Phosphate recovery from water using cellulose enhanced magnesium carbonate pellets

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Abstract

Phosphorus is an essential and limited nutrient that is supplied by a depleting resource, mineral phosphate rock. Eutrophication is occurring in many water bodies which provides an opportunity to recover this nutrient from water. One method of recovery is through adsorption; this study focused on fabricating a porous and granular adsorptive material for the removal and recovery of phosphate. Magnesium carbonate was combined with cellulose in varying weight ratios (0, 5, 10, 15, 20%) to synthesize pellets, which were then calcined to increase internal surface area. Physiochemical properties such as surface area, thermal degradation, surface morphology, elemental composition, and crystal structure of the materials were characterized using Brunauer, Emmett and Teller (BET) surface area analysis, thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The pellet proved to be uniform in composition and an increase in BET surface area correlated with an increase in cellulose content until pellet stability was lost. Phosphate adsorption using the pellets was studied via batch kinetics and sorption isotherms. The *pseudo*-second-order kinetics model fit best suggesting that the adsorption occurring was chemisorption. The isotherm model that fit best was the Langmuir isotherm, which showed that the maximum equilibrium adsorption capacity increased with an increase in cellulose content between 10% and 20%. The average adsorption capacity achieved in the triplicate isotherm study was 96.4 mg g^{-1} for pellets synthesized with 15% cellulose. Desorption of the phosphate back into solution was studied using solutions that changed pH and only up to 4% was desorbed. Overall, using cellulose and subsequent calcination created additional internal surface area for adsorption of phosphate and suggests that granular materials can be modified for efficient removal from water and need to be studied further for recovery of phosphate post adsorption.

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List of Symbols and Abbreviations

ADP	Adenosine diphosphate
ATP	Adenosine triphosphate
BET	Brunauer, Emmett, and Teller
C	Carbon
Ca	Calcium
c_o	Initial adsorbate concentration
DAP	Diammonium phosphate
DNA	Deoxyribonucleic acid
E33	Bayoxide® E33 Adsorptive Media
EBPR	Enhanced biological phosphorus removal
EDS	Energy-dispersive X-ray spectroscopy
Fe	Iron
GAOs	Glycogen accumulating organisms
HABs	Harmful algal blooms
HCl	Hydrochloric acid
HPO_4^{2-}	Hydrogen phosphate
IJC	International Joint Commission
K	Potassium
k_1	*Pseudo*-first-order rate constant
k_2	*Pseudo*-second-order rate constant
k_f	Freundlich adsorbent adsorption capacity
k_L	Langmuir constant
La	Lanthanum
LDH	Layered double hydroxide
Mg	Magnesium
$MgCl_2$	Magnesium chloride
$MgCO_3$	Magnesium carbonate
MgO	Magnesium oxide
MgOH	Magnesium hydroxide
$MgSO_4$	Magnesium sulfate
N	Nitrogen
NaOH	Sodium hydroxide
NH_4^+	Ammonium
O	Oxygen
P	Phosphorus
P_2O_5	Phosphorus pentoxide
PAOs	Poly-phosphate accumulating organisms
pH	$-\log[H^+]$
PHA	Polyhydroxyalkanoates
PO_2	Phosphorus dioxide
PO_3	Phosphorus trioxide
PO_4^{3-}	Phosphate
q_{max}	Langmuir maximum sorbate amount per unit mass of adsorbent

RNA	Ribonucleic acid
rpm	Revolutions per minute
SEM	Scanning electron microscopy
Tg	Teragram (10^{12} g)
TGA	Thermogravimetric analysis
USEPA/EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
XRD	X-ray diffraction

Chapter 1: Introduction

1.1 Literature Review

1.1.1 Background

The story of phosphorus (P) began with the search for the philosopher's stone that led to Hennig Brandt[1], or Henning Brand[2,3] depending on the source, discovering the elemental form of phosphorus in 1669. Brandt was attempting to find the secret to gold but instead found a glow in the dark material that emits a green glow when reacting with atmospheric oxygen[1–3]. Daniel Kraft piggybacked off of this discovery in 1675. The material was named phosphorus from Greek to mean 'light bearer'[1]. Johann Kunckel made P in 1676[1] followed by Robert Boyle in 1680[1–3] but it wasn't until 1780 that Antoine Lavoisier recognized it as an element[1]. Brandt had created this material from urine but it was discovered later that other parts of the body were much more abundant sources with 0.7 kg of P stored in bones and teeth as well as soft tissue and extracellular fluids[1,3]. Even the blood contains about 0.4 g of P per liter. In 1769, Gahn and Scheele discovered that calcium phosphate makes up bones and were able to isolate phosphorus in bone ash[3]. Arthur Albright was able to use bones to make phosphorus in 1849[2].

The early uses of the element were questionable including medicinal purposes in the 17th and 18th century and military applications in the 20th century. P is the 15th element in the Periodic table as part of the nitrogen group with a few common allotropes like white P, red P, less common violet P and black P[1,3]. White phosphorus was used as a flammable source since it would ignite spontaneously and then produce a biocidal poison[1]. P was known as the "Devil's element" for its use in incendiary devices, bombs and poisons in World War I and II[3]. Following the questionable uses, people began to recognize that phosphorus was essential to all life forms as phosphodiester bridges that link nucleotides in DNA and RNA, as ATP that carries chemical energy in cells and is the most abundant biomolecule in nature, as phospholipids that are part of cell membranes and in lipoproteins for blood plasma[1,4,5]. Phosphorus is used for the phosphorylation process and is so highly reactive that it is mostly found in oxidized forms[3]. Phosphorus is needed for cell growth and making fruits and seeds[1]. It is the limiting nutrient meaning once the supply of phosphorus runs out, the plant will no longer grow[4]. Unfortunately, unlike carbon, hydrogen, nitrogen, and oxygen, phosphorus does not circulate freely in the atmosphere and can only be absorbed by plants as orthophosphates dissolved in soil solution[1,4]. In order to grow, plants need three important macronutrients: nitrogen, phosphorus and potassium. Plants need carbon, hydrogen and oxygen but this is readily available in the atmosphere; plants also need calcium, sulfur and magnesium which are sometimes added if soil is not rich enough. Micronutrients, like boron, chlorine, copper, iron, manganese, molybdenum and zinc, are needed in much smaller supply so these are generally available[6].

Phosphorus does not travel well and is not readily bioavailable for environmental systems but does move quickly within organisms. When enzymes, like phosphatase, phytase and nucleases, are present, phosphate hydrolyzes into a form that can be used by plants and some plant roots, or mycorrhizal fungi coating the roots, can produce enough organic acid to dissolve the mineral P[3,5]. This symbiotic relationship will occur less as the soil becomes sterile from over-application of fertilizers[3]. Mineral P can also weather due to carbonic acid, caused by biochemical respiration releasing carbon dioxide that increases acidity. Once mineral P dissolves, it becomes an organic form in plant tissue and begins to form biomolecules for photosynthesis and metabolism. The phosphorus cycle varies but the goal is to find equilibrium between soil being recycled and replacing what is lost through erosion of P-mineral bearing rocks[5]. Unfortunately, topsoil is being eroded and removed around 1% annually with losses of nutrients into water bodies. Over the next half century, 26% of arable land base could disappear due to erosion, salinization and waterlogging. Soil organic matter content has decreased significantly so increasing fertilizer will be necessary for keep soil fertile as the soil food web loses diversity[3].

The method of adding phosphorus to soil has changed throughout the years. Phosphorus can come naturally from rock through erosion and then become part of the sediment allowing for plant uptake or water transport through runoff[7]. Originally, the existing P in the soil came from 10-15 million years of erosion and deposition of mineral apatite[1,8]. This nutrient is one of the least biologically available so one style of converting it into a useable form was through ‘firestick’ farming. At least 40,000 year ago, this method of burning soil to create an inorganic form of P in the ash was used for creating more fertile lands. In Europe, this method was called ‘swidden’ and involved rotational style burning. Another early method of providing nutrients to agriculture was through ‘night soil’ from humans, pigeons, bats, birds, etc[1]. The organic cycle involves animals consuming the plants containing phosphorus then the animals’ excrement reenters the soil and the cycle repeats[7]. The Industrial Revolution and the Sanitary Revolution were turning points in how nutrients were managed. Cities began to industrialize making agriculture too far away to return nutrients through ‘night soil’. The original flush toilet meant waste was collected in cesspools which filled with disease so public health was the forefront of concern related to excrement. Sewers were built to carry this waste away from the centers of the cities with simple slow sand filtration and chlorination for treatment. No longer was waste disposed of through the land but rather through the water which meant phosphorus was no longer being recycled[1,2]; instead only 10% of waste was being recirculated[8].

Following these revolutions was the Green Revolution which led to a dependence on mineral phosphate rock for providing the nutrients that were no longer being recycled through waste disposal. Justus von Liebig confirmed that decaying plant matter was providing nutrients but this cycle was broken by a need for increased food production. Since the organic cycle was broken, external sources of fertilizers became popular in Europe and the US such as importing crushed bones or resources from the 'Guano Islands'[1]. Guano was rapidly used up so mining of phosphate rock really took off in the 1950s[8]. After World War II, phosphate mining became the only way to keep up with the fertilizer demand caused by invention of the Haber-Bosch process for nitrogen. Fertilizer was used seven-fold more from 1950-2000 than ever before with increasing crop yields and nutritional intake per capita. Plant decay, urine and feces were no longer sources for nutrient recycling because of public health concerns, public awareness, especially from the Great Stink of 1858, and increased food production[1].

The inorganic cycle involves phosphorus-rich rocks being eroded into sediment and the sediment being transported through water bodies to eventually be uplifted geologically as rock again. The natural inorganic cycle can take millions of years so phosphate rock is mined and processed to meet the quality standards required for its application[7]. The most common P-bearing minerals are fluroapatite, the igneous rock form, and authigenic carbonate-fluorapatite, the sedimentary rock form[5]. Phosphate rock mainly contains calcium phosphate apatite which has a strong affinity for heavy metals[2]. Phosphate rock provides the source of phosphorus for fertilizers but how is this resource part of the marine cycle? Nearly all, 85%, of the deposits are sedimentary marine phosphorus rocks known as phosphorites, which have mainly fluorapatite and carbonate fluorapatite minerals[9]. Phosphorites are sedimentary deposits high in phosphorus concentration, at least 9% by weight, which form by two processes. The first stage for either process is phosphogenesis, which involves the formation of P-bearing minerals in sediment, and generally leads to carbonate fluorapatite formation. Following this, either chemical or physical dynamism lead to the formation of the rock deposits. The chemical process is controlled by biogeochemical factors that concentrate the minerals while the physical process can rework sedimentary capping and concentrate the chemically mobilized P. Neither process is 100% efficient and it is difficult to quantify. These deposits form in continental margin sediments or deep sea oozes and survive countless tectonic, geochemical, sedimentological and oceanic conditions[10].

Phosphorus is a limiting nutrient especially in the ocean where concentrations are low and half of the phosphorus is caught in mineral lattices, like with iron and manganese[5]. The average P content in mined ore has declined from 15% to 13% just from 1970 to 1996 and off-shore mining will be a focus as the land resources are further depleted. The flux before human activity began to affect the cycle was about 1 Tg of P annually for dissolved P and 1-2 Tg of potentially soluble P annually. The time it takes to regenerate this material is thousands of years and the overall concentration in the ocean is low as it recycles with only 1.5 µM – 2.5 µM total P in the deep ocean. The concentration is especially low in surface waters where phytoplankton use the nutrient to form ATP and ADP that are necessary for photosynthesis energy and phospholipids to form cell membranes. Phosphorus accumulates more when phosphorites are not forming and the bulk of the rock reserves are known as the “Phosphorite Giants”, which have 100 times the normal concentration of P in sedimentary rocks. The times when phosphate rock deposition occurred in high volume represent when processes acted in unison; namely, the cycle of sediment-bound P, dissolved P, P-limiting biological productivity and the recycling or final burial of P. About half of the P involved in the marine cycle is trapped in mineral lattices and does not fully cycle through the biogenic process and some remains trapped in organic matter and sediment[10]. The phosphorus cycle has had several large variations that lead to global redistribution of the resource like the weathering of the Himalayan-Tibet Plateau that delivered the nutrient into the ocean or the “biogenic bloom” of the late Miocene, but recently the cycle has been dominated by agriculture and human activity. Nutrients have leached into water sources from fertilizers, deforestation, soil loss and sewage sources which leads to eutrophication because phosphorus is critical to photosynthesis and metabolic pathways. The overall global phosphorus cycle varies but net input of dissolved P from land to the ocean is 4-6 Tg annually[5].

Phosphorus is used in water treatment, flame retardants, corrosion inhibitors, paints, food and beverage, and pharmaceuticals[11]. Phosphorus has been used to make bronze, in detergents until that was banned, in production of fine china, as an organic compound in “Roundup” and as phosphoric acid in carbonated beverages to sharpen flavor. It has high demand for feeds, pesticides, plastics, computer chips, lubricants, chemical extractants, toothpaste, and car batteries[12]. All of these applications require a varying amount of processing to remove impurities in the mined rock. Eventually, agriculture became dependent on phosphorus in fertilizers and this application dominated the phosphorus market[3].

1.1.2 A nonrenewable resource

Phosphorus comes from a nonrenewable resource but there is uncertainty in how long the resource will last. Indicators of resource scarcity include the resource lifetime, trends in price, ore grade, discovery rates and Hubbert curve extrapolation. Reserves are the economically extractable resources while the resource base includes resources that are not yet available but are expected to be with improvement in technology[13]. Hubbert curves can be used to predict peak production of phosphate rock but have only proven successful for resources that have alternatives; unfortunately, phosphorus does not have an alternative[14]. The overall flow of phosphorus has increased four times since phosphate rock mining began in 1950 with most of the material flowing from agriculture to lakes and oceans. In 1938, Franklin D. Roosevelt pointed out the need to start conserving and recovering phosphorus but efforts are still being made to figure out how[15].

Unfortunately, the overall use of phosphorus is not very efficient. More than half of the phosphorus mined has been lost between the farm and human consumption, mostly through soil leaching and erosion[8,15]. Even though 90% of mined P goes to food production, only about 15-30% of applied fertilizer is actually taken up by crops due to runoff, erosion, bioavailability, etc[15–17]. About five times the amount of phosphorus consumed by humans is actually being mined. Unfortunately, 25% of phosphorus mined since 1950 has been lost to water bodies or landfills[8]. About 30-40% of food is wasted which means wasting this valuable nutrient. Humans lose about 1.2 grams of phosphorus daily in excrement[15]. Livestock use more nutrients to produce than crops and people are starting to include more meat and dairy in their diets[8,15]. Another consideration for increasing demand is the biofuel industry which will grow crops in competition with the food industry[8]. Biofuels could be created from algae, but either way crops and algae require phosphorus to grow so peak oil and peak phosphorus begin to be a focus together[3].

