ADSORPTION EXPERIMENTS IN SWINE LAGOON WATER**

Having established eggshell as an adsorbent of Cu ions in wastewater, the next step was to explore the efficacy of eggshells for use in other agricultural wastewaters. One such type of wastewater is swine lagoon effluent. Swine lagoons are ill-suited for conventional water treatment methods due to the low capacity for capital investment in the agricultural sector. Volumes for treatment are prohibitively large and precipitant sludge production by coagulation methods are not desired (AWWA, 2011; Salman et al., 2015). Swine lagoon effluent is often contaminated with copper due to supplemental dosing to prevent enteric pathogens in swine herds (Barker, 1996; Suzuki; Price et al., 2001). Reports by Suzuki et al. (2010) indicated that swine manure may contain 135-374 mg g⁻¹ (dry basis) of copper. Similarly, Cestonaro do Amaral et al. (2014) reported that swine wastewater may contain up to 15 mg L⁻¹ of copper. At present, there is no information about the efficacy of eggshell as an adsorbent for removing Cu for swine lagoon wastewater. Hence, additional studies were performed to study removal of Cu from swine lagoon wastewater over a pH range of 2-9 to assess the possibility of minor pH adjustment in batch adsorption systems. The pH of the solutions was adjusted initially and then allowed to rise as the system buffered (p<sub>ka</sub> 7.8).

Figure 8 shows the fractional removal of Cu from swine lagoon wastewater for a pH range of 2-9. Removal of Cu via adsorption reached a maximum at a pH of 4. For aqueous systems whose pH are greater than 4, removal of copper occurs mainly via precipitation. Our results suggest that raw eggshell (without modifications) may not be able to remove Cu from lagoon
wastewater via adsorption. However, eggshells may be chemically modified via various facile surface treatments to enhance adsorption capacity of copper under alkaline conditions. Further, our data suggested that raw eggshells are suitable for adsorbing Cu from wastewaters from other sources such as battery manufacturing, copper plating, or metal etching industries, where the effluent is acidic in nature. In addition, we observed that copper was strongly bound to eggshells and exhibited minimal leaching into solution suggesting that spent eggshells could easily be disposed of.

CONCLUSIONS

Study results show that eggshells sequester copper ions from aqueous solution. Eggshells are best suited for acidified industrial wastewaters with limited scope for use in agricultural or municipal wastewater unless modified chemically to enhance adsorption under alkaline conditions. Copper-loaded onto the eggshell surface shows a low proclivity for dissolution and is likely present as a low-solubility precipitant covering the particle surface. This enables safe and convenient disposal of eggshells in landfills. Based on the experimental investigations, the following mechanistic conclusions can be made:

Figure 8. Effect of initial pH on removal mechanism of Cu by eggshell in swine lagoon effluent. Precipitation at infinity model (MINTEQ) for 40mg L\(^{-1}\) Cu in deionized water provided as a baseline comparison.
• Removal mechanism of Cu from solution by eggshell was a continuum between adsorption and micro-precipitation onto the eggshell surface. Relative proportions were dependent on initial Cu concentration and solution pH.

• Cu removal can be described by the second-order kinetic model and was mass transport limited with an activation energy of approximately 27 to 29 kJ mol\textsuperscript{-1}.

• The maximum copper adsorption capacity (20°C) was 4.3 mg g\textsuperscript{-1}. Copper removal performance can be improved at elevated temperatures and occurs at a pH of 6.

ACKNOWLEDGEMENTS

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CHAPTER FOUR: EVALUATION OF FACILE SURFACE MODIFICATIONS OF EGG SHELLS FOR ADSORPTION OF COPPER

4.1 Introduction

Anthropogenic emissions of metals are a burgeoning environmental and public health concern. Toxic metals such as copper are commonly released into the environment through wastewater. Municipal and industrial wastewater from chemical, electroplating, metal finishing, mining, and textile production may contain elevated copper concentration. These waste effluents must be treated to reduce copper to permissible levels before release into natural waterways. Many conventional treatment methods are available such as coagulation, electrochemical, flocculation, ion exchange, precipitation, and reverse osmosis (AWWA, 2011; Salman et al., 2015). Unfortunately, these methods may be impractical or cost-prohibitive for certain situations and some marginalized industries.

This underserviced gap in wastewater treatment has generated strong interest in recent years for identifying metal adsorbents that can be cheaply and locally sourced. Waste materials as diverse as aspen wood shavings, kudzu cuttings to wheat bran have been investigated for their metal adsorptive properties (Demirbas 2008; Gupta 2009). As a general rule, biomass adsorbents are considerably less efficient than commercially available adsorbent materials in terms of adsorbate capacity to mass ratio. The overall cost of adsorbate removal is lower but the volume of adsorbent material may be excessive and cumbersome to convenient disposal. A compromise between these two priorities may be the use of facile surface modifications to increase adsorbate capacity while maintaining economy.

This study has chosen to survey prospective low-cost surface modification techniques for use with waste eggshells. Eggshells are a by-product of both household and industrial food production with few alternative uses. Eggshells are well-suited for metal sequestration due to their primarily mineral composition (93%), alkalinity, strong mechanical properties, and resistance to degradation (Guru and Dash 2014). Eggshells have been studied for their adsorption capacity of many metals including arsenic, cadmium, chromium, copper, iron, and lead. (Yeddou and Bensmaili 2007; Oke 2008; Ahmad 2012). Ahmad (2012) measured eggshell’s capacity for copper adsorption to be 2.0 mg g⁻¹. Vijayaraghavan (2005) measured
the maximum capacity as 5.03 mg g\(^{-1}\) while previous work by the author has measured a similarly low 2.6 mg g\(^{-1}\) (Hess unpublished).

Due to its low adsorption capacity but ideal physical properties, surface modifications were chosen that used the eggshell particle as a base to layer on more effective adsorbents that lack stable mechanical properties. Iron oxide, magnesium oxide, and crosslinked tannins were evaluated for use on eggshells. Iron oxides are commonly used as flocculants in municipal drinking water treatment and have a high affinity for metal ions due to its ability to exchange ions with both anions and cations. It is not well-suited for use as an adsorbent in its hydrated state, however, due to its bulky amorphous gel structure. Iron oxide physical properties can be improved by coating onto substrate materials such as filtration sand or as in this study, eggshell particles (Benjamin 1996). Similarly, manganese oxides are commonly coated onto sand substrates for use in metal removal from drinking water (Fan and Anderson 2005). Tannins are high-molecular weight polyphenols with strong metal binding properties. They are often the responsible metal removing component in agricultural waste biomass adsorbents. Extracted or in native biomass, tannins are prone to solubilizing in solution. Immobilization onto a stable substrate can be carried out through the use of a cross-linking agent such as formaldehyde or glutaraldehyde (Yurtsever and Sengil 2009).

The objective of this study was to evaluate the sorption capacity of potential surface modifying agents, iron oxide, manganese oxide, and cross-linked tannins applied onto an eggshell substrate for the removal of copper.

4.2 Materials & Methods

4.2.1 Materials

Copper stock solution (1000 mg L\(^{-1}\)) was prepared by dissolving 99.999% purity elemental copper (Sigma-Aldrich) in nitric acid and diluting with ultra-pure water. All other chemicals and solvents were purchased from Fisher Scientific (Fairlawn, NJ) and were of ACS grade. Commercial eggshells produced in the state of North Carolina were collected from local grocery stores. Inner contents were removed and the eggshell and attached membranes were thoroughly washed in deionized water. Eggshells were dried at 50°C and ground to a uniform size with laboratory mill fitted with a 1mm screen. The final particles were then washed three times with deionized water to remove fine dust and stray
contaminants. Washed particles were dried at 50°C for 24 hours and stored until use in a desiccator.