Phosphorus is a finite resource that is mined from the earth where it is the 11th most abundant element. Igneous rocks deposits represent 13:87 as compared to sedimentary rock deposits, with 80% of phosphate coming from sedimentary rocks. Most of this rock is surface mined but about 25% of it is mined underground[17]. The mined rock is not pure so other metals have to be removed before it can be used; this is especially crucial for fertilizer production because impurities like cadmium and uranium cannot be added to cropland[7]. Mining of this rock is only 39% efficient and results in waste rock, phosphatic tailing, and process water[9] as well as phosphogypsum, a compound with high levels of radiation[4]. In order to use the mined phosphorus-containing rock, other elements like calcium, sodium, iron, magnesium, cadmium and uranium need to be considered. Sedimentary rocks have a higher metals content. Radionuclides and phosphogypsum are health hazards. The phosphorus content of rock can vary from as high as 40% to less than 5% so purification is necessary to increase this content[17]. These heavy metals and radioactive substances could contaminant soil and water if handled improperly. Mineral fertilizers are produced from mining rock and purifying it through a thermal or wet route. The thermal route involves pelletizing the rock and baking it to release other metals associated with the rock. The wet route uses sulfuric acid to create phosphoric acid, which is highly impure, but this method requires less energy[2,11].

The supply of natural phosphorus-containing rock is decreasing. The phosphate rock reserves are becoming less and less pure and only represent 20% of the resources that are feasible to use[14]. Ore grade is measured in Bone Phosphate of Lime and used to be over 70 but is now less than 50. The process of getting phosphorus from rock and into food is not efficient; 20-30% of phosphorus is lost in spoil just from mining and beneficiation. Phosphogypsum is a byproduct of the wet-process of producing phosphoric acid that could contain 2.5% phosphorus[6]. Ore grade is decreasing as phosphate rock is associated with cadmium and uranium[14]. The element complexes with hexavalent uranyl so phosphate rock is often contaminated with uranium[3]. The mining process produces significant carbon emission, radioactive by-products and heavy metal pollutants like uranium, thorium and cadmium[8]. The low quality rock is not worth the expense of mining considering both the economic cost as well as the environmental cost from mining, processing and transporting. Phosphorus is mined from phosphate ores that generally contain 30% P_2O_5[13]. Although phosphorus is the 11th most abundant element in the earth's crust, the average amount of phosphorus in earth's upper crust is 0.1% and the sedimentary and igneous rocks that are phosphorous rich only contain 5-13% phosphorus[4]. Eroding soil leads to nearly 8-30 million tons of phosphorus being lost annually; phosphorus lost to oceans is too difficult to extract since overall concentration may only be 0.06 mg/L. Phosphorus leaves agriculture in livestock and supplies upwards of 1500 mg/person/day to people in the United States, which is mostly excreted[6]. The phosphorus content of rock is declining by 1% per decade and lower quality rock is far more expensive, uses more chemicals and uses more energy to purify for use. Other factors affecting the cost of fertilizers are: accessibility of the ore, degree of purification, capital investment, operating costs, availability and costs of other resources needed. Fertilizer use is expected to grow 4% annually as the population grows and more countries develop more robust agricultural practices so phosphorus will be depleted[17].

Unfortunately, phosphate rock is not being discovered much currently and reserves are only located in a few countries. Discovery over the last century has been limited to four specific discoveries, two in Morocco and two in North Carolina, finding 74% of the phosphate rock discovered during this period[14]. Around 30 countries produce P rock for trade but only three represent two-thirds of the production: USA, China and Morocco[3,8,17,18]. USA and China combined have 20% of the resources[17]. About 80% of the resource is distributed between these few countries[19]. The United States produces and consumes the most fertilizer, but only has 25 years of domestic reserves left[8]. China also has some of the largest reserves and has an export tariff of 135% to keep the reserves from leaving the country[8].

Africa exports the most since the largest reserve is in Morocco but this is a geopolitically sensitive area so the United Nations condemns importing phosphate rock from this region[8]. Morocco has the greatest supply with maybe 77% of the overall reserves remaining, depending on the survey, approximately 50,000 million tons, but only produced about 15% in 2010. In order to maintain the supply for the growing demand, Morocco will need to increase production by 700% over the next 100 years and will eventually have complete control over the market, unless significant changes are made. This kind of control can be compared to OPEC's control over oil except that OPEC is a group of countries and P rock is controlled by mostly one individual over the majority of the reserves. Not only are the reserves concentrated in one place, but international law against exists that makes it difficult to use the reserves in the Western Sahara which has been occupied by Morocco since 1975[20].

In Europe and North America, agricultural practices have involved enough fertilizer that the demand is considered stabilized but this is not true of Africa and Asia where fertilizer has not been so widely spread[4,8]. Similar analyses have been completed for oil, but the difference is renewable energy sources are being discovered that could provide an alternative to oil whereas the same is not true for phosphorus. Instead of focusing on an oil-based economy, phosphorus-based economics focus on a resource without any alternative that is running out[18].

In 1998, the annual production of P_2O_5 was about 40 million tons with 80% of that being used for fertilizer, 12% used for detergents, 5% used for animal feeds and the remaining 3% for specialty needs. Production of P is driven by the need for fertilizer which stems from the need for agricultural crops for feeding an increasing population. The population is growing at 1.5% annually and is especially occurring in developing countries where crop yields and fertilizer use are also still developing. An increase in wealth can be accompanied by this population growth trend which means concern for higher dietary standards. Unfortunately, the cereal required to feed a population meat is a ratio of 3:1 for poultry, 4.5:1 for pork and as high as 6:1 for red meat. At least half of the nutrients used in agriculture are used for cereal production, with around 2000 million tons produced each year. All of these crops require phosphorus so fertilizer use has increased tenfold since 1930. The peak year for consumption predicted by Steen was 1988 with 37.7 million tons of P_2O_5. The production capacity is estimated at 50 million tons annually. Eventually the phosphate will be depleted and some predictions say this could take 60-130 more years[17].

Based on a Hubbert's peak curve analysis by Cordell et al, which considers the amount of phosphorus that is feasible for use rather than actual 100% depletion, peak phosphorus is going to occur in 2033 before it becomes too low quality to be worth mining[8]. Some estimates of how long phosphorus will last range from 30 years to 300 years, showing how imminent a threat it is that phosphorus will no longer be available[4]. The best-case scenario according to Van Vuuren et al is that depletion by 2100 will only be 20-35% and the worst case is 40-60% so overall a short-term phosphorus depletion crisis is not likely. Trade of phosphorus will need to increase since most the resources are in Africa and Asia[13]. According to Liu et al, estimates of rock remaining say it may only be 7000 million tons, which gives the resource only 100-250 years until depletion[19].

A table in the Cooper et al study reveals the reserve-to-production ratios calculated based on all the collected data with Morocco having the highest ratio. The global ratio allows for 370 years until rock supply reaches a peak, but this relies heavily on Morocco. Without Morocco, the reserve-to-production ratio globally is only 100 years. After 100 years, only seven countries could even contribute to the reserves but these are in countries that are currently not producing much. China and the US are lead producers with only 50-60 years left in reserves. Unfortunately, the future of phosphorus regulation and technology is unknown for how it will affect mining price and accessibility, but with the assumptions used, the future will not be very long. Using the ratios and assuming demand increase based on population growth from 2011-

2100, the future of the global phosphate rock reserves was predicted. Overall, reserves that are used for 70% of the current production will be depleted in just 100 years. Demand for food and fertilizer is on the rise and authors for this study assumed a 1% increase in production annually. The peak production is estimated to be anywhere from 195 million tons annually to 383 million tons/year in the next 100 years. Cooper et al assumed 260 million tons as the peak production. Not only is demand increasing, but quality of the rock reserves has decreased from 31.4% P to 30.6% which makes extraction that much more difficult[20].

Although predictions like this and even from Thomas Malthus in 1798 saying the global population would be constrained by food supply existed, it was not until the 21st century that perceptions shifted from phosphorus as a pollutant to phosphorus as a resource. Echoing M. King Hubbert's peak oil production concept, peak phosphorus has been predicted to have already occurred in 1989 or will occur as early as 2030 or 2040[1]. A survey by USGS predicted 16 billion metric tons of reserves whereas the International Fertilizer Development Center predicts 60,000 mega tons, 3.8 times the reserves and even 7.4 times the reserve base[1,14]. This shows how difficult it really is to pinpoint the exact number of reserves remaining for predicting the peak phosphorus. One early scare of an 800% price spike for phosphate rock in 2008 represents where the global population could be very soon again. That price spike also affected future trade since China added the 135% tariff to export phosphorus[1]. In 2011, the baseline price was about $90/ton of phosphate rock but the 2008 spike led to $431/ton. Some believe that change will be made once the price reaches $100/ton because it will even the playing field enough[16,21]. With the available phosphate rock decreasing, the price has increased 133% over the last 30 years while consumption has increased as well by 25%[22].

Until faced with imminent resource scarcity, society may never make severe enough changes to see an effect. Phosphorus scarcity relates to energy scarcity, water pollution and greenhouse gas emissions so it is important to keep in mind how resources are intertwined[14]. Fluxes to consider include yield, trade, consumption, soil erosion, fertilization and recycling of waste containing phosphorus. The most important consideration is how much phosphorus is truly available to plants in the soil and this distribution is not consistent across the globe since the history of agricultural practices varies so much. By studying these fluxes, one can determine if it is possible to replace the depleting mineral fertilizer with enough recycled material to supply the phosphorus that plants need to grow. Dumas et al built a model in terms of crop yield that considers the total phosphorus in soil and what is actually available to plants. Phosphorus in soil is generally part of three chemical classes: organic compounds, mineral precipitates or surface complexes with metal oxides/clays. The way phosphorus exists in the soil affects the ability of plants to actually use it. Some soils are considered stable in available phosphorus and may not even need external fertilizers for a long time, but weathered soils predominantly have phosphorus that is only available to plants on a slow-release basis and cannot possibly provide enough without external fertilizers. Soil, therefore, is classified into three conditions: calcareous soils, slightly weathered soils and highly weathered soils. Data is needed to fill in the information about soil classifications. A large data set has not been collected with regards to phosphorus in soil so it is difficult to assess phosphorus fluxes. Instead, information has been gathered regarding the availability of phosphorus-containing rock for providing mineral fertilizer. The place to really focus is not on how much mineral fertilizer can be produced, but rather on how much phosphorus is available in soil and how much really needs to be added[23].

1.1.3 A source of pollution

Lakes have three trophic levels which come from an increase in nutrients and biological activity from oligotrophic to mesotrophic and finally to eutrophic. Nutrients enter water from septic systems, landfill leachate, wastewater plant discharge, lawn and road runoff, animal feedlots, agricultural runoff and rainfall[24]. Historically, algal blooms have been studied since as early as 1890 through the science of limnology. The term eutrophication comes from the word eutrophic, which comes from Greek and means 'rich in food'. Eutrophication describes the process by which lakes become rich in nutrients and the symptoms that accompany this condition. Originally, it was believed that eutrophication occurred naturally from lakes becoming full of sediment which increased the concentration of nutrients in the smaller and smaller amounts of water. In the mid-20th century, however, it became clear that this process is accelerated by human activity leading to increased nutrient input[25]. Eutrophication of lakes leads to hypoxia, high turbidity, formation of disinfection by-product precursors and excess algae[24]. The condition also leads to foul water with taste and odor problems and dead zones from oxygen depletion that kills fish and bottom-dwelling animals[26]. The over-enrichment of nutrients leads to overproduction of autotrophs. High respiration rates of the algae growing leads to hypoxia and anoxia and the low dissolved oxygen kills aquatic animals and releases more phosphorus from the sediment[27]. The algae dying off causes an aerobic decomposition process that depletes the water of oxygen which further kills off organisms in the water[3].

Phosphorus is the most common cause of these conditions in freshwater systems whereas nitrogen is generally the key nutrient for oceans[26,27]. Trace amounts of phosphorus may enter the atmosphere from volcanoes, but otherwise, phosphorus does not have a gaseous form[27]. Phosphorus occurs almost entirely as orthophosphate in water with small proportions of PO_2 or PO_3 present under anoxic conditions[24]. Other forms include pyrophosphate, longer-chain polyphosphates, organic phosphate esters, phosphodiesters, and organic phosphonates. Enzymes hydrolyze organic forms of phosphorus into phosphate and even sediment-bound phosphorus can be converted under the right conditions. Once phosphorus enters water, it is effectively trapped as the limiting nutrient for the ecosystem[27]. The P cycle is one of the slowest biogeochemical cycles because of the slow movement in soil and water[3]. As water moves, phosphorus can travel in spiral by detaching and re-attaching to the sediment so both dissolved and particulate phosphorus play roles[27]. A reducing environment can solubilize iron and manganese, cause phosphorus to be released from sediments, and convert nitrogen to ammonia[24].

The highest flows of phosphorus lost from the farm to fork system are agricultural runoff and erosion and animal wastes. Runoff represents 46% of lost phosphorus with high flow rate and low concentration and animal waste represents 40% of what is lost with low flow but high concentrations[28]. Wastewater contains nutrients since humans excrete 0.75 kg of phosphorus every year so releases of this add to the eutrophication as well[3]. Organic phosphorus from animal waste can be converted into inorganic phosphate and is more feasible to control than runoff. Runoff is generally a non-point source so it is difficult to capture and control. The phosphorus content in freshwater is at least 75% greater than it was before phosphate rock mining became so popular in the industrial age. Phosphorus flows in the ocean have increased from 8 to 22 million tons causing over 400 dead zones and rising 10% each decade[28]. The dead zones affect at least 245,000 square kilometers with hypoxia occurring when the dissolved oxygen levels fall below 2 mg/L and mass mortality occurring at levels below 0.5 mg/L[29].

The poor use of this nutrient is causing it to become a pollutant to water bodies, like Lake Taihu and Lake Erie, and yet also leading to uncertainty about the amount left for future use[12]. Eutrophication was first used in 1907 to describe wetlands but has since expanded to lake classification based on primary production. Various factors, like nutrient loading, light, temperature, oxidative stressors, interactions with other biota, surface water conditions, vertical stratification and water residence time, affect eutrophication but a full understanding has not yet been reached[30,31]. A eutrophication symposium was held in Wisconsin in 1969 and the American Society of Limnology and Oceanography had a symposium shortly after in 1972, but neither focused on specific solutions[30].

For some time, it was thought that phosphorus, nitrogen, carbon, trace elements and major ions all played a role in eutrophication, but in the 1970's scientists started to convince policy makers that phosphorus was the target nutrient to decrease in order to reduce eutrophication. Richard Vollenweider reviewed case studies on different scales of projects where nutrients were studied for the relationship with eutrophication. He made the first models for relating the two, like in 1976 he put together a model to predict algal growth by P input, average water depth and outflow of a lake[27], but was not taken seriously for years to come and in fact, his work was never published in a peer-reviewed journal. From Vollenweider's review, J.R. Vallentyne started to review the Great Lakes in Canada and W.E. Johnson started studying whole lakes with the Freshwater Institute with the hope that these experiments could convince policy makers that phosphorus was the nutrient to control. Johnson's study began around 1968 and included 50 small lakes and watersheds in Ontario. Several lakes in the Johnson study showed the importance of P; Lake 226 was split into two basins, one with nitrogen and carbon inputs and one with solely phosphorus, but only the phosphorus basin had algal blooms. At least 35 different lakes documented an improvement in eutrophication from reduction of phosphorus alone. The same cannot be said for nitrogen, however, and it is much more expensive to control nitrogen in water treatment. Nitrogen emissions, of course, should be controlled as they play a role in other aspects that burden the environment but is not the key nutrient to control for eutrophication.