4.2.2 Iron Oxide Coated Eggshell

Eggshells were modified using methods adapted from Chen (2016), Khaodhiar (2000), and Pokhrel (2008) as follows: A 50mL supersaturated solution of FeCl₃ was mixed with continuous stirring and the pH adjusted to 11.0 by addition of NaOH pellets. The slurry was then allowed to react for three hours. The resulting slurry was incorporated onto ground eggshells to achieve “wetness”, uniformly coated in the red-brown slurry. The coated eggshells were dried at 70°C for 24 hours and then washed with deionized water until the pH of the water returned to neutral and ran clear. The final orange-colored eggshells were dried at 70°C overnight and stored in a desiccator until use.

4.2.3 Manganese Oxide Coated Eggshell

Method modified from Fan and Anderson (2005). A 20mL supersaturated solution of Mn(NO₃)₄ was mixed with continuous stirring. Next, the slurry was incorporated onto 20g ground eggshells (1mm) to achieve “wetness”. The eggshells were dried at 70°C for 24 hours and washed with deionized water until the pH of the water returned to neutral and ran clear. The final light yellow-tinted eggshells were dried at 70°C overnight and stored until use.

4.2.4 Phenolic Resin Coated Eggshell

Tannin extraction was carried out following method by Massie (2015). A 200g portion of peanut skins were extracted with 70% (v/v) ethanol in water solution at a 1:5 ratio. The resulting polyphenolic extraction was a deep red-wine color. The polyphenol extraction was acidified to a pH of 2 with HCl and 37% formaldehyde was added drop-wise until a gel precipitant formed. Precipitate was separated from the supernatant liquid and mixed with 20g eggshell. The gel was annealed to the eggshell surface by heating to 65°C until the ethanolic content evaporated to dryness. The coated eggshells were washed with deionized water to remove excess unbound tannins. The final red-brown eggshells were air-dried overnight.

4.2.5 Loading Capacity Determination

Adsorption experiments were conducted under isothermal conditions at room temperature (20°C). The effect of initial adsorbate concentration was investigated at varying concentrations (0-120 mg L⁻¹). An accurately measured 0.5 g portion of selected adsorbent
material was added to each 50 mL aliquot. Adsorbent materials were equilibrated for 72 hours under constant agitation (350 rpm) to facilitate mass transport of metal ions. Final equilibrium concentrations of Cu were measured by flame atomic absorption spectrophotometry using ASTM standard method D1688 (1995). Experiments were carried out in triplicate and the results averaged for analysis. The amount of Cu adsorbed was determined via equation (4.1):

\[ Q = \frac{(c_o - c_{eq})v}{M} \]  

(4.1)

where \( Q \) is the adsorption loading capacity (mg g\(^{-1}\)), \( c_o \) is the concentration of Cu at \( t = 0 \) (mg L\(^{-1}\)), and \( c_{eq} \) is the concentration of Cu at equilibrium (mg L\(^{-1}\)), \( V \) is the volume of the solution (L), and \( M \) is the mass of the adsorbent (g). The data collected from the experiments were fit to equilibrium adsorption isotherms listed in Table 4.1.

<table>
<thead>
<tr>
<th>Model</th>
<th>Eqn (#)</th>
<th>Equations</th>
<th>Fitted Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir[^a]</td>
<td>(4.2)</td>
<td>( Q = Q_{max} \frac{bC}{1 + bC} )</td>
<td>( b ) (L mg(^{-1})) ( Q_{max} ) (mg g(^{-1}))</td>
</tr>
<tr>
<td>Freundlich[^b]</td>
<td>(4.3)</td>
<td>( Q = k_fC^n )</td>
<td>( n ) ( k_f ) (L mg(^{-1}))</td>
</tr>
</tbody>
</table>

\[^{a}\] \( Q_{max} \) is the maximum loading capacity (mg g\(^{-1}\)); \( b \) Langmuir rate constant (L mg\(^{-1}\))

\[^{b}\] \( k_f \) is the Freundlich rate constant (L mg\(^{-1}\)); \( n \) is an affinity term

### 4.3 Results & Discussion

#### 4.3.1. Iron and Manganese Oxide Modified Eggshell

Mineral oxides have been extensively studied for their adsorptive properties to understand their role in the partitioning of free ion species in natural soil and water systems (Gao and Mucci 2003). In neutral pH soil, oxide surfaces adsorb nearly all free copper ions and are an important sink for other dissolved ions as well (Khaodhiar 2000). Mineral oxides
are commonly used in conventional drinking water treatment. Iron oxides are formed to coagulate influent suspended particles to reduce turbidity. Freshly formed hydrous oxides are also capable of co-precipitating other free metal ions and possess a high ion exchange capacity for both cations and anions (Karthikeyan 1997; Benjamin 1996). Adsorption of metal ions, however, is not a common use of hydrous mineral oxides in water treatment due to its poor mechanical properties and bulky floc structure (Benjamin 1996).

Use of mineral oxides for its adsorptive characteristics has focused on the creation of compact, mechanically stable forms by granularization or annealing onto substrate material such as activated carbon, sand, zeolite, or biomass (Fan and Anderson 2005; Ioannou 2012; Pokrel and Viraraghavan 2008; Uwamariya 2015). This study has chosen to anneal iron oxide and manganese oxide onto an eggshell substrate. Eggshells are primarily composed of calcium carbonate crystals structured by an inner protein matrix (Zhou 2017). Devi (2014) found that mixed systems of iron-oxide coated sand and calcium carbonate from limestone removed more iron and arsenic from contaminated water than coated sand alone. Extending this thought, Chen (2016) improved adsorption of phosphate and hexavalent chromium complexes by coating waste eggshell with iron oxide. Similarly, Ahmad (2012) successfully adsorbed copper from solution onto mixture of iron oxide, powdered eggshell, and iron-oxide coated eggshell. Adsorption from Ahmad’s adsorbent mixture removed 44.8 mg g⁻¹ copper, respectively 9 and 2 times more than eggshell or iron oxide alone.

This study’s results, however, did not find similar success for either iron oxide coated or manganese oxide-coated eggshells. Adsorption isotherm of iron oxide-coated eggshell versus native eggshell is shown in Figure 4.1. Isotherm data was fit to the Langmuir and Freundlich models of adsorption and resulting parameter fits of each for along with other modified eggshell results are listed in Table 4.2.
Figure 4.1 Isotherm and Langmuir model fits of iron oxide-coated eggshell versus native eggshell adsorbents (Cu 0-60mg g\(^{-1}\), pH unadjusted, 72 hour equilibrium time, 20°C)

Table 4.2 Isotherm constants for the adsorption of Cu(II) onto native and modified eggshells

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(b) (±SD)</td>
<td>(Q_{\text{max}}) (±SD)</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----------</td>
<td>-------------</td>
</tr>
<tr>
<td>Eggshell</td>
<td>0.381 (0.043)</td>
<td>2.7 (0.3)</td>
</tr>
<tr>
<td>Fe Oxide Coated Eggshell</td>
<td>0.938 (0.240)</td>
<td>1.7 (0.1)</td>
</tr>
<tr>
<td>Mn Oxide Coated Eggshell</td>
<td>0.344 (0.385)</td>
<td>1.2 (0.1)</td>
</tr>
<tr>
<td>Tannin Coated Eggshell</td>
<td>0.852 (0.413)</td>
<td>2.1 (0.1)</td>
</tr>
</tbody>
</table>

The Langmuir isotherm provided the best fit for native, iron oxide-coated and manganese oxide-coated eggshells. Unmodified eggshells had the highest maximum copper loading capacity of 2.7 (±0.3) mg g\(^{-1}\). Iron oxide-coated eggshells maximum copper loading capacity fell nearly 40% to 1.7 (±0.1) mg g\(^{-1}\). These results are contrary to previous findings of Chen (2016) and Ahmad (2012) but may be the results of two notable differences between
this study and the previously cited. Chen (2016) used iron-modified eggshells to adsorb phosphate anions and As(III), which forms a negatively charged complex in aqueous solution. Coating with iron oxide resulted in round a three-fold increase in the adsorption of each by increasing the surface area and number of protonated hydroxyl groups in acidic solution. This study was carried out at a similar acidic pH range which likely resulted in electrostatic repulsion between the positively-charged adsorbent surface and copper cations. Ahmad (2012) and Devi (2014), however, found that the presence of calcium carbonate increased adsorption at slightly higher pH ranges (6-7) closer to the hydrolysis point of each target metal ion (p$_{ka}$ Cu 7.5, Fe 9.4) but below the expected zero-point charge of the adsorbent material (7.9-8.9). These studies contained physically separate mixtures of iron oxide and calcium carbonate. As stated by Devi, calcium carbonate neutralizes acidity in solution allowing the hydrolysis of free metal ions into less soluble species that precipitate on the adsorbent surface. Therefore, chemically bonding a layer of iron oxide onto the eggshell surface may act in three ways to reduce that adsorption of cations: (1) create an electrochemically unfavorable surface and (2) prevent the dissolution of calcium carbonate that enhances metal precipitation onto the iron oxide surface and likewise (3) prevent metal ions from contacting the eggshell surface where adsorption/surface precipitation would normally occur.

Similar results were found with manganese oxide-coated eggshells, the maximum copper loading capacity fell further to 1.2 (±0.1) mg g$^{-1}$. Decreased efficiency likely follows the same mechanism encountered with iron oxide modification; bonded manganese oxide is less suited as an adsorbent in the solution conditions than the native eggshell and its presence serves only to occupy binding sites and prevent copper ions from reaching the eggshell surface. Further affecting the efficacy of iron and manganese oxide amendments to eggshell is that in the facile modification method used, deposited crystal structure of the oxide is not strictly controlled. A discrete oxide top layer may not be achieved on the eggshell surface but rather a thin amorphous crystal structure of mixed hydroxide and carbonate. Crystal component and morphology of mineral oxides can possess vastly different adsorption capacities for copper as shown in Table 4.3.
Table 4.3 Variances in copper adsorption capacity by various mineral oxides.

<table>
<thead>
<tr>
<th>Study</th>
<th>Adsorbent</th>
<th>Qmax mg g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boujelben 2009</td>
<td>Naturally iron-oxide coated sand</td>
<td>2.04</td>
</tr>
<tr>
<td>Ionnou 2012</td>
<td>Geothite (α-FeOOH)</td>
<td>69</td>
</tr>
<tr>
<td>Lai 2001</td>
<td>Iron oxide coated sand</td>
<td>0.259</td>
</tr>
<tr>
<td>Zhu 2015</td>
<td>α-Fe₂O₃ coated volcanic rock</td>
<td>58.1</td>
</tr>
<tr>
<td>Shipley 2013</td>
<td>Hematite (α-Fe₂O₃) nanoparticles</td>
<td>2.34</td>
</tr>
<tr>
<td>Grover 2012</td>
<td>Hematite (α-Fe₂O₃) nanoparticles</td>
<td>26</td>
</tr>
<tr>
<td>Chen and Li 2010</td>
<td>Nano-geothite (α-FeOOH)</td>
<td>149</td>
</tr>
<tr>
<td></td>
<td>Nano-hematite (α-Fe₂O₃)</td>
<td>85</td>
</tr>
<tr>
<td>Feng 2007</td>
<td>Birnessite (K₀.₀₅MnO₂₀₁(H₂O)₀.₆₅)</td>
<td>80.6</td>
</tr>
<tr>
<td></td>
<td>Todorokite (Mg₀.₁₇MnO₂₀₉(H₂O)₀.₈₈)</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Hausmannite (MnO₁.₃₃(H₂O)₀.₁₄)</td>
<td>12</td>
</tr>
<tr>
<td>Han 2006</td>
<td>Manganese oxide coated sand</td>
<td>0.339</td>
</tr>
<tr>
<td>Zou 2006</td>
<td>Manganese oxide coated zeolitic tuff</td>
<td>4.59</td>
</tr>
</tbody>
</table>

5.3.2 Tannin-Modified Eggshells

Tannins are high molecular weight (500+ Daltons) polyphenols produced by plants (Sengil and Ozacar 2008). Tannins serve many functions within the plant; deterring predation, providing color and protection against UV radiation, and possessing antifungal and antibacterial protection (Daniel 1999, Schijlen 2004, Dixon 2005). The tannin compound is a large branched structure containing many hydroxyl groups as illustrated in Figure 4.2. This imparts a high capacity for metal adsorption through bidentate chelation of metal ions between adjacent hydroxyl groups (Yurtsever and Sengil 2009).
Figure 4.2 Example of a procyanidin condensed tannin structure.

Peanuts skins are an excellent potential source of condensed tannins for development as adsorbents as they contain 17% by weight procyanidins (Karchesy and Hemingway 1986). Furthermore, peanut skins are produced at a rate of 750,000 tons per year with a mere value of $20 per ton due to their few commercial uses (Sobolev and Cole 2003). Peanut skin tannins are easily extracted in aqueous or ethanolic solution (Nepote 2005). Being water-soluble, however, tannins must be immobilized before use as an adsorbent. This can be achieved through the use of polymerizing agents such as formaldehyde, which forms methylene (—CH₂—) and methylene ether (—CH₂-O-CH₂—) bridging structures across sacrificial hydroxyl groups. This lessens the metal chelating capacity of the tannin but forms an insoluble resin (Sengil and Ozacar 2008). This study chose to apply the resin to an eggshell substrate to form a larger particle, more mechanically favorable adsorbent. Similar adsorbents have been tested by Yong (2013) who immobilized persimmon tannin onto activated carbon and Yang (2007) who applied tannins onto duck feathers. Adsorption performances of their studies and other relevant studied of tannin resins are listed in Table 4.4. Additionally, Nasrollahzadeh (2016) demonstrated the use of polyphenols to reduce copper ion to zero-valent copper metal onto eggshells for use as a catalyst. Nasrollahzadeh (2016) was able to load 11% copper by weight onto the eggshell substrate in the presence of Orchis mascula L. leaf extract with mild heating.
### Table 4.4 Performance of cross-linked tannin adsorbents.

<table>
<thead>
<tr>
<th>Study</th>
<th>Adsorbate</th>
<th>Adsorbent</th>
<th>Qmax (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liao 2004</td>
<td>Cu(II)</td>
<td>Myrica rubra tannin - collagen fiber</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>black wattle tannin - collagen fiber</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>larch tannin - collagen fiber</td>
<td>6.3</td>
</tr>
<tr>
<td>Oo 2009</td>
<td>Cu(II)</td>
<td>mangrove tannin</td>
<td>8.78</td>
</tr>
<tr>
<td>Palma 2003</td>
<td>Cu(II)</td>
<td>Pinus radiata tannin resin</td>
<td>3.53</td>
</tr>
<tr>
<td>Sengil &amp; Ozacar 2008</td>
<td>Cu(II)</td>
<td>mimosa tannin</td>
<td>43</td>
</tr>
<tr>
<td>Sengil 2009</td>
<td>Cu(II)</td>
<td>valonia tannin gel</td>
<td>44</td>
</tr>
<tr>
<td>Sun 2011</td>
<td>Cu(II)</td>
<td>collagen-tannin resin</td>
<td>16.9</td>
</tr>
<tr>
<td>Tondi 2009</td>
<td>Cu(II)</td>
<td>mimosa/pine tannin foam</td>
<td>12</td>
</tr>
<tr>
<td>Yang 2007</td>
<td>Cu(II)</td>
<td>tannic acid modified duck feather</td>
<td>48.9</td>
</tr>
<tr>
<td>Yong 2013</td>
<td>Pb(II)</td>
<td>persimmon tannin activated carbon</td>
<td>12.4</td>
</tr>
<tr>
<td>Yurtsever &amp; Sengil 2009</td>
<td>Pb(II)</td>
<td>quebracho tannin resin</td>
<td>86.2</td>
</tr>
</tbody>
</table>