The key nutrient to control, as shown by countless historical records, is phosphorus[25]. As early as 1971, the International Joint Commission (IJC) recommended that P input control was necessary for decreasing the eutrophication in the Great Lakes. Luckily, technology already existed at this time to remove phosphorus from waste water treatment facilities. At the same time, the IJC requested that detergent companies reduce the phosphorus in product because it was found to be at least 50% of the human phosphorus input into the Great Lakes. The detergent companies pushed back with studies showing that carbon was the element to decrease, which slowed the progress of phosphorus control becoming implemented via the Great Lakes Water Quality Agreement[25]. In 1974, J.R. Vallentyne predicted the year 2000 would be the Algal Bowl[1].

From a study done in China, evaluation of eutrophication should be based on productivity of macrophytes and phytoplankton, but these are difficult to access so common indictors used are nitrogen, phosphorus, transparency and chlorophyll a. Eutrophication is defined by these indicators and has the following thresholds in the study: 0.035 mg/L of phosphorus, 0.008 mg/L of chlorophyll a, and transparency less than 3 m. If the nitrogen to phosphorus ratio in algal cells is less than 7:1 then blooms are more likely to occur. The factors that affect blooms include nutrient concentrations, light, temperature and hydrodynamic force. Overall, the ecosystem responses seen in China from eutrophication were: extinction of submerged plants, frequent cyanobacterial blooms, increased microbial biomass and productivity, decreased biodiversity, accelerated cycles, less efficient use of nutrients, simplification of biotic community structure, instable ecosystems and much more turbid, algae-dominated waters[32].

Case studies have shown that phosphorus control reduces eutrophication and that carbon and nitrogen reduction does not contribute to this water quality improvement. Another case study involved Lake Washington in Seattle when W.T. Edmondson used the data to persuade the city to re-route sewage from entering this lake[25]. Studies of lakes in Canada by The Freshwater Institute and the study of Lake Washington in Seattle both showed that phosphorus is the limiting nutrient for lakes and nitrogen is a close second in importance. Nitrogen can, however, be fixed by some bacteria from the atmosphere and decreasing silica favors development of this nitrogen-fixing cyanobacteria. Carbon was found to have a response to eutrophication, but not be a cause even though some believed that for a while. Point sources of phosphorus and external loading can be controlled to reduce eutrophication but diffuse sources and internal loading will be difficult to control and overall the lakes will take years to recover[30]. Models have been created by Larson, Mercier, Vollenweider and Carlson to relate phosphorus concentration to algal production and transparency of water[24]. The Redfield Ratio, 15:1 of nitrogen to phosphorus, can be used to predict growth as long as significant changes in the nutrient concentrations have not happened recently[27]. In 2008, the EPA sponsored a roundtable discussion regarding eutrophication and harmful algal blooms so the scientific community could come to a consensus on the matters. Seven statements were agreed upon with support provided for each and are generally centered around the importance of nutrients in the spread of harmful algal blooms. The quantity, the composition, and the long-term and short-term delivery are all factors influencing how nutrients impact this growth[33].

Algal blooms are becoming more problematic as population increases and land-use leads to more and more nutrient release into water bodies. Toxic forms of algal blooms are common when the ratio of N:P is low[25]. Cyanobacteria, or blue-green algae, can outcompete phytoplankton and even eukaryotic algae at higher water temperatures. Cyanobacteria make up harmful algal blooms because they produce toxic secondary metabolites that affect the hepatopancreatic, digestive, endocrine, dermal and nervous systems. When enough algae grow, the cells not exposed to the surface can die and lysing of the cells releases the toxins as well as additional nutrients to add to the growth[31]. Nitrogen can be fixed from the atmosphere by cyanobacteria when there is unavailability in the water. Microcystis is a cyanobacteria that is actually toxic, but cannot fix nitrogen. Cyanobacteria generally cannot form in high salinity waters[34], so harmful algal blooms are more common for freshwater ecosystems.

Wastewater has phosphorus concentrations anywhere from 0.5 mg/L to 10 mg/L, but the EPA limit for acceptable phosphorus levels is only 0.1 mg/L or lower[28,35]. Even a level of 100 µg/L of phosphorus can lead to eutrophication[3]. Some guidelines even restrict P in effluent to 5 µg/L, so technology needs to be employed to recover as much P as possible to reach this limit[21]. In general, only a few micrograms of phosphorus per liter of water can saturate algal growth and the average concentration in rivers was 130 µg/L from 1974-1981[27]. The EPA regulates concentrated animal feeding operations through the Clean Water Act and any point source must have a National Pollutant Discharge Elimination System permit to release into US waters through the Clean Water Act. All other agricultural sources are considered nonpoint and are not regulated by federal law and agricultural storm water discharges are specifically exempt from point source definition. The EPA gives money to states to develop programs for control nonpoint source pollution but, as of 1998, only 22 states had quantitative limits, 12 had general narrative criteria and 21 did not have phosphorus standards[36].

Eutrophication is estimated to cost $2.2 billion/year due to loss of property value, additional water treatment costs from taste and odor or toxicity and other water quality loss, loss of recreational water usage and increased spending to recover endangered species especially with decrease in biodiversity[21,37]. The current methods are only able to remove about 30% of phosphorus and the cost to achieve the EPA limit across the United States is estimated to be $44.5 billion with current methods[35]. By decreasing the amount of phosphorus entering water bodies, lakes can begin to recover from eutrophication. Only 15-25% of phosphorus originally added to soil is used up immediately whereas most is stored as insoluble phosphorus until that resource needs to be used. If more soluble phosphorus is added, eventually, the insoluble phosphorus cannot be contained in the soil and is released into soil soluble which increases leaching and runoff into water. Fertilizer needs to be used more efficiently to decrease demand on phosphate rock and reduce eutrophication in nearby water bodies[3].

1.1.4 Reducing demand

In order to avoid the phosphorus release into water bodies causing eutrophication, phosphorus has to be controlled in agriculture. Agriculture is the largest contributor of P into the environment and management of this practice is difficult due to complex watershed processes, variability in management and climate. Conventional conservation of fertilizers may not be enough because both chronic and acute sources come into play with nutrients. The way water flows over agriculture can easily change a small source of phosphorus into a significant load. Intensity and duration of rain storms and soil conditions, including tilling practices, affect how the water impacts the land. Even if the application of phosphorus is considered in balance with the plant withdrawal, diffuse chronic sources are present from accumulation of the nutrient in soil and water. This means that focusing on how plants uptake phosphorus alone cannot solve the problem. The dissolved phosphorus in runoff, background levels, how quickly P is sorbed into soil, magnitude and duration of P transfers, soil erosion, how much P is attached to soil particles, and mobilization of dissolved P are all parts of the phosphorus in agriculture that need to be considered when agronomic practices are changed to avoid impacting aquatic ecosystems. Phosphorus leaches vertically through the soil and then laterally towards water bodies and impacts the water through decreasing the water quality in ways that reduce aquatic resources, expand toxic algal blooms, and affect human consumption and recreation. Runoff can lead to 20-40% of total phosphorus loss from agriculture so critical source area management is important for reducing this overall problem. Regulators need to decide if P concentrations or P loads should be the overall target in management practices, but regardless, education, social capital, and public participation are critical for resolving this problem[38].

In order to better use this declining resource, less phosphorus should be applied to crops and other agricultural strategies can be utilized to help in the effort. The modern agricultural ecosystems are depleting resources that are not at all infinite like land, water, energy and nutrients. Land can be optimized by finding a balance between high productivity per hectare that allows for more limited land demand. Meat and dairy use the most land for production. Another strategy for reducing phosphorus demand is to prevent erosion and improving the infiltration capacity of soil. Soil quality is important for assuring that phosphorus will be used efficiently and is fully available to the crops. pH, organic matter, resilience and fertility are factors to manage to help keep high quality soil. Other strategies include improving fertilizer techniques, improving crop genotypes, exporting phosphorus-containing manure, modifying livestock diets and adjusting livestock densities. All of these strategies can help to reduce the amount of phosphorus needed to support crop production necessary to supply enough food to a growing population[39].

Part of improving the use of phosphorus in the US and even globally is understanding where losses are occurring and how efficient each step in the process of the food system is. The major losses are occurring in livestock production, crop cultivation, food waste, mining waste and fertilizer manufacturing waste. Humans consume twice the phosphorus that they need and are relying more on a diet of meat and dairy, which require the highest number of nutrients to produce. More than half of the phosphorus that is lost is through livestock and crop production so improving these yields without additional phosphorus will improve the food system. Reducing household food waste is another effective method of reducing phosphorus losses[40]. The control measures possible for keeping nutrients from entering water include decreasing fertilizer use, containing and treating manure, tilling to conserve soil, vegetated buffers and wetlands[26].

Legacy phosphorus is phosphorus that has accumulated in the soil and can be remobilized to provide a continuing source for years. These legacy sources can mask how much the reduction in phosphorus loading and losses are affecting an ecosystem. Generally, legacy phosphorus builds up in downslope areas in the land-freshwater continuum where phosphorus cannot be used as quickly as it is supplied. Land legacy phosphorus comes from nutrient management for agriculture especially where total P concentrations can be two- to ten-fold greater than in forests. Crop and livestock production results in localized manure imbalances that get stored in the soil. Phosphorus is present in solid phases in the soil because it is highly reactive. Cascades, influenced by hydraulics, hydrology, geomorphology and land management, can transfer nutrients from land through runoff into water bodies where dissolved chemicals can remain for a long time. Soil conservation techniques like no-till, cover crops, buffers, grass waterways and diversion drainage, can be used to avoid erosion and release of soils downstream. The biogeochemical cycles of nitrogen, phosphorus and carbon are closely related so changes in one can affect the rest downstream. Spiraling is a phenomenon to describe the movement of the compounds downstream as they experience precipitation, dissolution, mineralization, uptake, influence of primary producers and microorganisms and diffusion. Targeted use of amendments to capture phosphorus during the spiraling effect can be a management strategy. Management strategies can lead to release of legacy P so monitoring needs to be used until full recovery of a system is reached. Legacy P in groundwater, for example, can have residence times from less than a year to more than 50 years which makes it difficult to control[41].

1.1.5 Removal techniques

Typical methods for removing phosphorus from wastewater treatment systems include enhanced biological phosphorus removal (EBPR) and chemical precipitation. Perhaps the most conventional method for removal is biological phosphorus removal that creates a phosphorus rich sludge. A combination of anaerobic and aerobic stages is used to encourage bacteria to take up phosphorus to help with growth[11]. It uses polyphosphate-accumulating organisms (PAO) to remove phosphorus and convert it into sludge. These organisms can take in more phosphorus than necessary for growth which makes them better for this purpose[35]. In the anaerobic stage of the process, PAOs hydrolyze stored polyphosphate in order to take in carbon sources as PHA to provide energy. In this stage, orthophosphate is actually released in order to take in sufficient energy[42]. Polyphosphate and glycogen provide energy for biochemical reactions and acetate and glucose can provide additional carbon sources for this stage[43]. The aerobic stage involves growth of PAOs using the PHA as energy to take in orthophosphate to recover the polyphosphate level and remove phosphorus from the water[42,43]. This method requires adding acetic acid or sodium acetate to provide enough chemical oxygen demand in the reactor[11].

EBPR can remove over 85% of phosphorus, but does have some drawbacks. For example, the PAOs only store phosphorus while the conditions in the system are aerobic and will release some if the system goes anaerobic. Also, the sludge does not contain a high percentage of PAOs so generally it has to be recycled through an aerobic-anaerobic cycle to enrich the sludge. This can take days or months and is not very efficient. EBPR is difficult to control and it is unclear how conditions like temperature and pH affect the species formed[35]. This process depends on numerous factors: carbohydrate content, pH, chemical oxygen demand, P, Mg, Ca, K, incubation time, sludge retention time, temperature, aeration, time aeration starts, and the number of glycogen accumulating bacteria (GAOs). Polyphosphate accumulating organisms can also be used for denitrification under the right conditions but exposure to high nitrite concentrations can impact the phosphate uptake as well. One problem for understanding EBPR fully is the ability to characterize the bacteria that are acting as PAOs[43]. This uncertainty in the reliability of the system makes it a system that still needs review.

Since EBPR is a bit of a mystery, de-Bashan et al studied various factors that include: the microorganisms responsible for EBPR, isolation of polyphosphate accumulating organisms, microbial diversity of EBPR sludge, biochemical metabolisms of PAOs, energy budget in PAOs metabolism, denitrification by PAOs, and the role of GAOs. In general, EBPR is stable except when there is excessive rain, the loading is too high, potassium is not readily available, aeration is excessive and nitrate loading is high in anaerobic zone. Fundamental understanding of EBPR is lacking because it is difficult to determine the microbiological and biochemical aspects of the process. For a long time, Acinetobacter was considered the primary bacteria responsible for EBPR, but later cultures have shown that it is only about 10% of the total bacteria responsible. The sludge is not dominated by a single type of bacteria but rather by groups of bacteria and isolation is essential for understanding these PAOs. Another important component is understanding the energy budget and how chemicals interact so PAOs can uptake phosphorus. PHA is an important carbon source that can be converted from acetate with reducing powder, which comes from degradation of stored glycogen. Acetate is an important carbon source, but the ratio of carbon source taken up to phosphate released varies so it is difficult to understand. The enzyme AMP-phosphotransferase is responsible for energy conservation of PAOs, but these organisms can have an energy wasting metabolism. One important note from the authors is that PAOs are different from GAOs because GAOs take up organic substrates in anaerobic phase without release phosphorus. Denitrification is possible through EBPR if anoxic conditions are used because PAOs can use nitrate like oxygen, but with less efficiency. Overall, EBPR is still not understood enough to really optimize the process but it is an effective way to remove phosphorus from water[42].

The ASM2d model was extended to include the role of potassium and magnesium in addition to calcium for enhanced biological phosphorus removal. Synthetic wastewater was created with various compounds to represent a typical wastewater including a magnesium sulfate, calcium chloride and potassium phosphate. The simulation focused on how potassium and magnesium affect the phosphorus removal ability of the EBPR plant and found that both are co-transported with phosphorus into and out of bacteria because both are needed for electroneutrality of the cells. The potassium and magnesium cannot substitute for each other and magnesium was found to be more critical than potassium. Calcium was not found to be involved in the phosphorus removal. Under the right anaerobic conditions, magnesium ammonium phosphate will form, but this was not expected here[44]. About half of the phosphorus contained in wastewater is removed by enhanced biological phosphorus removal, 11% is removed with primary sludge and 28% is removed in biomass. Sludge can be handled through a wet chemical technology by adding acid or base to remove insoluble compounds then phosphate is handled separately through further processing. Another method is thermochemical and involves incineration of sludge to vaporize heavy metals[7].