Metal adsorption capacity of tannin-based adsorbents varies largely and is dependent of a number of factors: extraction source, preparation method, chosen substrate if applicable, and metal solution conditions. The adsorbent produced in this study, peanut skin tannin-modified eggshells, performed on the low end of the range seen in literature for copper adsorption. The maximum loading capacity as determined by the best fit Langmuir model ($R^2=0.97$) was 2.1 mg g⁻¹, less than unmodified eggshell. However, it should be noted that the annealing of tannic resin of the eggshell surface changed the dominant adsorption mechanism from surface precipitation to chemisorption at active hydroxyl functional groups. This can be noted by the greater conformance of the tannin-modified eggshell to the Langmuir adsorption model versus unmodified eggshell.

Resulting low adsorption capacity of the tannin-eggshell adsorbent is likely the result of two factors; (1) poor control of cross-linking extent in the preparation method resulting in less available hydroxyl groups and (2) reliance on Ca⁺² chelation to bond the tannin resin to the eggshell surface further reducing available hydroxyl groups for free ion chelation. Albeit possessing reduced adsorption capacity, tannin-modified eggshells may have better uses in applications where divalent metal specificity is preferred or adsorbent regeneration is desired as chelated copper would be released by washing in acidic solution. Metal ions are precipitated onto unmodified eggshells with less specificity and are harder to remove for
regeneration. Further research should be devoted to controlling extent of cross-linking to increase the metal capacity of the proposed adsorbent.

4.4 Conclusions

This study attempted to improve the copper adsorption capacity of eggshells using three different facile surface modifications: iron oxide, manganese oxide, and tannins. None of the proposed modifications produced a higher adsorption capacity than the unmodified eggshell. Modification by mineral oxides interfered with the metal adsorption mechanism onto eggshells and vice versa. Modification by annealing tannins onto the eggshell substrate, slightly decreased the maximum copper adsorption capacity but increased specificity towards divalent metals and capacity for adsorbent regeneration. Further research is needed to determine preparation methods’ effect on the extent of cross-linking in the tannin resin and find the ideal balance between tannin insolubility on the eggshell surface and maximum available hydroxyl binding sites.
REFERENCES


CHAPTER FIVE: EFFECTS OF CO-OCCURRING SPECIES PRESENT IN SWINE LAGOONS ON ADSORPTION OF COPPER ON EGGSHELL

Abstract
Anthropogenic discharge of metals into water is a burgeoning environmental and public health concern. Agricultural animal production facilities release metal ions and present both chemical and financial obstacles to conventional water treatment methods. Hence, in this research, adsorbents derived from waste chicken eggshells were evaluated for performance in abating copper contamination from swine farm wastewaters. In addition, potential confounding components of swine wastewater: acetate, ammonia, and zinc were evaluated for their effect on the efficacy of eggshell adsorption performance. Maximum copper loading capacities were measured under three swine-lagoon relevant concentration levels of each co-occurring species. The selected co-occurring species were not found to be an unsurmountable barrier towards developing eggshell adsorbents as a low-cost solution for heavy meal abatement in agricultural wastewaters.

5.1 Introduction
Anthropogenic metal pollution is a burgeoning environmental and public health concern. Once released into the air, soil, and waters by human activity, metal ions are persistent contaminants that cannot be degraded or destroyed. Many transitional metals pose serious health hazards to humans or severely damage the stability of natural ecosystems (DeForest and Meyer 2015). Toxic metals are released into the environment through the wastewater of various production industries including swine farming.

Hog farms use large open-air anaerobic bio-digesters called “swine lagoons” to treat the waste of housed pigs. Swine lagoon effluent is commonly contaminated with copper due to supplemental dosing to prevent enteric pathogens in swine herds (Barker, 1996). Swine lagoons may also be concentrated in other metals originating from the animal’s feed; arsenic, cobalt, and zinc (Nicholson 1999). Unlike textile dying or metal etching industries, however, swine lagoons are concentrated in many other components as well. Swine lagoons are a potent soup of raw hog waste, nutrients, living and dead micro-organisms, and their metabolic by-products including; volatile fatty acids, acetate, ammonia, hydrogen sulfide, and methane.
Many conventional treatment methods are available to this end such as coagulation, electrochemical, flocculation, ion exchange, precipitation, and reverse osmosis (AWWA, 2011; Salman et al., 2015). However, swine lagoons are ill-suited for conventional water treatment methods due to their large footprints and low capacity for capital investment in the agricultural sector. Hence simple, suitable, and practical solutions are needed to mitigate metals from swine lagoon wastewater.

Adsorption is one such technology that is relevant and applicable for swine lagoons. Adsorption is a physico-chemical process in which contaminant molecules are concentrated on a solid surface via hydrogen and covalent bonding. Hence, there has been a great interest in recent years for identifying adsorbents for removal of metals that can be inexpensively and locally sourced.

One such possible adsorbent is chicken eggshell. Eggshells are a by-product of both household and industrial food production with few alternative uses. In the United State alone, over 100 billion eggs are produced annually (USDA NASS) resulting in about 660,000 MT of eggshells (John-Jaja 2016). Eggshells are well-suited for metal sequestration due to their primarily mineral composition (93%), alkalinity, strong mechanical properties, and resistance to degradation (Guru and Dash 2014). As a result, eggshells have been studied for their adsorption capacity of many metals including arsenic, cadmium, chromium, copper, iron, and lead. (Yeddou and Bensmaili, 2007; Oke et. al., 2008; Ahmad et. al, 2012). Flores-Cano et. al (2013) cited thermodynamic evidence that metal adsorption occurs onto eggshells via two mechanisms; reversible ion-exchange and non-reversible chemisorption and/or precipitation. Geochemical studies of analogous material, calcite, supports these proposed mechanisms (Schosseler et al., 1999). Ahmad (2012) measured eggshell’s capacity for copper adsorption to be 2.0 mg g\(^{-1}\). Vijayaraghavan (2005) measured the maximum capacity of 5.03 mg g\(^{-1}\) while previous work by the authors reported a similar adsorption capacity of 4.6 mg g\(^{-1}\) (Hess unpublished).

Most of the previous studies with eggshells to this date have been limited to pure aqueous solutions with single, binary, or rarely tertiary metal components. However, in swine lagoons, copper always co-occurs with other pollutants such as zinc, acetate, ammonia, volatile fatty acids, hydrogen sulfide, and methane. To our knowledge, there is no information on how copper adsorption occurs in presence of other commonly occurring
species in water. Studying the effects of aforementioned co-occurring compounds on the
efficacy of eggshells for mitigation of copper will uncover valuable information on the
applicability of eggshells in swine lagoons. Hence the objective of this research was to
investigate the adsorption of copper in presence of acetate, ammonia, or zinc at
concentrations relevant to swine lagoons.

5.2 Materials and Methods

5.2.1 Materials

Copper (Cu) stock solution (1000 mg L\(^{-1}\)) was prepared by dissolving 99.999% purity
elemental copper (Sigma-Aldrich) in nitric acid and diluting with ultra-pure water. All other
chemicals and solvents were purchased from Fisher Scientific (Fairlawn, NJ) and were of
ACS grade. Commercial eggshells produced in the state of North Carolina were collected
from local grocery stores. Inner contents were removed and the eggshell and attached
membranes were thoroughly washed in deionized water. Eggshells were dried at 50°C and
ground to a uniform size with laboratory mill fitted with a 1-mm screen. The final particles
were then washed three times with deionized water to remove fine dust and stray
contaminants. Washed particles were dried at 50°C for 24 hrs and stored until use in a
desiccator.