The next technology is chemical precipitation, which involves adding a metal salt into the water that can react with phosphate to precipitate an insoluble metal phosphate. After precipitation, this material can be filtered out from the water[35]. Metal precipitation is a common method for removing phosphorus but does not necessarily allow for recycling because of the contaminated precipitate recovered[43]. Various metals, divalent and trivalent, have been used to achieve this precipitation like iron, aluminum chlorides, sulfates, lime, anionic polymers[11] as well as magnesium, and calcium[35]. Aluminum is considered promising since it is currently used for coagulation[35] but aluminum is toxic to plants if used as a fertilizer[28]. Iron forms a precipitate quickly but it is important to use ferrous oxide since it is cheaper then provide oxygen to the system so it converts to ferric oxide which is better for removing P[35]. Various forms of iron have proven successful such as in the form of blast furnace slag[43]. Iron phosphates, however, are not available to plants[28]. Magnesium can be used in the presence of ammonium to form struvite in basic pH conditions. Calcium can be used similarly and can be taken from bio-waste like oyster shells[35]. Magnesium and calcium based precipitates could both be available to plants in fertilizers[28]. Overall, however, precipitation seems to be the least effective way to remove phosphorus[35]. Metal salt precipitation is expensive and leads to an increase in sludge volume and, depending on the metal used, may create something that cannot be reused[45].

EBPR and chemical precipitation are common but a few other removal technologies exist. Constructed wetland systems are generally low in cost and technology and use plants as biofilters. The selection of plants is important because some plants can remove certain pollutants better than others. The system can be engineered to control during changes in climate and wastewater source. Microorganisms with the plants can adsorb nutrients and other contaminants of concern[43]. A few other technologies include ion exchange, magnetic attraction and adsorption with materials like activated alumina, half-burned dolomite and red mud[11]. Ion exchange can be made to be selective and reversible[28]. Other methods include crystallization, acid-leaching and thermochemical methods. Hydroxyapatite can be crystallized out of wastewater and is comparable to rock phosphate for other purposes besides just fertilizer such as production of chemicals, flame retardants and lithium-ion phosphate electric-vehicle batteries. Struvite precipitation is a common method, but the money made from this form of fertilizer only accounts for about 1/3 of the cost of the chemicals needed for this method. Struvite only removes nitrogen and phosphate in a 1:1 molar ratio so it does not provide a way to achieve both discharge limits since nitrogen is generally in excess[21]. Struvite is now explained further.

1.1.6 Struvite

Struvite was identified as early as 1939 and was seen as a nuisance that caused pipe blockages by crystallizing in pipes and reducing the diameters[46,47]. The smaller pipes made pumping more expensive and led to overall decreased efficiency. The most common place for struvite to form is in areas of increased turbulence and where pH increases, which leads to a decrease in the compound solubility[46]. The crystals are practically insoluble in neutral and alkaline solutions, but are readily soluble in acid. Struvite is a soft mineral with molecular weight around 245 g/mol and specific gravity of 1.7 with rod-like orthorhombic structure[19]. Struvite requires a 1:1:1 molar ratio of magnesium, phosphate and ammonium for precipitation as well as alkaline pH and appropriate mixing conditions[48]. Domestic sewage generally has a molar ratio of 8:1 of nitrogen to phosphorus[45]. In 1991, the EC Urban Waste Water Treatment Directive was put into place to keep sewage sludge from directly entering water bodies and to limit nitrogen and phosphorus to reduce eutrophication[47]. Until 2006, struvite was seen as a nuisance that occurred spontaneously in treatment systems in places that reduced overall plant efficiency like valves, joints and aeration assemblies where water rushed through with a high turbulent flow. Precipitation can be controlled in a way to benefit a water treatment system especially for the purposes of recovering nutrients for a slow release fertilizer, which has proven successful as an alternative to conventional fertilizer with recovery efficiency as high as 90% in some cases. Struvite recovery has the potential to reduce mining of phosphate rock by about 1.6%. Struvite should be further investigated for the possibility of using it as a slow-release fertilizer because it is easy to make, pure, easy to handle, concentrated, granular, non-sludgy and non-odorous[48]. In the 1970s, crystallization reactors to create calcium phosphate or magnesium ammonium phosphate started being implemented. Fluidized or fixed bed reactors can be supplemented with seed materials that encourage the nucleation of these crystals[11].

If the formation and collection can be controlled, the magnesium ammonium phosphate crystal can be used as raw material for fertilizer and other industrial purposes. The conditions necessary are high concentrations of phosphorus and ammonium with a $Mg:NH_4:PO_4$ molar ratio of 1:1:1 at least, the pH should be above 7.5, and the suspended solids concentration should be low. In combination with phosphoric acid, this material can be manipulated to be a faster release fertilizer when necessary[43]. Crystallization occurs in two stages: nucleation and growth[19,48]. This technique has been proven with various water sources like leather tanning wastewater, swine wastewater, wasted sludge, industrial wastewater, municipal landfill leachate and poultry manure wastewater. Two different reactors have been used for crystallization: a mechanically stirred reactor and a fluidized bed reactor. The nucleation is influenced by pH, mixing energy, super saturation and presence of foreign ions and the ‘induction time’ may only take a few minutes while the growth could take up to 180 minutes depending on crystal size[19]. The factors that affect struvite precipitation include degree of supersaturation, molar ratio of reacting species, kinetics, presence of seed crystals and counter-reacting ions[45].

Large scale use of this technology has not been adopted, however, because of various drawbacks that mostly trace back to the cost. One cost to consider is the pre-treatment that can be associated with implementing struvite recovery; ions like calcium and iron may need to be removed to allow for precipitation which can add pre-treatment like anaerobic digestion, acid base leaching, chelating agent treatment, microwave treatment, or enhanced biological phosphorus removal to make struvite precipitation possible. Not only is pre-treatment a possible cost, but the ratio of magnesium, ammonium and phosphate may not be right for struvite recovery so adjustments may need to be made. This adds the cost of the chemicals needed to supplement the additional part of the perfect struvite ratio[48]. A more alkaline solution was shown to work better as increasing the pH from 10 to 12 increased the phosphorus removal from 55-100%. Increasing the pH shifts the phosphorus equilibrium and leads to supersaturation with HPO_4^{2-} and PO_4^{3-} reacting with magnesium[49]. Therefore, another chemical additive is for adjusting the pH; usually sodium hydroxide is used for this, but could be magnesium hydroxide, calcium hydroxide, lime or with carbon dioxide stripping. One drawback of this technique is these added chemical expenses[19,45].

Cost also needs to consider the savings associated with removing phosphorus from a waste stream, however, which allows for safe disposal of the waste and a lower sludge volume overall[48]. Struvite crystallization from digester supernatant was evaluated from an economic perspective in a study by Shu et al and compared with other methods for removing phosphorus from water systems. Using this technique, 1 kilogram of struvite can be crystallized from 100 m^3 of wastewater which could provide enough fertilizer for 2.6 hectare of agriculture. This could reduce phosphate rock mining by as much as 1.6%. This method is profitable compared with chemical and biological methods because it does not require as many chemicals as used for precipitation and leads to less sludge formation than both chemical and biological methods. Profit from struvite might be \$0.07-0.74 per kilogram, but the initial costs of crystallization could not be recovered from selling struvite alone. The market for struvite is not yet available to farmers so storage may be necessary until this method becomes more profitable. The payback period for a plant that processes 55,000 m^3/day could be less than five years[50]. Several considerations must be researched further in order to guide the conversation regarding the implementation of struvite as a recovery method: alternative magnesium sources, different seed materials, nitrogen conservation and fertilizer value[48].

Generally, magnesium is not present in high enough molar concentration for struvite to form readily so a magnesium supplement is provided to add slightly more than equi-molar amount of magnesium[19,45]. The most common magnesium sources are pure chemicals that are highly reactive but also expensive; examples include $MgCl_2$, $MgSO_4$, and MgO. The cost of this source alone can contribute to up to 75% of the overall production cost, making this an area for close review. A few possible other sources which are much more available include sea water, bittern and magnesite ($MgCO_3$). Sea water contains numerous ions but magnesium is the second most abundant from the weathering of Mg-rich minerals on the sea floor. When sodium chloride from brines and/or sea water is crystallized, bittern can be formed. Magnesite is a by-product of MgO production. Sea water and bittern both have shown promising phosphate recovery but require more magnesium than phosphate, 1.5:1. Magnesite has low water solubility so a high dose is needed to achieve precipitation, but acid dissolution and thermal decomposition are two methods for increasing the solubility. Both treatments make magnesite cheaper than pure materials. One consideration with impure magnesium sources is the other ions included in the source because these may not be desirable and would require treatment[48]. Sulfate and nitrate forming with magnesium is very soluble and magnesium fluoride is slightly more soluble than magnesium phosphate so inorganic ions would not impact phosphate removal. Magnesium phosphate will form first and will not re-dissolve once precipitated because the solubility is too low[49].

A seed material can be added to provide a template for nucleation which results in a faster induction time and provides a surface area immediately for growth of struvite crystals. The seed material must also be inert to the solution where crystallization is occurring and have isomorphism with the precipitating crystal[48]. Examples of seed materials include sand, quartz, silica sand, anthracite, magnesia clinker, pumice, clays, struvite powder or steel/wood/rubber devices[19,47]. The seed materials can increase the reaction, the crystal size and crystal settling, but the seeds do reduce purity of the struvite crystals and add an expense from the material cost, the extra pumping and mixing, and from recycling loops[19]. Magnesium phosphate rather than calcium phosphate should be used, but sand is generally used. The seed material can make the crystal impure so using a magnesium phosphate provides the purer compound[49]. Another potential seed can be small struvite crystals that could not be used as a fertilizer material[45]. Struvite fines are under strong consideration for the best seed material while non-struvite seeds like sand, stainless steel mesh, pumice stone and borosilicate glass do not produce the same low induction time and quick crystallization rate. The factors that need to be considered when looking for the ideal seed material for precipitation are surface roughness, dosing, grain size and super-saturation of solution[48].

Analysis of crystals may mislead how much struvite is truly part of the precipitate and pure struvite actually forms best at a very slow rate at pH 7-7.5. The more basic pH favors conversion of ammonium to ammonia which is not the form of nitrogen that struvite needs for crystallization. Precipitation of a pure struvite crystal could take three months at room temperature so various acceleration techniques like electrochemical deposition, use of crystal seeds, and increasing thermodynamic driving force, are needed to speed up the process. The faster precipitation may lead to smaller crystals which will not provide as much phosphate as desired. Struvite may only be as good as other mineral fertilizers, but is much more expensive to produce and releases the nutrients far slower than other forms of fertilizers[51]. A few drawbacks are that more nitrogen is required for agriculture than phosphorus but increasing dose to achieve higher nitrogen may also increase pH and the Mg:Ca ratio in the soil which will not help with growth. Also, struvite does not have any potassium which is an important nutrient so struvite in combination with other fertilizer is the optimum use for a balance NPK ratio. Acidic soil conditions are best for adsorbing phosphorus from fertilizer and struvite works about the same as conventional fertilizer in these conditions. Struvite actually outperforms conventional fertilizer in alkaline soil conditions and nitrogen leaching loss is insignificant. Of 19 studies completed regarding fertilizer ability for various plants' uptake of nutrients, 14 showed that struvite was superior to conventional fertilizer[48]. The final form of struvite is best for uptake by plants if the material is granulated[45].

Another consideration with struvite precipitation is the possibility that it can conserve nitrogen especially related to food waste compost quality. Nitrogen can be lost through gaseous emissions from compost up to 42% and control measures make processing expensive. When struvite precipitation is used for composting, however, the nitrogen concentration increases and stabilizes. Additional magnesium and phosphate may need to be added to maintain the perfect molar ratio, which can reduce microbial activity so an optimum level of 20% of the initial N is suggested for the Mg and P dose. This method has been shown to conserve up to 60% of nitrogen specifically for food waste composting[48].

An important consideration for further use of the material as a fertilizer is the purity as related to the essential nutrients. Struvite contains about 12.6% phosphorus, 5.6% nitrogen and 9.9% magnesium that can be released slowly to plants. The crystals may not be pure based on seed crystals and competing ions so purification may be necessary for use as fertilizer. In general, however, the crystals do not contain heavy metals and will not burn plant roots. The slow-release would mean less frequent application and is especially good for grasslands, forests and coastal agriculture. Several methods of decomposition, pyrogenation, distillation with a caustic addition, and electrolysis, could be employed if the goal was to recycle parts of the material separately. Magnesium ammonium phosphate is a good fertilizer for climate change since the nitrogen is not readily released to form N_2O and NO emissions, the uptake of nutrients is efficient, and less nitrogen will be lost overall. Struvite fertilizer compares well with conventional soluble fertilizers, so this is a good option for recovering phosphorus from water bodies for reuse[19].

In the United Kingdom, the Slough Sewage Treatment Works studied trying to form struvite in a controlled manner because the system supports 250,000 customers with a large percentage being industrial effluent. Controlling struvite precipitation could mean recovering phosphorus from leaving the facilities and causing eutrophication in the receiving waters. The treatment facility had to raise the pH, usually with sodium hydroxide, and add magnesium, in the form of magnesium chloride, to keep the components of struvite in the right overall molar ratio.

The best stage of the treatment process to control struvite crystallization was in the centrifuge liquor with an annual yield of 42-1000 tons depending on the conditions. The crystallization process is expensive. The revenue from selling struvite may only account for one-third of the overall cost of the chemical addition necessary to control the precipitation. Another consideration is removing suspended solids prior to precipitation which could add more expense for overall processing. Jaffer et al found, for Slough Sewage Treatment Works, that the chemical cost may be 50,000 euros/year with the pH adjustment chemical making up 97% of the cost. Although the revenue could be 8400-20,000 euros/year and the precipitation could lead to 97% phosphorus removal to help meet the Urban Wastewater Treatment Directive, the overall cost is a considerable drawback[46].

Struvite was tested for phosphorus uptake in low phosphorus sandy soil with two different crop types, buckwheat and spring wheat, to compare with di-ammonium phosphate and triple super phosphate fertilizers. Buckwheat was able to use struvite phosphorus much better than spring wheat so a mixture of struvite and DAP could be used to fertilize spring wheat. Conventional fertilizers are highly water-soluble and lead to high soil solution phosphorus that is immobilized onto soil particle surfaces. This leads to limited phosphorus supply for later stages of growth. Slow-release fertilizer like struvite would reduce this soil immobilization, improve fertilizer recovery, reduce crops using photosynthate to use soil P, and reduce risk of phosphorus lost in runoff. For early plant uptake, a mixture of 70-80% of di-ammonium phosphate with struvite could be used then struvite would provide a more efficient long term use of phosphate. Plants can exude organic acids to dissolve struvite and uptake phosphorus. This method of fertilization is more sustainable than using mineral phosphate rock fertilizers especially since phosphate rock is a resource in decreasing supply[52].