5.2.2 Loading Capacity for Copper in Deionized Water

Adsorption experiments were conducted under isothermal conditions at 25°C in a
water bath. The effect of initial copper concentration was investigated at varying
concentrations (0-150 mg L\(^{-1}\)) buffered to a pH of 5.5 using 0.1M 2-(N-morpholino)
ethanesulfonic acid (MES). An accurately measured 1.0 g portion of eggshell was added to
each 100 mL replicate. Adsorbent materials were allowed to equilibrate for 240 hours under
constant agitation (50 rpm) to facilitate mass transport of metal ions. Solution pH was
maintained by additions of 1.0N HNO\(_3\) as needed every 24 hours. Aliquots were sampled
after the appropriate equilibrium time and preserved with a 0.2 mL addition of concentrated
nitric acid until analysis. Final equilibrium concentrations of copper were measured by flame
Experiments were carried out in triplicate and the results averaged for analysis.
5.2.3 Loading Capacity for Copper in Presence of Interfering Species

Three potential interfering species that are commonly found in swine lagoon wastewater were selected; acetate, ammonia, and zinc. Adsorption experiments (0-150 mg L\(^{-1}\) Cu, pH 5.5, 1.0 g eggshell, 100 mL) were repeated under isothermal conditions (25°C) at three levels (high, medium, or low) for each species as follows: acetate (1000, 500, and 250 mg L\(^{-1}\)), ammonia (1000, 500, and 250 mg L\(^{-1}\)), and zinc (100, 50, and 25 mg L\(^{-1}\)). Adsorbent materials were allowed to equilibrate for 240 hours under constant agitation (50 rpm). Aliquots were sampled after the appropriate equilibrium time and preserved with a 0.2 mL addition of concentrated nitric acid until analysis. Untreated aliquots of varying copper concentrations were retained and analyzed to adjust for background solution effects during copper concentration measurement.

5.2.4 Analysis

Experiments were carried out in triplicate and the results averaged for analysis. The amount of Cu adsorbed was determined via equation (5.1):

\[
Q = \frac{(C_0 - C)V}{M}
\]

(5.1)

where \(Q\) is the adsorption loading capacity (mg g\(^{-1}\)), \(C_0\) is the concentration of Cu at \(t = 0\) (mg L\(^{-1}\)), and \(C\) is the concentration of Cu at equilibrium (mg L\(^{-1}\)), \(V\) is the volume of the solution (L), and \(M\) is the mass of the adsorbent (g). The data collected from the experiments were fit to equilibrium adsorption isotherms listed in Table 5.1. Data analysis was performed using Windows Excel and a software program entitled JMP Pro 10 (SAS Inst., Cary NC). Multi-linear regression has performed using the linearized Langmuir equation.
Table 5.1. Adsorption Isotherm Models Used to Evaluate Data (Zhu et. al., 2009; Worch, 2012)

<table>
<thead>
<tr>
<th>Model</th>
<th>Eqn (#)</th>
<th>Equations</th>
<th>Fitted Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir[a]</td>
<td>(5.2)</td>
<td>( Q = Q_{max} \frac{bC}{1 + bC} )</td>
<td>( Q_{max} ) (mg g(^{-1}))</td>
</tr>
<tr>
<td>Freundlich[b]</td>
<td>(5.3)</td>
<td>( Q = k_f C^n )</td>
<td>( k_f ) (L mg(^{-1}))</td>
</tr>
</tbody>
</table>

\[a\] \( Q_{max} \) is the maximum loading capacity (mg g\(^{-1}\)); \( b \) Langmuir rate constant (L mg\(^{-1}\))

\[b\] \( k_f \) is the Freundlich rate constant (L mg\(^{-1}\)); \( n \) is an affinity term

5.2.5 MINTEQ Modeling

Chemical speciation was modeled using Visual MINTEQ version 3.1 software (MINTEQ, 2013) to provide further insight. As exact lagoon conditions were logistically inconvenient to replicate, experimental conditions and anticipated lagoon conditions were both modeled for comparison. Lagoon conditions were approximated using average compound concentrations specified by the American Society of Agricultural and Biological Engineers (ASAE D384.2 MAR2005) for lagoon supernatant water with <0.5% solids as listed in Table 5.2 along with other relevant studies of lagoon supernatant. Chloride and sodium ions were designated as counter-ions to maintain neutral charge of solutions as needed. Solution pH was set to 8.0 in lagoon approximations and to 5.5 in experimental models. Solutions were modeled with adsorbent dosed at a 10mg L\(^{-1}\), specifying calcite in lieu of eggshell as a finite solid.
Table 5.2. Chemical concentrations in swine lagoon supernatant waters, <0.5% solids.

<table>
<thead>
<tr>
<th>Study</th>
<th>Concentration (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total N, P as P₂O₅, K as K₂O, Ca, Mg, Zn, Cu, Mn, Na, Fe, S</td>
</tr>
<tr>
<td>ASAE D384.2</td>
<td>575, 336, 731, 103, 55, 3.6, 2.4, 1.2, 216, --, 37</td>
</tr>
<tr>
<td>Westerman and Bicudo 2000</td>
<td>765, 80, 764, 90, 21, 0.8, 0.4, --, 166, 5.1, --</td>
</tr>
<tr>
<td>Makris 2008</td>
<td>--, 43.2, --, 58.2, 1.75</td>
</tr>
<tr>
<td>Lovahn 2009</td>
<td>916, 180, 844, 101, 22, --, 0.415, 1, 252, 10.7, 36</td>
</tr>
</tbody>
</table>

5.3 Results & Discussion

Co-occurring species present in solution may affect the metal adsorption mechanism in a various number of ways: (1) metal adsorption may be lower as additional species compete for binding sites on the adsorbent surface (2) adsorption may be prevented as species form non-adsorbing aqueous complexes with metal ions in solution (3) species may form ternary complexes at the adsorbent surface which may enhance or diminish metal adsorption or (4) additional species may have no effect on the adsorption process at all (Benjamin and Leckie 1981; Buerge-Weirich 2003; Davis and Leckie 1978). This is illustrated in Figure 5.1. Outcome of adsorption of the metal ion in the presence of additional species is dependent upon metal speciation, chemical structure of the additional species, and the effect of solution conditions on the interplay between the two (Benjamin and Leckie 1981; Izquierdo 2013). Experimental conditions were conducted at pH 5.5, just below the hydrolysis point of copper, to minimize effects of precipitation contributing to the copper uptake onto the eggshell surface. At the highest copper concentration evaluated, 98% of copper in solution would be present as a free ion and the remaining present as aqueous complexes. Effects may therefore be primarily attributed to adsorption processes. Predictive modeling was then used to identify possible complexes or effects on copper speciation in solution that may affect the adsorption process for each surveyed co-occurring species; acetate, ammonia, and zinc. The effect on maximum loading capacity at three different levels was then measured and is presented herein.
5.3.1 Effect of Acetate

Acetate (CH$_3$COO$^-$) is present in swine lagoons as a metabolic by-product of microbial growth. Loughrin (2012) reported acetate concentrations to fluctuate in swine lagoons from below limits of detection to 1370±430 mg L$^{-1}$ between warm and cool seasons. In this research, acetate concentrations up to 1000 mg L$^{-1}$ as an average between the highest and lowest reported.