Another study focused on whether or not precipitated phosphates could be used effectively as a source of phosphorus for plants. Eleven different materials were evaluated including struvite from various wastewater discharge, laboratory synthesized struvites, a synthetic iron phosphate and a recovered calcium phosphate. Most of the materials were magnesium ammonium phosphate but struvite could also be a magnesium potassium phosphate. Pot experiments were conducted to compare these precipitated materials with monocalcium phosphate. The experiments were conducted in sandy loam and sandy clay loam soils with perennial ryegrass as the test plant. Superphosphates and fertilizers like monocalcium phosphate have high water solubility so the nutrients were released very quickly to the soil whereas struvite was a slow-release fertilizer. Overall, the various precipitated phosphates were not significantly different from each other nor were they significantly different from the monocalcium phosphate. This means that struvite could be used to remove phosphorus from water systems and then be used as a fertilizer that will produce nearly the same crop yield as standard fertilizers. The recovered phosphates had smaller dry matter yields consistently but not significantly smaller than the control fertilizer. Calcium phosphate had the lowest apparent effectiveness at 69% of the monocalcium phosphate and iron phosphate had 85% effectiveness[53].

A final case study was at the Murcia Este Wastewater Treatment Plant in Murcia, Spain, which had been experiencing blockage in the distribution system and worked to discover what was happening and why. The pipe blockage and equipment accumulation of a crystalline precipitate was forming mostly during and after the anaerobic digestion process in the treatment facility. The plant used biological phosphorus removal to achieve an effluent with less than 1 gram of phosphorus per cubic meter of water. This process involved phosphates and metal cations being taken up in bacteria as polyphosphates and the bacteria was removed as excess sludge. Parameters analyzed to understand the precipitation better included total suspended solids, volatile suspended solids, total phosphorus, phosphate, ammonium, alkalinity, pH, total and soluble calcium, total and soluble magnesium and total and soluble potassium. The anaerobic digestion of this sludge led to an increase in pH, ammonium and soluble magnesium which created the right conditions for precipitation to occur. Around half of the phosphate was available for reaction and the precipitate forming was made up of ammonium struvite and hydroxyapatite with the remaining available phosphorus adsorbing onto the surface of solids post digestion. Even though potassium was present, it was not precipitating as a struvite. The hardness of the water was found to affect the precipitation due to competition between the calcium and magnesium ions[54].

1.1.7 Opportunity for recovery

Phosphorus is a resource with a limit fast approaching and demand ever growing so recovery methods are essential for maintaining, and likely increasing, the amount of phosphorus available for reuse. Both nitrogen and phosphorus are valuable nutrients, about 3.5 cents for every cubic meter of sewage, that should be recovered for potential reuse as a fertilizer rather than just removed in a form of waste[45]. Overall, no one technology can meet all of the important considerations like maximum recovery rates, removal of hazardous substances, low environmental risks, good plant availability, ease for spreading as fertilizer, and economic efficiency[55]. There will always be a trade off in deciding the best technology for the situation.

Only about 6% of wastewater is reused and the primary means of reuse is for agriculture through wastewater effluent reuse or land application of sewage sludge[21]. Bio-solids have been applied to land as a way to return nutrients to soil, but this can be worrisome because the sludge can contain other contaminants that are harmful to soil and crops[43]. Land application is subject to regulation due to potential for heavy metals input so only 55% of US sewage sludge is used this way[21]. Supernatant recovery rates are only as high as 25%, but the cost is low and the implementation is rather simple for making clean, plant-available materials. Most technologies produce struvite with 10-12% phosphorus or calcium phosphate with 13-17% phosphorus[55]. Sometimes incinerating the sludge and using the ash as a soil amendment is a good option because it has 4-11% P by weight which is comparable to the 13% for mined P rock. Using soil amendments like this has added benefits for improved water retention, better soil health, filtering of pollutants and supplying other trace minerals needed for growth[21]. The sludge recovery process is complicated with higher recovery rates around 40-50%, but also very high heavy metals content unless an additional processing step is included. Sludge ash has the highest recovery rates from 60-90% and costs could be kept low but considerations again need to be made for potential pollutant content[55]. Another strategy for conserving this resource is to focus on recycling livestock waste since it contains five times more phosphorus than human waste and the population is ten times higher. Human waste phosphorus can be recovered through struvite precipitation in wastewater treatment facilities but livestock waste does not have this opportunity[18].

“Green chemistry” focuses on development of benign products and processes, elimination of waste, use of renewable (secondary) resources and design of output-drive production systems with minimum requirements and maximum efficiency. This way of looking at a problem presents three sustainability challenges with phosphorus: how to consume less phosphate rock and with greater efficiency, how to minimize phosphorus losses and generation of waste P that cannot be reused and how to set economically, socially and environmentally acceptable target to low phosphorus demand. Currently, maybe only 20% of phosphorus is being recycled but strategies like direct land application, assuming the right nutrient ratio without contamination, and biological or chemical recovery methods can increase this percentage. Regional variation and food consumption patterns affect what will be the best strategies. The environmental factor for phosphorus, which represents the ratio of waste generated to unit of product process, is 30. This leaves a lot of opportunity to improve the process. Phosphate rock contains heavy metals, which need to be co-extracted for potential use as well. The stripping of these materials could be costly. The mining process involves using sulfuric acid to dissolve phosphorus from rock, which produces harmful by-products. Hydrochloric acid could be used to avoid some of these wastes[12].

Today, only about one-third of demand could be met with recovering phosphorus; the remaining demand must be brought down through increasing efficiency and behavior change. Cordell et all suggest a systems framework needs to be followed to achieve the best method of avoiding a phosphorus scarcity disaster. The first key step in the framework is to identify the key drivers for recovery; namely, why should anyone care about recovering phosphorus? The most apparent reason is for pollution prevention as eutrophication is becoming more common and public. As stated before, phosphorus is essential for food production so another reason to recover phosphorus is to create a renewable fertilizer which is also locally available to farmers. Some of the recovered phosphorus will go to other purposes in industry as well. Additionally, by removing nutrients from wastewater, the sludge remaining is far less difficult to treat and will allow for less maintenance of wastewater treatment plants[16].

The next few pieces of the framework to consider are the system boundary, the quantity/quality of sources available and the stakeholders. When trying to solve this problem, the system boundary could be as small as a household to as large as a country so it is important to keep in mind that appropriate strategies are dependent on boundaries. Within the boundary, sources include wastewater, human excrement, greywater, animal manure, and crop residues. The quality of the source is important because the cost to recover it will increase with a decrease in quality. This is the problem with phosphate rock reserves as well; the sources are no longer very pure so extraction of the phosphorus is far more expensive than the amount mined is worth. The amount and quality of phosphorus sources will vary based on population size in the boundary, daily food intake, dietary preferences, livestock number, animal type-specific excretion, feed type, supplements, commodities produced, location of final consumption in comparison to production and efficient of the food chain. Since the sources can come from a variety of places, the stakeholders vary greatly as well depending on the boundary chosen. Stakeholders could include: phosphate mining companies, fertilizer manufacturers, farmers, food producers, retailers, nutritionists, consumers, water/sanitation service providers, environmental managers, and policy makers[16].

Several reuse strategies already exist and have been employed on a case by case basis with some success. Struvite precipitation is one such strategy and accounts for 13-14% phosphorus by weight; this strategy is, however, limited by the amount of magnesium in wastewater. Decentralized systems are becoming more popular as the infrastructure for the centralized systems is aging; moving large volumes of water a long distance is difficult and does not allow for specific treatment as needed. Source separation is one method of making recovery easier down the pipe and can be accomplished upfront in decentralized systems. Any system put in place to fix this phosphorus scarcity problem must also consider other environmental challenges that will be affected such as climate change, fossil fuel scarcity, water scarcity, and eutrophication and population trends. Another barrier to change is human behavior and how people feel about reusing excrement for food production, for example[16].

Unfortunately, a method for recovering this element from water sources is not always environmentally beneficial just because it alleviates the need for mineral fertilizers. Other factors have to be considered when selecting the best method for phosphorus recovery, so a thorough life cycle assessment was completed by Bradford-Hartke to address this issue[22]. Other literature had assessed specific recovery methods for more limited environmental effects, which led to contradiction in the results, so the goal of this life cycle assessment was to be thorough in addressing environmental factors. Factors that were considered include: global warming, ozone depletion, toxicity, salinization, eutrophication, and mineral depletion. The functional unit used to assess each recovery technique was 1 kilogram of plant available phosphorous that is able to offset the use of synthetic mineral fertilizer, specifically DAP and urea[22].

The assessment was conducted using six different wastewater treatment facilities in Australia; two were decentralized plants and four were centralized. Each facility had a different phosphorus recovery approach including recovery from urine, biosolids and precipitation of struvite. The system boundaries included effluent discharges, direct gaseous emissions, production of energy, chemicals and materials required for construction and/or operation of new infrastructure as well as awarding credit for offsetting fertilizer needs. The assessment assumed 50 years of operation of these facilities including transportation of recovered materials to agriculture. Overall, recovering phosphorus from urine reduced global warming and ozone depletion potentials, but adversely affected the terrestrial ecosystem by increasing toxicity and salinization. Chemical-based recovery methods require too much resource input to offset the resources required for mineral fertilizer production so this method is more of an environmental burden than a benefit. Struvite precipitation, specifically from solids dewatering more so than brine streams, benefit the terrestrial eco-toxicity, reduce the eutrophication impact on freshwater, and the energy and chemical savings are enough to offset the resources needed for mineral fertilizer production. The phosphorus-density of struvite is higher than that of urine and biosolids, which is why the energy savings can offset the energy needed for fertilizer production. Although this resource needs to be recovered, this life cycle assessment shows that avoiding fertilizer production cannot be the only consideration when choosing the best recovery technique[22].

Other resources that can be recovered in coordination with P include energy like methane and hydrogen, nutrients like nitrogen, other metals, like gold, and water. Currently, energy and nutrients are only recovered from 25-30% of the total available waste biomass. These two resources can be recovered at the same time by starting treatment with hydrolysis of organic solids. Energy can be recovered by anaerobic microbial technology and then pre-treatment of these systems can improve P solubilization to allow for more efficient recovery of P as well. Although recovery of nitrogen is considered low priority since it can be fixed from the atmosphere through processes like the Haber-Bosch, the energy cost and greenhouse gas emissions associated with this process will soon make recovery more economical. Metals that are found in higher abundance in wastewater include sodium, calcium, phosphorus, potassium, magnesium, iron, aluminum and titanium at levels as high as 30 g/kg. Potassium is not a concern since potash is cheap, but this should be considered for recovery with P and N since it is an essential macronutrient and used in fertilizer. Potassium struvite is one recovery method from urine that includes all three macronutrients. Water is one of the most important resources and is mostly recycled in less than 10% of wastewater systems so reuse of non-potable water and potable water is essential for the future[21].

Other considerations include the social impact of recovering resources for food production from water. Even a loss of just 1 meter of water clarity can result in up to 34% decrease in property value so maintaining high water quality is essential. Landfill fees continue to increase which motivates the need to recycle food waste and the associated nutrients. By recovering resources for fertilizer, poverty can be relieved by reducing fertilizer costs, malnutrition can be reduced by providing healthier food and income can increase from the crop market. In order to achieve all of this recovery, technological advances need to be coupled with improved business models, systems-level understanding, policy support and increased public acceptance[21].

1.1.8 Adsorption as a recovery technique

One method of recovery is through adsorption. Adsorption can occur any time a solid is exposed to a fluid, whether it is a gas or a liquid[56]. Adsorption is a viable technology for separating contaminants from fluids using solids due to low initial cost, simple design, easy operation, insensitivity to toxic substances and complete removal of pollutants even when the contaminants are at low concentrations[57]. Generally, it leads to an enhancement in the concentration of one component of the interaction, but this process is very dependent on the surface area available. Adsorption can be used for purification of liquid, pollution control, controlled drug delivery, etc[56]. It can be combined with coagulation. This technique, however, can have high operational costs, large reactors and possible effluent neutralization requirements[28].

This process has been used for a long time, connecting back to ancient times where it was used for clarifying fat and oils, for example. Charcoal was the earliest adsorbent studied extensively and connects to materials still studied today like activated carbon. Scientists have been studying this process for years with the earliest concept of an isotherm introduced in 1971.

In 1881, an isotherm with a solid/liquid interaction was discussed which led to the first mention of an ‘equilibrium concentration’. Freundlich focused on the importance of the solid surface in 1907 and McBain coined the term ‘sorption’ shortly after to explain adsorption in two stages as well as penetration in narrow pores. Zsigmondy noticed the important role of capillary condensation in physical adsorption. Langmuir published several papers in 1916-1918 that have influenced the way adsorption is characterized even today with regard to the ‘monolayer’. This method, however, was recognized by Langmuir to be over-simplified for materials with pores of a certain size. In 1938, three authors, now known as BET, noticed that a number of isotherms were S-shaped and came up with a method that is now standard for determining surface area of powders and porous solids[56]. Adsorption has a long history of study.

Various definitions have become standard when discussing adsorption and help to characterize the adsorbent. Two different types of adsorption were distinguished: physisorption, which involves van der Waals interactions, and chemisorption, which involves chemical bonding. Activated adsorption occurs when the temperature increase leads to an increase in adsorption. Pores in an adsorbent material have been categorized into three categories: micropores, mesopores and macropores. The three categories are differentiated by the internal width; micropores are less than 2 nm, mesopores are 2-50 nm and macropores are greater than 50 nm. A compact is an agglomerate that was formed by compacting powder. Adsorption hysteresis is the difference between the amounts adsorbed versus desorbed which is evident from gas-adsorption isotherms. Sphericity is used to estimate the surface area of materials by relating the shape of the particles to spheres. Porosity is found by dividing the volume of pores/voids by the total bulk volume of the solid. Pore structure can be created by a constitutive process or by a subtractive process, where pores are created by thermal decomposition of a compound[56].

Activated carbon is a very common adsorbent due to its large porous surface area, controllable structure and general stability[57]. The best adsorbents for industrial purposes have a surface area of at least 100 m^2/g. Surface area and pore size distribution are actually determined using controlled gas adsorption[56]. Not only is surface area an important factor, but other surface properties provide key factors to the success of an adsorbent. Detailed characterization must be completed to fully understand the properties of each adsorbent as well as adsorption isotherms which characterize the material related to temperature[56].

Adsorption is modeled using an isotherm that describes the dynamic equilibrium relationship between the pollutant and the solid to understand the mechanism pathways, the surface properties, the adsorption capacities of the solids and how best to design adsorption systems. Adsorption models are often linearized to understand the adsorption phenomenon occurring and extract essential adsorption parameters but nonlinear models should be further understood to provide even better understanding of the models and perhaps lead to less error[57]. Adsorption isotherms define the relationship between the amount adsorbed by a unit mass of solid and the equilibrium pressure at a known temperature. Gas-solid physisorption isotherms can be classified by common shapes. Only molecules that were physisorbed can be desorbed into the solution in its original form. Chemisorption alters the molecules so they might not desorb; chemisorption for gas-solid isotherms are described by a curve similar to the Langmuir isotherm with ‘monolayer’ adsorption. Adsorption from solution follows a Type L or Type S isotherm. Adsorption energy is controlled by the adsorbent/adsorbate pair and is difficult to quantify, but diffusion plays a critical role in this process[56]. The three fundamental approaches to isotherms consider kinetics, thermodynamics, and generating a characteristic curve. Isotherms can be based around two parameters like the common Langmuir and Freundlich models or three parameters like Redlich-Peterson and Sips models. At least 15 different isotherm models can be used to model adsorption with varying amounts of error. The main isotherms of interest include Langmuir, Freundlich, and BET. The most common method for accessing the goodness of fit of each model is linear regression with about 95% of studies of liquid-phase systems using linearization to understand models[57].

Adsorption is an appealing removal strategy because it allows for the option to then desorb phosphorus back from the material for reuse. One group of materials that have been studied are metal oxides and hydroxides like aluminum and iron materials. These materials work via ligand exchange and seem to be most effective in neutral or acidic conditions. Another material is furnace slag which contains silicates and amorphous glasses, but in small amounts only. It seems to have much lower capacity than alternative materials. Fly ash can be modified into zeolites with high cation exchange capacity, but does not prove effective in low concentration water systems. Clay is found naturally in high quantities which makes it cost effective. It is a layered alumina-silicate material like vesuvianite, montmorillonite and bentonite. Since it has layers, the interlayer spacing can be increased by adding various pillars like aluminum, iron, or lanthanum for example. Clay has a high negative surface charge which makes it good for adsorption. Equilibrium can be achieved as early as 5 hours, which is very attractive for this technology. Vesuvianite provides an interesting quality because it can float on the surface of the water for potentially easier removal from the system. Bio-waste materials are areas for further research because they are environmentally friendly, economically efficient and would be otherwise wasted materials if not for this opportunity for recycling. A couple examples are waste from oranges and egg shells. Egg shells have proven an adsorption capacity of 23.02 mg/g[35]. Adsorption has proven a simple technique with materials like calcium silicate hydrates, iron-rich sand, synthetic filtration materials and industrial by-products. Polymeric hydrogels with ion-exchangeable ceramic beads has proven successful for phosphate binding[12]. Other materials used for adsorption include phyllosilicate minerals, oxides and oxyhydroxides, porous nanosilicates, layered double hydroxides, polymer ligand exchangers, and mining, metallurgical and industrial by-products[9].

One difficulty with adsorption is the separation of the sorbent from solution once capacity has been reached. One way to avoid this trouble is to make the sorbent magnetic. Each sorbent needs to be tested for suitability as a fertilizer based on mineral composition as well as stability in weathering processes. The sorbent should not be toxic to the plants. Mono-calcium phosphate is water-soluble and completely plant-available so it is a good point of comparison for other sorbents. Zeolitized fly ash, layered double hydroxides, lithium-intercalated gibbsite, Diaion WA20 anion exchange resin, lanthanum-modified zeolite, and hybrid polymeric anion exchangers all showed potential for use directly as fertilizer[9].

Table 1 represents various adsorptive materials, like mentioned in the paragraphs above, used for recovering phosphate from water categorized by the main element or base material modified to create the adsorbents. The range of adsorption capacity is from 0.28 to 326.63 mg of phosphate adsorbed per gram of adsorbent.

Table 1
Phosphate adsorption capacity, surface area, pH, and temperature for various adsorbents.

Adsorbent	Capacity (mg g^{-1})	Surface area (m^2 g^{-1})	pH	Temperature (°C)	Reference
Clay					
Kaolinite in Iran	0.32	3.66	2-10	25	58
Bentonite in Iran	0.28	84.98	2-10	25	58
Tunisian kaolinite	38.46	68.5	3-9	25	59
Tunisian smectite	42.19	106.2	3-9	25	59
Kanuma clay with corn starch and CaO tablet	4.39	15.401	2-12	288.15, 298.15, 308.15K	60

Kanuma clay with corn starch, Fe powder, white cement and CaO tablet	3.61	15.59	2-12	288.15, 298.15, 308.15K	61
Electrochemically modified Kanuma clay tablet	5.36	16.12	2-12	288.15, 298.15, 308.15K	61
La modified bentonite	0.93	N/A	3-11	25	62
LaAl/Al pillared montmorillonite	13.022/10.307	N/A	3-8	25,30,35	63
Phoslock®	10.54	39.3	5-9	10,23,35,40	64
Zenith/Fe bentonite	11.15	N/A	5-9	15,25,35	65
Layered Double Hydroxides (LDH)					
Calcined Mg-Al-CO$_3$ LDHs	187.1*	82.5-143	3-11	25	66
Calcined hydrotalcite at 500C	244.58	250-300	9	25,45,65	67
Calcined hydrotalcite at 400C	192.9	250-300	9	25,45,65	67
Calcined Zn-Al LDH	41.26	81.2	N/A	25	68
Calcined MgMn LDH in seawater	7.5	68	3-10	10,25,40	69
Mg LDH	61	202	3-12	25	70
Dolomite LDH	36	80	3-12	25	70
Synthetic hydrotalcite	47.3	N/A	7.8	25	71
Mg-Al LDH	26.4*	64.4	7	10,25,50	72
Hydrotalcite	60	44	9	25,45,65	67
Zeolite					
Zeolite in Iran	0.37	13.83	2-10	25	58
Hydrated aluminum oxide modified natural zeolite	7	17.8	2-11	21	73
Zeolite/lanthanum hydroxide	71.94	55.69	2.5-10.5	25	74
Synthetic zeolite	52.91	74.5-174.4	3-9	25	59
La/Al modified zeolite	2.429	N/A	2-12	10,20,30	75
HUD synthetic zeolite	79.4	500	2.5-10	298K	76
Al modified HUD zeolite	75.8	642	2.5-10	298K	76
Zeolites from fly ash	11.79-47.17	29-91.49	1.58-12.11	25	77
Lanthanum					
Lanthanum hydroxide-doped carbon fiber	16.1	N/A	2-12	25	78
Commercial/synthesized lanthanum hydroxide	55.56/107.53	31.1/153.3	1.5-13	25	79
La doped silicate	26.7	763.2	2-12	25,35,45	80
La doped vesuvianite	6.7	N/A	3-13	5-35	81
La(OH)$_3$ modified vermiculites	79.6	39.1	3-11	25,30,35,45	82
La loaded granular ceramic	0.9015	26.83	2-12	20,30,40	83
Calcium					
Monohydrocalcite	1.67-3.63*	16.4	8-9	15,25,35	84
Calcite in Iran	1.82	0.98	2-10	25	58

Calcined waste eggshell	23.02	19.32	2-10	25,35,45	85
Freshwater mussel shells	6.95	N/A	1.5-9.5	25	86
Wasted scallop shell	23	N/A	2-10	15,25,35,45	87
Recycled crab shells	108.9	N/A	2-10	15-45	88
Calcite/aragonite in seawater	0.4/1*	N/A	7.2-9	5-45	89
Gas concrete	17.32	22	2,5,11.5	20,55	90
Magnesium					
MgOH in situ from diatomite	52.08	72.53	5-10	288, 298, 308, 318K	91
MgO microspheres made in water	3.17	1.82	5	30	92
MgO microspheres made in PSS	75.13	72.10	5	30	92
Natural palygorskite	3.73	206	4-9	25	93
Acid treated palygorskite	6.64	342	4-9	25	93
Acid/thermal treated palygorskite	8.31	287	4-9	25	93
Thermally treated palygorskite	42	47	3-9	25	94
Magnesium modified corn biochar	200-239	382-494	6-10	288,303,318K	95
Calcium and Magnesium					
Magnesium amorphous calcium carbonate	199.44*	70.45	6-10	25	96
Ca-Mg loaded biochar made at 600C	326.63	487.49	4-10	288, 303, 318K	97
Natural calcium-rich attapulgite	3.32	N/A	4,7,10	25	98
Half-burned dolomite	10	N/A	7.5-8.5	25	99
Dolomite	48	0.14	1-11	20,40,60	100
Iron					
E33	37.74	140.4	7	21	101
E33 coated with Mn	30.96	102.8	7	21	101
E33 coated with Ag I/II	25.52/38.80	124.6/142.0	7	21	101
FeO tailings	8.21	47.9	3-10	5,20,35	102
FeO anion exchange resin	48	N/A	7.2-7.6	24	103
Goethite	144	316	5,6.7	25,45,65	67
Zr coated magnetite nanoparticles	42.19	152.46	3-10	N/A	104
Magnetic Fe-Zr binary oxide	13.65	106.2	3-11	25	105
Iron sludge	18.7	113	7.6	N/A	106
Other					
Mesoporous ZrO_2	29.71	232	3-11	25	107
Calcite and Fe-rich calcareous soils	26	0.6	5-8	25	108
LaO on Fe_3O_4@SiO_2 magnetic nanoparticles	27.8	47.73	2-12	25	109
2 sedimentary apatites	0.31/1.09	0.72/0.57	8	22	110

3 igneous apatites	0.41/0.37/0.28	0.53/0.48/0.58	8	22	110
Aluminumoxid S	34.57	200	6	25,45,65	67
Activated alumina/2 Al-impregnated silicates	53.7/81.9/58.8*	155/343/328	6.4-7.2	25	111
Dewatered alum sludge	3.5	N/A	4.3-9	20	112
Hydrothermally synthesized silicate nanoparticles	93.46	N/A	7	303-323K	113
Alkaline residue (AR)	134.8	28.7	10.83	25	114
AR treated with NaOH	211.9	14.1	11.58	25	114
AR treated with HCl	2.2	100.6	3.96	25	114
AR calcined at 800C	139	29.31	2.5-11.5	25	114
Chitosan modified with zirconium ions	61.7	7.39	2-10	4,15,23	115
Drinking water treatment residuals	4.17-8.20	21-74	5,7,9	N/A	116
Calcined paper sludge	~113.96*	N/A	2-12	10,40,60	117
Fly ash	32	1.42	3,5,7,9,11	25,40,50,60	118
Slag	60	1.29	3,5,7,9,11	25,40,50,60	118
Portland cement	83	1.38	3,5,7,9,11	25,40,50,60	118

*Converted from original units

Adsorption does suffer from bottle-necking, which means that a material will become saturated and adsorption will no longer occur. The ideal adsorbent has high capacity for phosphate and can be reused directly or will desorb phosphate and regenerate. Fine powder is not easily reused because separation from liquid is difficult. Granulation is one technique to overcome the issue with separation but this will reduce the surface area available for adsorption[109]. Many of the above materials are powder-based or incapable of being used directly as fertilizers so these drawbacks need to be addressed. Adsorptive materials need to be durable, effective, easy to handle and allow for the option of recovering the phosphate after exiting the water system. The ideal material for this purpose would have high phosphate capacity and selectivity even in the presence of competing ions, would be capable of rapid kinetics, is low in cost especially if any separation or purification is needed, can make the phosphorus bioavailable and is highly permeable to avoid clogging. Adsorption provides a cost-effective way to recover phosphorus from liquid onto a solid for potential direct reuse or the phosphorus could be easily desorbed[9].

1.1.9 Magnesium as an adsorptive material

Hyperphosphataemia can occur in patients with chronic kidney disease that are undergoing dialysis. This condition can cause disturbed bone and mineral metabolism, cardiovascular disease and secondary hyperparathyroidism. Phosphate binders can be used to keep the phosphorus from entering the bloodstream. Calcium binders can lead to hypercalcaemia and aluminum binders are toxic. Sevelamer and lanthanum based binders are expensive. Magnesium binders may work just as well as calcium binders, but are generally combined together to reduce the calcium loading while still binding phosphate effectively. At least 12 different studies used magnesium-based binders with varying success. Magnesium hydroxide had poor gastrointestinal toleration so magnesium carbonate became more prevalent since the 1980s[119].

In a different study, two groups of patients were studied to compare treatments for hyperphosphatemia; one with calcium acetate/magnesium carbonate alone and the other with an added concurrent phosphate binder. Both groups had decreased levels of serum phosphorus at the checkpoints and were mostly able to lower phosphorus levels enough to meet the Kidney Disease Outcomes Quality Initiative target. Using this treatment was effective for binding phosphate but did increase magnesium levels enough that 67% of patients experienced some hypermagnesaemia. The ideal phosphate binder would be inexpensive, bind phosphate without side effects and would not put a high pill burden on the patients. Other binders include sevelamer or lanthanum based materials, but these are far more expensive than calcium or magnesium based materials. Aluminum based binders were found to be toxic. Calcium alone can lead to hypercalcaemia so combining with magnesium decreases this risk[120].

Magnesium carbonate could be studied further as an adsorptive material for removing phosphate from water but the powder causes clogging in water systems. A previous study focused on four different magnesium carbonates to determine how roll compaction combined with dry granulation affected the tableting. The combination allows for better flowability, less dust and does not require solvents to be used, but the tablets had less tensile strength. The surface area of the materials ranged from 7.6 to 21.9 m^2/g and XRD analysis proved hydromagnesite was present in all four. Magnesium carbonate is a white odorless powder that is practically insoluble in water but does dissolve in dilute acid. It is used as a magnesium supplement, a component of antacids, a filler for tablet production, an additive for baking powder and to prevent salt lumping. The study found a positive correlation between surface area and tensile strength and a negative correlation between relative tablet density and tensile strength[121].

Magnesium, in the divalent form, is the fourth most abundant cellular metal ion, the second most abundant in the hydrosphere, and the sixth most abundant in the lithosphere. It is a cofactor for enzyme and RNA nuclease activity[122]. Magnesium is one of the essential macronutrients for crops as a participant in photosynthesis, chlorophyll production, and nucleic acid stabilization. Deficiencies can occur so some fertilizers contain magnesium as well[123]. Based on Table 1, magnesium and similar materials have been successfully used for environmental adsorption and magnesium has shown to be an effective phosphate binder for medical purposes. Based on using magnesium-based materials for phosphate binders in the medical field, the ability to make it into tablets and the general success of adsorption as a method for recovery phosphate from water, this current study was conducted.

1.2 Project Objective

The objective of this study was to optimize the phosphate adsorption capacity of pellets made from magnesium carbonate through addition of varying amounts of a cellulose binder. The binder material provided stability, but was removed enough through calcination to create pores in the pellet for additional adsorption surface area. The effect of mixing in cellulose and subsequent calcination was expected to impact several factors, as seen in Figure 1.