Research in the field of contaminated soil remediation has shown that soluble acetate can initiate the desorption of up to 60% of adsorbed lead ions from soil particles via the preferential formation of metal-acetate complexes in aqueous solution. Desorption, however, occurred at much lower pH of 4-6 and at higher concentrations (17-59 g L$^{-1}$) than those present in swine lagoons (Shen 2001; Qiang 1994). According to modeling predictions using MINTEq for swine lagoon-like conditions with the highest tested level of acetate (1000mg L$^{-1}$), copper-acetate complexes would only account for approximately 2.2% of all copper species present by mass. This would primarily be in the form of Cu-Acetate$^+$ as shown in Figure 5.2. Legros (2010) performed more in-depth modeling of copper speciation in swine...
lagoons using micro X-ray fluorescence spectroscopy (μXRF) and synchrotron-based X-ray absorption spectroscopy (XAS) of actual pig slurry. Legros measured 4% of copper exists as Cu-acetate complexes overall but may be enriched up to 28% of present mass in smaller particle size fractions as those encountered in supernatant waters. Although the reduced charge of the Cu-acetate complex would reduce electrostatic attraction to the adsorbent surface, the complex would bind more easily to single hydroxyl (OH\(^-\)) binding sites on the adsorbent surface. The complex would still likely adsorb to some extent as evidenced by Shen et al. (2001) who observed complexed Pb-acetate\(^+\) re-adsorbing to soil particle surfaces upon equilibrium. Decreased adsorption of lead and zinc onto montmorillonite clay in the presence of acetate has been observed as well (Ghayaza et al., 2011).

Figure 5.2. Relative abundance of copper-acetate complexes by molar ratio of acetate to copper. (a) Lagoon conditions: pH 8, Cu 2.4 mg L\(^{-1}\), acetate 0-1000mg L\(^{-1}\) (b) Experimental conditions: pH 5.5, Cu 150 mg L\(^{-1}\), acetate 0-1000mg L\(^{-1}\).

Our experimental results corroborate this prediction. Copper was adsorbed to eggshell under low, medium, and high acetate concentrations versus control samples (no acetate). Adsorption isotherms were fit to both the Langmuir and Freundlich models as shown in Figure 1 and model parameters listed in Table 3. The maximum loading capacity (Q\(_{\text{max}}\)) predicted by the Langmuir model (R\(^2\)>0.99) matched experimental values and was a better fit than the Freundlich model (R\(^2\)= 0.82-0.96). Effect on Langmuir maximum loading capacity only differed from the no acetate control at the highest dosage level (1000 mg L\(^{-1}\)).
Multiple linear regression of the data, however, using the Langmuir model resulted in
predictive equation ($R^2 = 0.97$) as below (equation 5.4):

$$
C_{eq}/Q_{eq} = 1.0123 + 0.00048*\text{Acetate} + 0.2130*C_{eq} + [(\text{Acetate} - 440.47) (0.0000795*(C_{eq} - 51.47))] \tag{5.4}
$$

Multilinear analysis of the data indicated an interaction effect (p-value = 0.02) between copper concentration and acetate concentration. The inhibitory effect of acetate concentration on adsorption, especially above 500 mg L$^{-1}$, became more pronounced as copper concentrations increased. Decrease in adsorption was likely the effect of complexation of copper in solution with acetate. As also observed by Shen et al. (2001), charged metal-acetate complexes adsorb to adsorbent surfaces (Surface-Cu-Acetate) at a reduced efficiency. Given the modest decrease in maximum loading capacity only at the highest level tested and the seasonally low concentration of acetate in swine lagoons during warm months, co-occurring acetate will not present a significant hurdle to eggshell adsorbent application.

Table 5.3. Isotherm constants for the adsorption of Cu(II) onto eggshells at varying acetate concentrations.

<table>
<thead>
<tr>
<th>Acetate Level</th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$ L mg$^{-1}$</td>
<td>$n$</td>
</tr>
<tr>
<td>No (0 mg L$^{-1}$)</td>
<td>1.42 (0.42)</td>
<td>0.26 (0.08)</td>
</tr>
<tr>
<td>Low (250 mg L$^{-1}$)</td>
<td>1.05 (0.17)</td>
<td>0.32 (0.04)</td>
</tr>
<tr>
<td>Medium (500 mg L$^{-1}$)</td>
<td>0.98 (0.17)</td>
<td>0.35 (0.04)</td>
</tr>
<tr>
<td>High (1000 mg L$^{-1}$)</td>
<td>1.20 (0.20)</td>
<td>0.22 (0.04)</td>
</tr>
</tbody>
</table>

$^a$ As determined by pairwise student’s t-test at 95% confidence interval.
5.3.2. Effect of Ammonia

Decomposition of protein in organic material in swine lagoons releases nitrogen as ammonia (Lahav 2013). Depending on swine waste loading rate and water temperature, lagoon supernatant waters may contain 300-1000 mg L\(^{-1}\) total elemental nitrogen (Lovahn 2009). Up to 85% of all nitrogen will be dissolved as protonated (pKa = 9.2) ammonium (NH\(_4^+\)) in the lagoon (ASAE D384.2 2005, Lovahn 2009, Westerman and Bicudo 2000).

Luo and Huang (1993) found that the presence of ammonia and its resulting complexation with copper to form Cu(NH\(_3\))\(_x\)\(^{+2}\) complexes suppressed adsorption onto metal hydroxides. Copper may complex with up to four ammonia ligands with each complex possessing a different binding strength to the potential adsorbent. Luo and Huang found metal hydroxides adsorbed more copper from copper-ammonia solutions with an average ligand number of two than those with higher or lower average ligands. A possible reason for this trend is that ammonia is a stronger ligand than water molecules and destabilizes the hydration sphere around the copper ion. More than two ammonia ligands, however, likely causes steric hindrance as they occupy more equatorial positions around the copper ion center. Total ammonia concentration and speciation, in fact, was the controlling factor for adsorption across three different adsorbents. Crawford (1997) found similar results for...
adsorption of Zn(II) and Ni(II) onto hydrous iron(III) oxide and hydrous chromium(III) oxide. However, only certain metals form ammine complexes. Kinetics of complexation is an additional factor as well. Crawford found that Cr(III) removal was completely unaffected by ammonia because Cr(III) formed ammine complexes slower than the adsorption reaction occurred.

Predictive modeling of the lagoon using MintEq estimated that 88% of copper would be associated with ammonia. This is likely an overprediction as the model does not account for the ready biological reduction of Cu(II) species to Cu(I) within the lagoon. Legros (2010) predicted 96% of all copper in pig slurry to be present as chalcocite, Cu(I)S₂, with ammine complexes possible only at higher pH (>8.8). Earlier studies by Robel and Ross (1975) and Kornegay (1976) are congruent with Legros’ measurements. Legros’ model is based on anaerobic slurry (8.0% solids) conditions rather than the more oxygenated top 18” supernatant (<0.5% solids) level of the swine lagoon where adsorbent material would likely be dispersed (Lovahn 2009). Using a different methodology, L’Herroux (1997) showed that post-oxidative treatment 66% of copper was associated with organic ligands such as ammines. Lacking comprehensive measurements of the exact speciation of Cu due to oxidation in the supernatant water, a predictive model for experimental conditions only are presented in Figure 5.4.