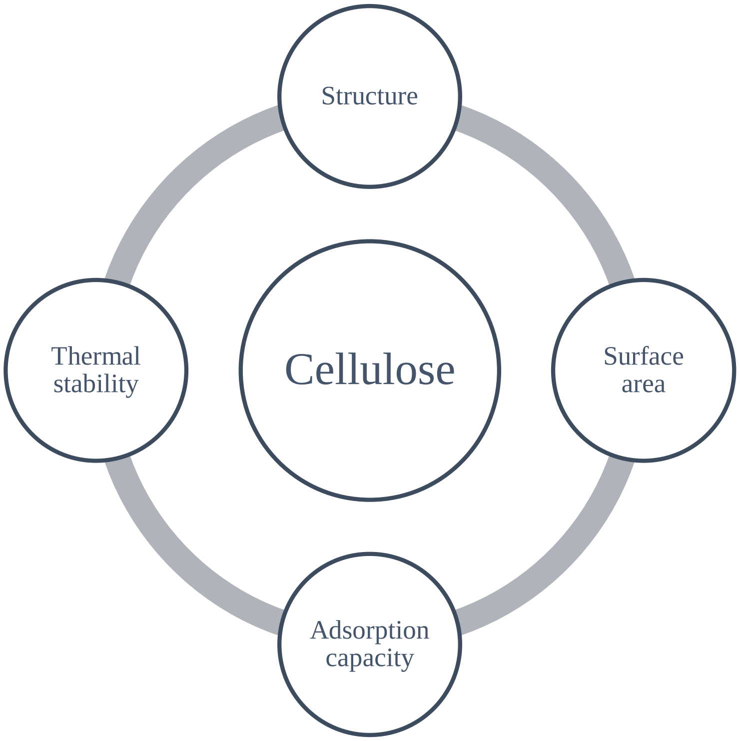


Figure 1 The factors adding cellulose impacted in the pellet synthesis and optimization for phosphate adsorption.

It was expected that calcination of the pellet with the most cellulose would have the highest surface area, which would increase the adsorption capacity. Mixing the two materials and calcining, however, changed the structure and affected the thermal stability of the pellet so an optimum level of cellulose was determined. Following pellet synthesis, physiochemical properties such as surface area, thermal stability, surface morphology, elemental composition, and crystal structure of the materials were characterized using Brunauer, Emmett and Teller (BET) surface area analysis, thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Phosphate adsorption was measured by batch studies which investigated the kinetics as well as developed isotherms for varying compositions of the pellets. Following adsorption studies, the pellets were also studied for potential desorption since the goal was to create a pellet that could adsorb phosphate and then be directly applied as a slow release fertilizer.

Chapter 2: Materials and Methods

2.1 Materials

Analytical grade $MgCO_3$ powder (Fisher Scientific) was made into pellets using the MZL Flat Die Pellet Mill (Xuzhou Orient Industry) as seen in Figure 2.

Figure 2 Pellets were synthesized with magnesium carbonate and cellulose for phosphate adsorption (photo by E. Martin).

A cellulose binder, average particle size of 20 µm (Sigma Aldrich), was used to optimize the pellet design. Pellets were made with a constant moisture content of 45% water to $MgCO_3$ weight ratio. Cellulose was added in varying weight ratios from 0 – 20%. Conditions for use of the pellet mill were kept as consistent as possible, but the instrument did allow for variation as related to the length of pellets made. After synthesis, the pellets were calcined at 300 °C in the A-550 oven (Ney Vulcan) for various times to remove cellulose for additional porosity without complete decomposition of the magnesium carbonate. The phosphate stock solution was created using analytical grade sodium phosphate monobasic dihydrate ($NaH_2PO_4 \cdot 2H_2O$) (Fisher Scientific).

2.2 Characterization

The BET surface area was determined using the NOVA 2000e Surface Area & Pore Size Analyzer (Quantachrome). Samples were first purged with nitrogen gas at 150 °C overnight before analysis. Pellet composition was examined using SEM-EDS (EDAX JEOL 7401) to perform both a line scan and cross section scan of the pellet. The uniformity was determined by comparing the percentage of carbon (C), oxygen (O) and Mg present across each scan. The thermal stability of the pellets was determined using TGA Q500 (TA Instruments) where temperature was first equilibrated at 50 °C then ramped up to 900 °C at 20 °C/min. The surface morphology of the $MgCO_3$ pellets was observed using SEM (Philips XL 30 ESEM-FEG) at an accelerating voltage of 30 kV. The crystal structure was determined using XRD (PANalytical X'Pert) with the 2-theta diffractometer under CuK_α radiation and a wavelength of 1.54 µm and the XRD patterns were analyzed using JADE software (MDI, Inc.)

2.3 Adsorption Experiments

Preliminary batch studies assessed the potential adsorption capacity of around 35 different combinations of cellulose ratio (from 0 – 20%) and calcination time (from five minutes to two hours and 17 hours) in order to limit the number of pellet recipes studied further through kinetics and isotherm tests. The studies provided a general sense of the capacities of each of the recipes without reaching equilibrium. One pellet from each recipe was placed into 125 mL polypropylene bottles (Nalgene) with 100 mL of a phosphate stock solution with target concentration of 160 mg L^{-1} and placed on a G10 Gyrotary shaker (New Brunswick Scientific Co., Inc., USA) at 150 rpm. Samples of the phosphate concentration remaining in solution were taken after one day and after five days to evaluate the effect of cellulose content and calcination time on the adsorption capacity. As part of the preliminary work to better understand phosphate adsorption, a buffer study was conducted in an attempt to control the pH of the solution. For attempting to maintain a pH 7 solution, propanesulfonic acid, aka MOPS buffer (Sigma Aldrich) was used. The MOPS concentration was varied from 1.5 mM to 15 mM to 150 mM to try to maintain a pH of 7 throughout the preliminary experiments. From these studies, five specific pellet conditions were selected for further study with regard to cellulose ratio and calcination time: 0% cellulose calcined for 17 hours (0%17), 5% cellulose calcined for 1 hour (5%1), 10% cellulose calcined for 2 hours (10%2), 15% cellulose calcined for 1 hour (15%1) and 20% cellulose calcined for 2 hours (20%2).

The optimum surface area was investigated through changing the length of the pellets used for adsorption. The goal was to determine if cutting the pellets into shorter pieces and using the same mass resulted in higher adsorption capacity. Three variations were considered: the full 380 mm^3 surface area, using two halves at 430 mm^3 together, and using four quarters at 550 mm^3 together. The pellets were placed into 125 mL polypropylene bottles with 100 mL of a phosphate stock solution with target concentration of 160 mg L^{-1} on the shaker at 150 rpm. Samples of phosphate concentration remaining in solution were taken daily over four days just to capture a change in adsorption capacity instead of waiting until equilibrium.

Kinetic experiments were conducted to understand the adsorption reaction rates between adsorbate and adsorbent phosphate concentration. The initial conditions for the kinetic study were: (i) adsorbent amount: one pellet, (ii) temperature: 22.7 °C ± 0.5, (iii) pH: 7.0 ± 0.1, (iv) target phosphate concentration: 160 mg L^{-1}, and (v) mixing speed: 150 rpm. The study was conducted with 125 mL of the sodium phosphate monobasic dihydrate stock solution mixed with the five different $MgCO_3$ pellet compositions in 125 mL bottles and placed on the shaker. Samples were taken at various times (1, 2, 3, 4, 7, 9, 11, 14, 18 and 25 days) to analyze for phosphate concentration remaining in the solution.

Next, an isotherm experiment was completed with varying sorbent masses, from 1 (~0.4 g) to 6 (~2.4 g) pellets, to find the maximum equilibrium adsorption capacity of each material. The phosphate concentration in the stock solution was first 160 mg L^{-1} then raised to 330 mg L^{-1} but, otherwise, the conditions were the same as for the kinetics studies. The various 125 mL bottles were left on the shaker for 25 days to reach equilibration and then analyzed for phosphate concentration remaining in solution. An additional isotherm experiment, with the 330 mg PO_4^{3-} L^{-1} stock solution, for the 15%1 pellet was conducted in triplicate to determine reproducibility. Otherwise, each adsorption experiment was conducted once and all of the analysis was conducted in duplicate and averaged. All of the samples from the adsorption studies were filtered using a 0.45 µm nylon syringe filter (Whatman) and analyzed for phosphate using a UV-Vis spectrophotometer (DR 2700, HACH) via the US EPA PhosVer 3® (Ascorbic Acid) method at 880 nm.

2.4 Desorption Experiment

Desorption experiments were conducted using 4 – 6 pellets from the isotherm adsorption experiment in various solutions to analyze the recovery of phosphate. Two solutions varied pH in an attempt to achieve desorption: 0.1 M HCl (pH <2) and 0.1 M NaOH (pH ~ 12.4). Pellets were also placed into deionized water (pH ~ 6.6) just to measure leaching. The spent adsorbents were placed in 125 mL bottles with 125 mL of each various solution and left on the shaker at a mixing speed of 150 rpm for 25 days, as with the isotherm experiments. The concentration of phosphate that returned to the solution was measured using the US EPA PhosVer 3® Method mentioned in Section 2.3 and the desorption percentage of phosphate was calculated. This experiment provided insight into the ability of the pellets to release phosphate as a potential slow release fertilizer.

Chapter 3: Results and Discussion

3.1 Characterization

3.1.1 General Characteristics

Pellets were synthesized with magnesium carbonate and cellulose in varying in weight ratios and calcined in the oven to create additional internal surface area. The pelletizer instrument allowed for variation in length of the pellets but diameter was controlled by the die hole size. This meant the standard deviation of diameter was small while the deviation in length was large. The volume and surface area were both influenced by the variation in length. Overall weight change caused from calcination reduced the pellets' weights by about half, which led to an average of 0.4 g per pellet. The variation in general characteristics is presented in Table 1. The weight change and weight were averaged across the different pellet recipes but were influenced by the amount of cellulose present in the recipe.

Table 1 General characteristics of pellets synthesized with magnesium carbonate and cellulose.

Characteristic	
Diameter	6.0 mm ± 0.05
Length	17.0 mm ± 2.13
Volume	480.8 mm^3 ± 61.56
Surface area	377.0 mm^2 ± 40.63
Weight change from calcination	-54% ± 7%
Weight	0.4 g ± 0.05

3.1.2 BET Surface Area

The BET surface area of each of the five chosen pellet recipes was determined and compared with the cellulose weight ratio to determine the effectiveness of calcination to create additional porosity as shown in Figure 3.

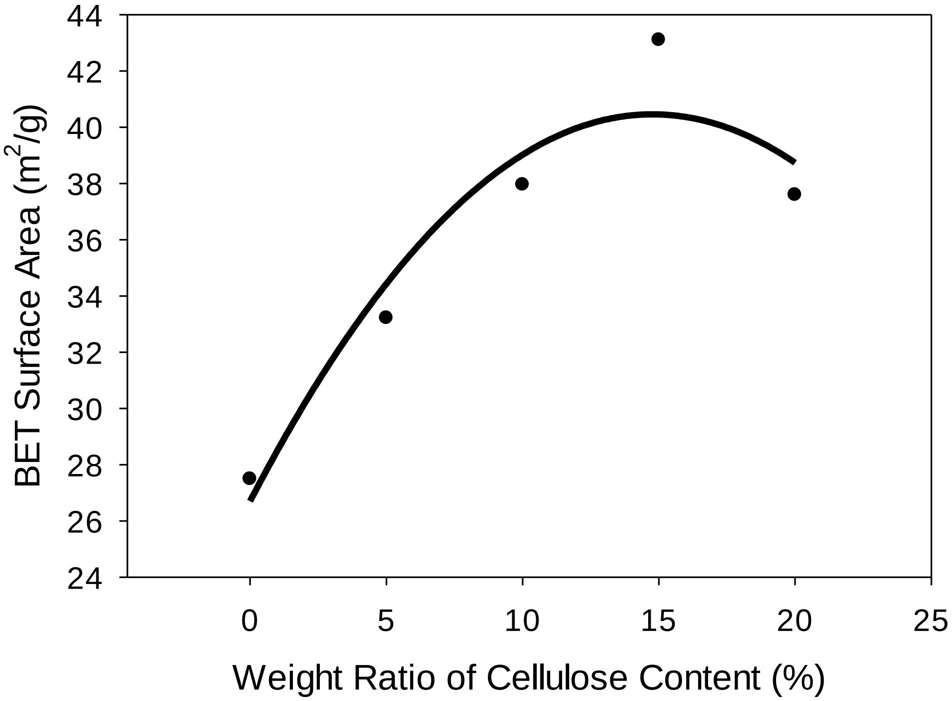


Figure 3 BET surface area compared with cellulose percentage for the four various pellet recipes.

The BET surface areas for the 0%17, 5%1, 10%2, 15%1, and 20%2 pellets were 27.5, 33.2, 36.9, 43.1, and 37.6 m^2 g^{-1}, respectively. As the ratio of cellulose increased, the BET surface area increased until the 20%2 sample. At this point, the stability of the pellet in water began to be lost and more char was present which accounted for the loss in surface area from clogging the pores. As expected, the addition of cellulose provided additional internal surface area.

3.1.3 Uniform Composition

The next step for pellet characterization was to ensure that the pellets were uniform in composition. Two separate batches of a pellet from the same recipe, namely the 15%1 pellet, were investigated for composition. One pellet from each batch was analyzed using SEM via a line scan as well as a cross section scan. The elemental composition of these pellets prior to adsorption was determined using EDS for Mg, O, and C. Figure 4 shows the percentage range of each element across the particular scan of the pellet.

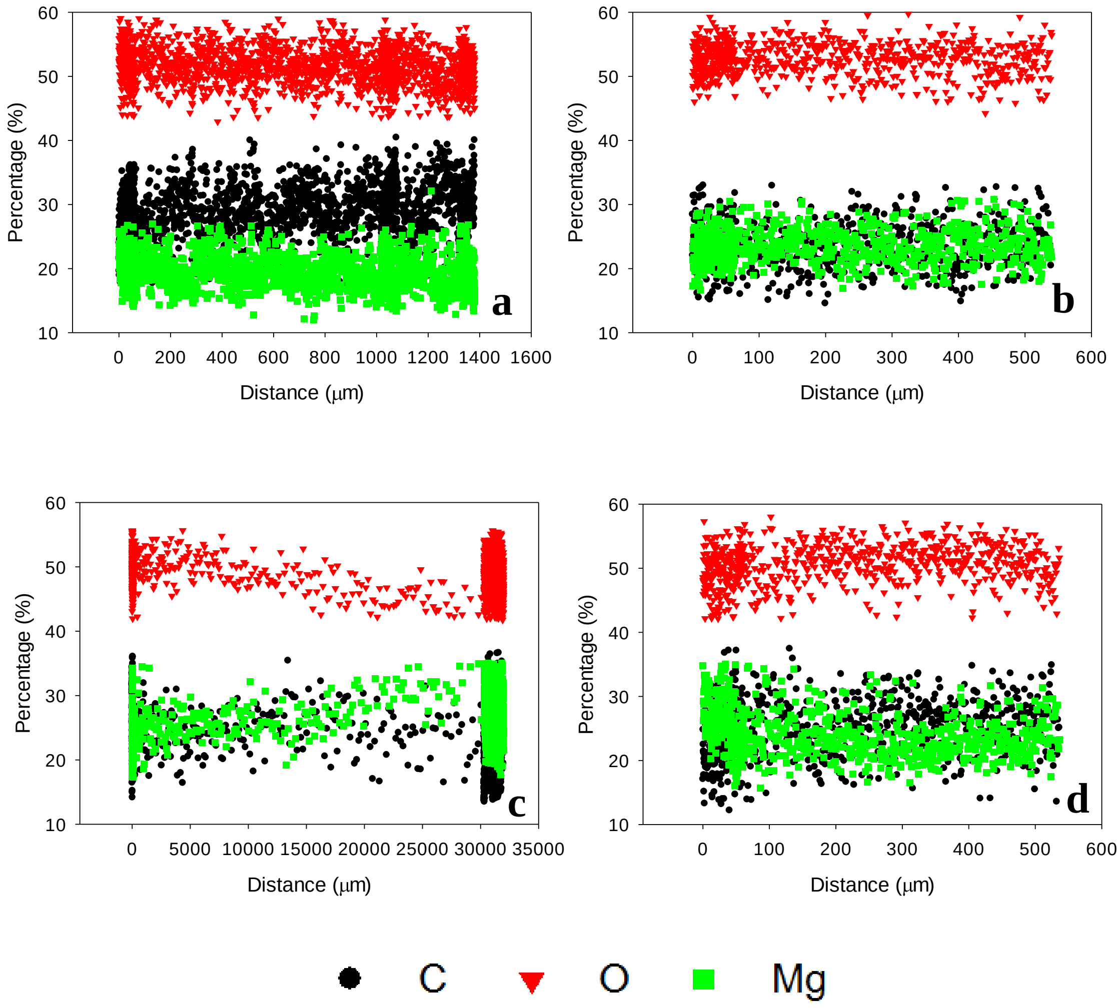


Figure 4 Line and cross section scans of two 15%1 samples for carbon, oxygen and magnesium;(a) line scan of sample 1, (b) cross section scan of sample 1, (c) line scan of sample 2, (d) cross section scan of sample 2.