![Figure 5.4. Relative abundance of copper-ammonia complexes by molar ratio of ammonia to copper (pH 5.5, Cu 150 mg L⁻¹, NH₄⁺ 0-1000 mg L⁻¹).](image)
By technical necessity, acidic experimental conditions were utilized to maintain constant copper and ammonia concentrations. This created fairly low amounts of copper-ammine complexes (<10%) with nearly the entirety associated with just one ligand, Cu(NH$_3$)$_{2}^+$. As found prior, copper adsorption onto eggshell was best fit by the Langmuir model ($R^2 > 0.99$). Ammonia concentration had a positive effect on total loading capacity ($p = 0.045$) but only the highest dose level Langmuir maximum loading capacity differed significantly from the control. Multiple linear regression of the data using the Langmuir model gave predictive equation ($R^2 = 0.99$):

$$C_{eq}/Q_{eq} = 2.8562 + 0.00085 \times \text{Ammonia} + 0.1968 \times C_{eq} + [(\text{Ammonia} - 456.52)(-0.000037(C_{eq} - 48.93))]$$ (5)

Our research suggests that the formation of ternary complexes may enhance the adsorption of copper ions onto the calcium carbonate eggshell surface in the higher concentration range tested in this research. Luo and Huang (1993) observed a peak adsorption in copper-ammonia solutions when the average ligand number was 2.0. The experiments conditions in this research had an average ligand number of 0-1.0 on the rising side of the trend. The speciation and relative abundance of copper-ammine complexation in swine lagoons could not be predicted by the selected modeling method and has not been directly measured to our knowledge. Experimentally the overall mass of copper associated in ammine complexation was low (<10%) and a statistically observable change (+30%) in loading capacity occurred only at the highest tested ammonia concentration. Given the likely low concentration of ammine-copper concentration in swine lagoons, ammonia would have little effect on the overall adsorption process in the lagoon matrix.
Figure 5.5. (a) Adsorption isotherms of copper onto waste eggshell at varied levels of ammonia. (b) Langmuir maximum loading capacity (Qmax) by ammonia concentration. (c) Langmuir rate constant (b) as affected by ammonia concentration.

Table 5.4. Isotherm constants for the adsorption of Cu(II) onto eggshells at varying ammonia concentrations.

<table>
<thead>
<tr>
<th>Ammonia Level</th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$ L mg$^{-1}$ (±SE)</td>
<td>$n$ (±SE)</td>
</tr>
<tr>
<td>No (0 mg L$^{-1}$)</td>
<td>1.42 (0.42)</td>
<td>0.26 (0.08)</td>
</tr>
<tr>
<td>Low (250 mg L$^{-1}$)</td>
<td>1.15 (0.17)</td>
<td>0.31 (0.04)</td>
</tr>
<tr>
<td>Medium (500 mg L$^{-1}$)</td>
<td>1.57 (0.25)</td>
<td>0.23 (0.04)</td>
</tr>
<tr>
<td>High (1000 mg L$^{-1}$)</td>
<td>1.04 (0.16)</td>
<td>0.35 (0.04)</td>
</tr>
</tbody>
</table>

a As determined by pairwise student’s t-test at 95% confidence interval.
5.3.3 Effect of Zinc

Elevated zinc levels occur in swine lagoons due to supplemental dosing of zinc oxide as a diarrhea preventative. Zinc supplementation is most common for nursery pig stocks (Bolan 2004; Nicholson 1999). Zinc levels in the lagoon, therefore, are dependent on the stock of the hog farm. Concentrations cited in literature are generally in the same order of magnitude as present copper concentrations (Table 5.2).

Co-occurring metals affect adsorption of the target metal depending on their comparative affinities to the adsorbent binding sites. Light electrolytic metals such as calcium, sodium, and magnesium do not compete for binding sites of target heavy metals (Sawalha 2009). Competitive effects between heavy metals is dependent on the adsorption mechanism. Adsorption of copper onto calcium carbonate surfaces are theorized to occur as follows: (a) dissolution of the calcite surface releases carbonate ions into solution resulting in the rapid stripping of the hydration sphere to form Cu(CO$_3$)$_2^{+2}$ complexes (b) adsorption at the surface and formation of monodentate complexes of square-planar and/or square-pyramidal coordination. This likely occurs at kinks and steps in the dissolved and reformed calcite surface and thus (c) slow incorporation of the smaller copper ion into the calcium crystal lattice via distortion of octahedral carbonate coordination geometry. (Elzinga and Reeder, 2002; Schosseler et al., 1999) as illustrated in Figure 5.6. Schosseler et al. (1999) theorized that the distortion of the crystal lattice by incorporated copper ions results in inhibition of further dissolution/growth of the calcite mineral and thus the adsorption/incorporation process is self-limiting. Increasing metal concentration in solution, however, may result in surface precipitation and the formation of a distinct precipitant phase covering the carbonate surface (Shosseler et al., 1999). Elzinga and Reeder (2002) found that copper and zinc follow similar adsorption mechanisms onto the surface of calcium carbonate minerals and thus are likely to compete for binding sites. Zinc, however, does that as readily replace calcium ions in the crystal lattice due to its propensity to form tetrahedral rather than octahedral complexes (Shosseler et. al, 1999).
As with acetate and ammonia, copper adsorption onto eggshell in the presence of zinc was best fit by the Langmuir model ($R^2 > 0.97$). Increasing zinc concentration showed deviation away from agreement to the Langmuir model as evidenced by decreasing coefficient of determination values that did not occur with the other co-occurring species. This trend may suggest a change in copper removal mechanism. Zinc concentration also did not have a statistically significant effect on total loading capacity ($p = 0.149$) in multiple linear regression analysis. The highest tested zinc concentration (100mg L$^{-1}$) showed a large jump in total loading capacity as well as a clear deviation away from the characteristic Langmuir adsorption isotherm shape as compared to the control. These two factors suggest the two metals precipitated onto the adsorbent surface or out of solution.

However, this was likely an experimental artifact and is unlikely to occur in the swine lagoon due to the low zinc and copper concentrations present. Therefore, multiple linear regression was re-analyzed excluding the 100 mg L$^{-1}$ zinc data set. At 0-50 mg L$^{-1}$ zinc concentration has a significant ($p < 0.0001$) negative effect on loading capacity. The model provided a predictive equation ($R^2 = 0.98$) as shown below (equation 5.5):

$$\frac{C_{eq}}{Q_{eq}} = 1.2042 + 0.1443*\text{Zinc} + 0.2373*C_{eq} + [(\text{Zinc} - 26.47)(0.000706*(C_{eq} - 55.70))]$$ (5.5)
Table 5.5. Isotherm constants for the adsorption of Cu(II) onto eggshells at varying zinc concentrations.

<table>
<thead>
<tr>
<th>Zinc Level</th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$ L mg$^{-1}$</td>
<td>$n$</td>
</tr>
<tr>
<td>No (0 mg L$^{-1}$)</td>
<td>1.42 (0.42)</td>
<td>0.26 (0.08)</td>
</tr>
<tr>
<td>Low (25 mg L$^{-1}$)</td>
<td>0.64 (0.08)</td>
<td>0.37 (0.03)</td>
</tr>
<tr>
<td>Medium (50 mg L$^{-1}$)</td>
<td>0.63 (0.21)</td>
<td>0.34 (0.07)</td>
</tr>
<tr>
<td>High (100 mg L$^{-1}$)</td>
<td>1.17 (0.24)</td>
<td>0.33 (0.05)</td>
</tr>
</tbody>
</table>

As determined by pairwise student’s t-test at 95% confidence interval.

Figure 5.7. (a) Adsorption isotherms of copper onto waste eggshell at varied levels of zinc. (b) Langmuir maximum loading capacity ($Q_{max}$) by zinc concentration. (c) Langmuir rate constant ($b$) as affected by zinc concentration.

5.4 Conclusions

Swine lagoons are a complex matrix that poses many challenges to implementing conventional water treatment methods. In this research, three representative contaminants, acetate, ammonia, and zinc were tested for effects on adsorption of copper on waste
eggshells. At the highest relevant concentrations, adsorption was negatively affected (<20%) by acetate and zinc. Ammonia was shown to enhance copper adsorption (30%) at the highest dosed level presumably by formation of ternary complexes. Results show that individually co-occurring organic species and zinc are not a barrier to developing eggshell adsorbents for further use in swine lagoons or mixed industrial/agricultural effluents. Moving forward, further research on synergistic effects of co-occurring species is suggested.

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APPENDIX: PRECIPITATION MODELS

Experimental conditions were conducted at pH 5.5, just below the hydrolysis point of copper, to minimize effects of precipitation contributing to the copper uptake onto the eggshell surface. At the highest copper concentration evaluated, 98% of copper in solution would be present as a free ion and the remaining present as aqueous complexes. This is illustrated in Figure A1 in which the most saturated species, tenorite (c) just breaks into positive saturation at the given pH. Furthermore, inclusion of increasing amounts of organic ammonium and acetate decrease precipitation of copper ions by forming aqueous complexes in solution (Figure A2 and A3). Inclusion of zinc also decreases the saturation of copper ions slightly (Figure A4). Unfortunately, the Minteq program does not include Cu,Zn mixed carbonate minerals in its database such as rosasite ((Cu,Zn)$_2$(CO$_3$)(OH)$_2$) or aurichalcite ((Zn,Cu)$_5$(CO$_3$)$_2$(OH)$_6$) so possible coprecipitant products cannot be modeled.
Figure A1. Precipitation model of 150 mg L$^{-1}$ copper in deionized water by varying pH.

Figure A2. Precipitation model of copper (30, 80, 150 mg L$^{-1}$) by varying acetate concentration (0-1000 mg L$^{-1}$).
Figure A3. Precipitation model of copper (30, 80, 150 mg L$^{-1}$) by varying ammonia concentration (0-1000 mg L$^{-1}$).

Figure A4. Precipitation model of copper (30, 80, 150 mg L$^{-1}$) by varying zinc concentration (0-100 mg L$^{-1}$)
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CHAPTER SIX: CONCLUSIONS AND FUTURE WORK

The goal of this research was to employ adsorption to mitigate heavy metals from swine lagoons via agricultural wastes. Specifically, this goal was defined by the following objectives: (A) Survey a selection of NC waste biomasses for copper adsorption efficiency. (B) Characterize one NC waste biomass to elucidate copper adsorption mechanisms. (C) Attempt modification of the biomass adsorbent surface to increase copper adsorption efficiency (D) Evaluate the adsorbent in the swine lagoon matrix and define limiting factors present within the lagoon. The findings of these studies are defined below:

1) Findings from studies to accomplish objective A:
   • Of the surveyed NC agricultural wastes, eggshells had the highest copper loading capacity (2.60 mg g\(^{-1}\)) versus peanut hulls (0.60 mg g\(^{-1}\)) and chicken feathers (0 mg g\(^{-1}\)) under similar conditions (Cu 0-80mg L\(^{-1}\), 72 hr, unadjusted pH).

2) Findings from studies to accomplish objective B:
   • Adsorption of copper followed a second-order kinetic model with an adsorption capacity of 4.3 mg g\(^{-1}\) (20°C, 240hr, unadjusted pH).
   • Eggshell adsorption was found to be a favorable process with an activation energy of approximately 27 to 29 kJ mol\(^{-1}\) and followed similar mechanisms as its calcite analog.
   • Removal mechanism of copper from solution by eggshell changing ratio between adsorption and micro-precipitation onto the eggshell surface dependent on solution conditions.
   • Copper adsorption can be improved at elevated temperatures and occurs best at a pH of 6. Adsorption does not occur above a pH of 7.

3) Findings from studies to accomplish objective C:
   • Facile surface modifications to deposit iron oxides, manganese oxides, and tannin resins onto the eggshell surface were not successful and did not achieve maximum copper loading capacities higher than untreated eggshells.

4) Findings from studies to accomplish objective D:
   • According to the Langmuir model, eggshells have a maximum copper loading capacity of 4.6 mg g\(^{-1}\) at pH 5.5, 25°C.
• Zinc has an inhibitory effect on eggshell copper adsorption.
• Ammonia and acetate do not detrimentally affect adsorption in the concentration ranges relevant to swine lagoons.

From this data, it can be concluded that solution pH is the greatest hurdle to implementing eggshell adsorbents in swine lagoon. For successful implementation, the adsorbent material would be immersed in the lagoon fluid, adsorb copper, and then extracted from the lagoon for disposal outside of the geographic region used for typical lagoon waste disposal. Precipitation or settling of the adsorbent material into the sludge layer of the lagoon is not desirable as it creates a copper-rich product which is limited in transport range. The adsorbent material is only viable if its use ultimately reduces the lifetime copper loading of the constrained geographic area surrounding high-density hog production. For eggshell adsorbents, copper precipitation out of solution occurs at a faster rate than adsorption above a pH of 7. Therefore, eggshell adsorbents have low viability for application in swine lagoons without pH adjustment. This is logistically infeasible due to the large volume of the swine lagoon, its high buffering capacity, and the resulting chemical cost to lower lagoon effluent pH.

The future use of adsorption technology for copper remediation of the swine lagoon is challenged by a number of constraints encountered in this study: (1) low availability of aqueous copper ions in swine lagoon effluent (4-28%) which are mostly complexed with acetate ligands that decrease adsorption capacity (2) adsorption must occur in high pH solution and adsorption kinetics must exceed the rate of copper precipitation out of bulk solution (3) adsorbent material must be mechanically stable for submersion, retrieval, drying, and transport while also being efficient, locally available in large volumes, and cheap. Selecting a potential adsorbent material to surmount all of the listed challenges will be extremely difficult if not impossible.

Eggshells may be better implemented as an immobilizing agent in fields where lagoon effluent are disposed. Eggshells have strong buffering capacities and can maintain high soil pH levels to prevent metal ion from solubilizing in rainfall. Lee (2013) found that a 5% eggshell inclusion rate into the soil reduced leaching of cadmium and lead even when washed with acidic rain. Ashrafi (2015) found that 5% eggshell reduced leachability of lead,
cadmium, and zinc even in already alkaline soil and encouraged mineralization of metal ions to residual and carbonate-bound fractions. Similarly, eggshell could be incorporated into riparian buffers to prevent run-off of metal species into surrounding water systems. This implementation scheme addresses water pollution concerns but does not consider long-term toxicity effects of metal concentrations in soil as addressed by Mcbride and Cai (2016), who found that even after “aging” conversion of metals to less labile species phytotoxic effects persisted in soybean crops. Systemic solutions to copper pollution from the swine industry should be considered for their efficiency versus economic merit; more controlled dosage or elimination of therapeutical copper dosing in pig populations and/or better establishment of lifetime soil loading limits of copper.

Despite challenges in implementation in swine lagoons, eggshells are well-suited adsorbents for mildly acidic industrial waste effluents and are resistant to the presence of co-occurring species. Some proposed future work to further this direction are listed below:

1. Further work is needed to assess any synergistic effects of multiple present species and to establish an affinity series of metals for eggshell adsorbents would also be helpful to establish best use scenarios. Response surface methodology would be an expedient method to determine the cumulative effect of several co-occurring species.

2. Copper uptake onto eggshell is likely a changing ratio of (1) adsorption by carbonate groups and subsequent integration into the mineral crystal lattice and (2) surface precipitation as a discrete layer over the eggshell surface. Surface characterization methods used in this study could not confirm the exact speciation of loaded copper. X-ray powder diffraction (XRD) should be used to confirm exact uptake mechanisms and if the mechanism changes through the adsorption process as might be inferred from the two-phase kinetics shown in this study.

3. Due to the mechanism of copper adsorption onto the eggshell surface, deposited copper is non-labile and suited for long-term storage of copper. Eggshell adsorbent, however, is not reusable and therefore other renewable sources of biogenic CaCO₃ such as oyster shells should be explored for their adsorptive properties to ensure a large and constant volume of available adsorbent material.
REFERENCES