The two cross section scans have the same distance scanned because the diameters of the pellets were limited to the diameter of the die hole on the pelletizer, which was about 6 mm. The line scans show the variety in length of the two pellets. Overall, the range of percentages of each element were consistent for the two pellets in both the line scan and the cross section scan. The carbon and magnesium percentages ranged from 15 – 35% and the oxygen ranged from 45 – 60%. This showed uniform composition between the two batches and demonstrated the random distribution of each element within the pellet.

3.1.4 Thermal stability of the pellets

The thermal stability of the pellets was investigated to determine if mixing cellulose, water and magnesium carbonate together to make pellets then putting the product into the oven would affect the decomposition temperature. The 0%17 pellet provided a control group to determine if adding cellulose alone affected the thermal stability. Figure 5 presents the loss in weight as the sample were exposed to higher temperatures.

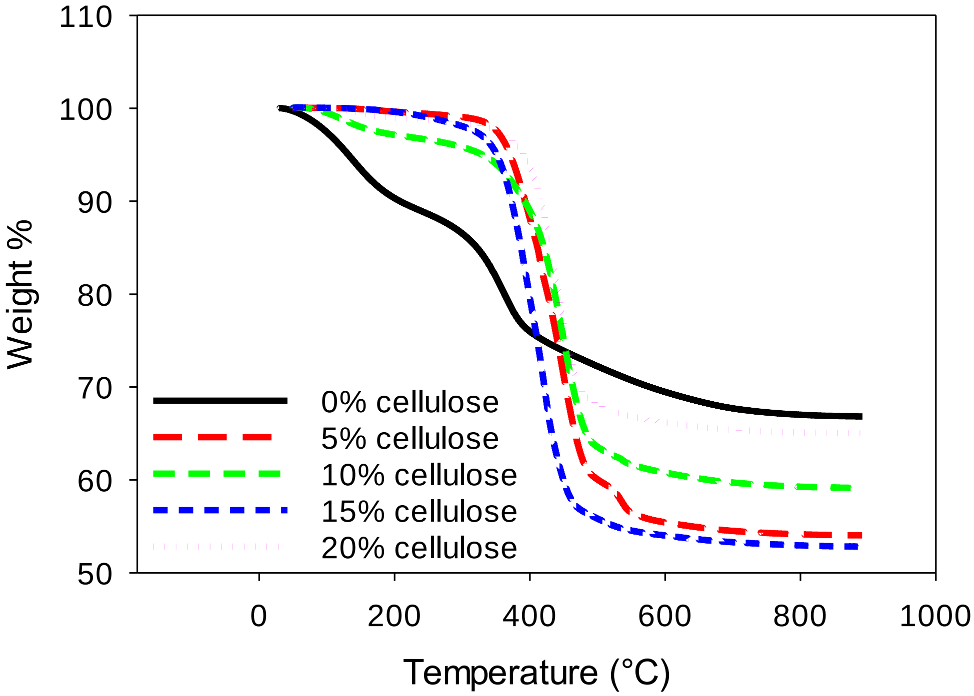


Figure 5 Thermal stability of the 5 various pellet recipes as compared to the $MgCO_3$ control.

The 0%17 pellet had a peak for onset degradation temperature at 319 °C as the baseline. The pellets with cellulose showed improvement in onset decomposition temperature. The onset decomposition temperatures for the 5%1, 10%2, 15%1, and 20%2 pellets were 384, 399, 364 and 403 °C, respectively. Cellulose provided binding and increased the thermal stability up until the 15%1 pellet where porosity took control and slightly decreased the stability; the 15%1 pellet, however, still had a higher onset degradation temperature than the 0%17 pellet. The 20%2 pellet increased in thermal stability again because this pellet had more char present on the surface and in the pores which added to thermal stability since carbon had higher stability than the original pellet.

3.1.5 Surface morphology of the pellets

Figure 6 shows SEM images of the surface of the 0% cellulose baseline pellet and the 10% cellulose pellet before and after phosphate adsorption. Many particulate aggregates were observed on the surface of the $MgCO_3$ pellets before phosphate exposure. To confirm phosphate adsorption on the surface of the pellet, the elemental composition was checked with EDS. A clear peak was seen for phosphorus on the 10%2 pellet while the 0%17 pellet did not have such a clear peak. This illustrated that increased cellulose content resulted in an increase in phosphate adsorption, as expected.

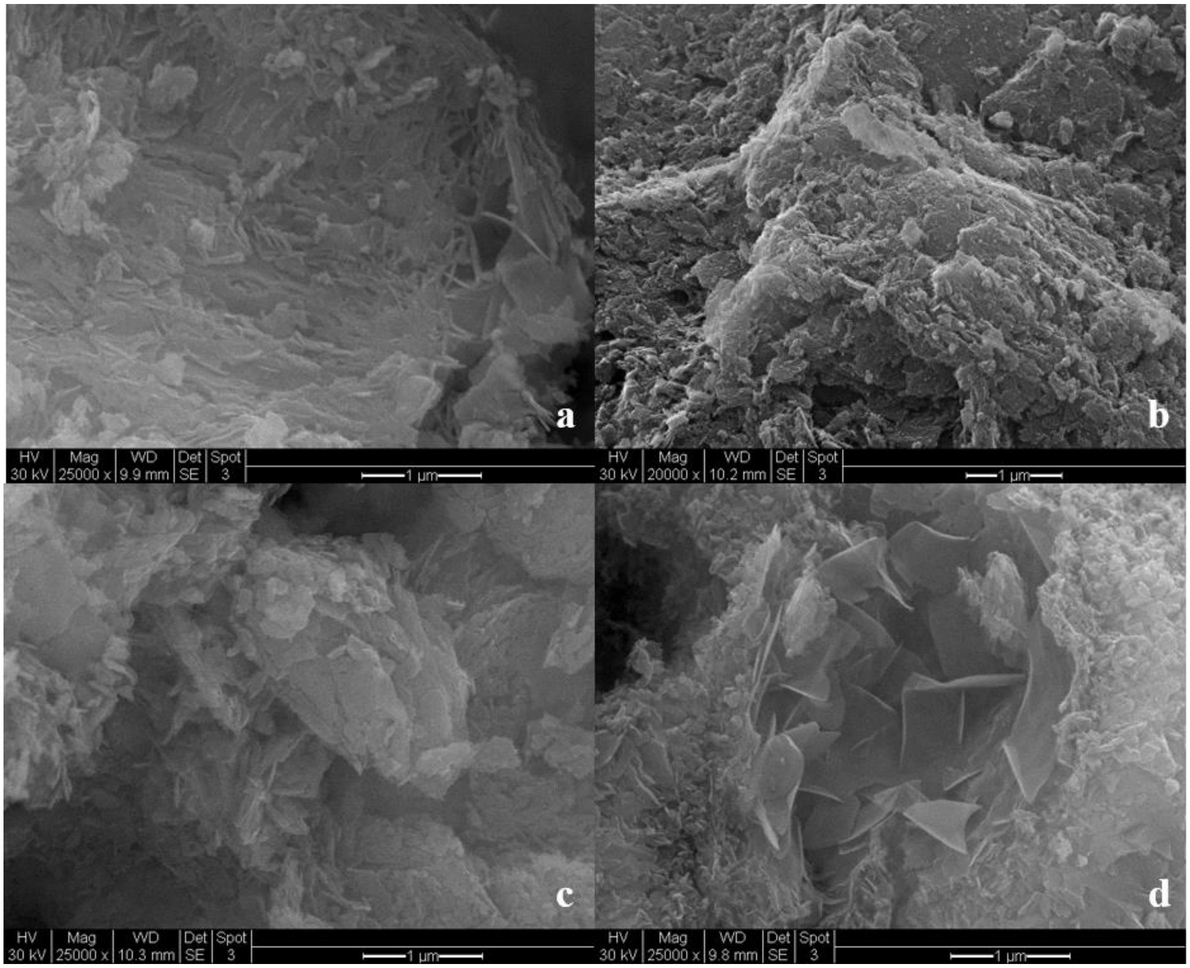


Figure 6 SEM images of (a) 0%17 pellet before adsorption, (b) 0%17 pellet after adsorption, (c) 10%2 pellet before adsorption and (d) 10%2 pellet after adsorption (all scale bars represent 1 µm).

3.1.6 XRD Analysis

The XRD patterns for each sample before and after an adsorption isotherm showed that cellulose, periclase (MgO) and brucite (MgOH) were present for the pellets before adsorption. As shown in Figure 7a, the pellets had both variations of magnesium present due to mixing magnesium carbonate with water and then calcining the pellets. After adsorption experiments were conducted, magnesium variations were detected mostly as hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) with some remaining brucite and magnesium phosphate (as cattiite) as shown in Figure 7b. The pellet with the most phosphate present was the 15%1 pellet as seen with the highest peak of cattiite. Finding magnesium phosphate after the adsorption experiments further confirmed that adsorption occurred and that the increased surface area from cellulose addition was providing additional adsorption capacity.

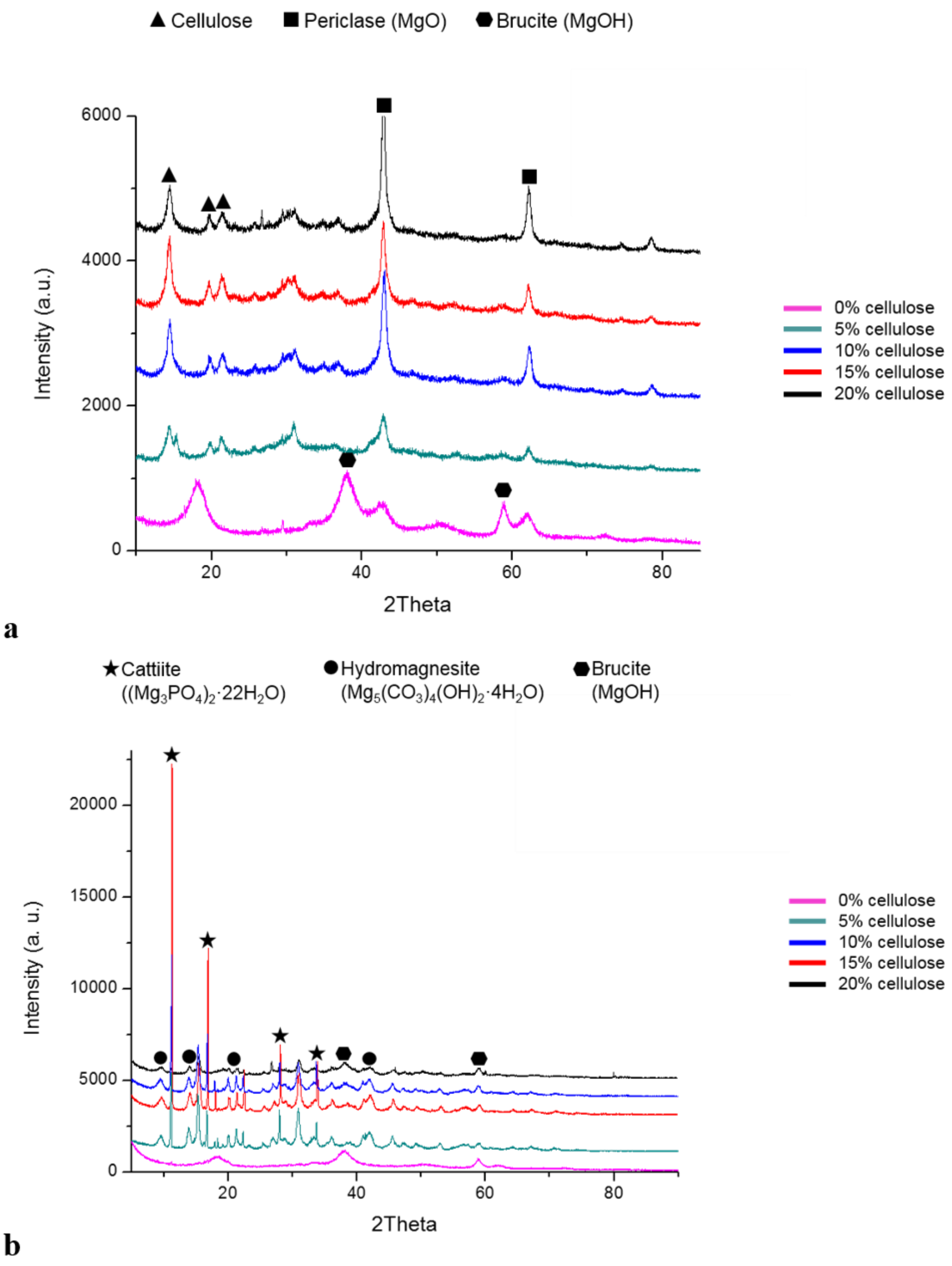


Figure 7 XRD patterns of the various pellets (a) before and (b) after adsorption isotherms were conducted.

3.2 Adsorption Experiments

3.2.1 Preliminary

$MgCO_3$ pellets were prepared with a constant weight ratio of water and varying ratios of cellulose. The pellets were then calcined at 300 °C for various times to achieve additional porosity without losing stability. Preliminary batch studies were conducted to determine the highest cellulose content that could be used before stability was lost through the calcination as well as to determine the best cure time for each pellet design. Stability was determined through a qualitative measurement when the pellet was put into water. Based on the best adsorption capacities from the preliminary studies, Figure 8 reveals a cellulose ratio curve indicating 10% cellulose as the potential optimum weight ratio with the capacity dropping as 20% cellulose was reached. The 20% cellulose pellet also had the least visual stability in water so no higher cellulose ratio was studied.

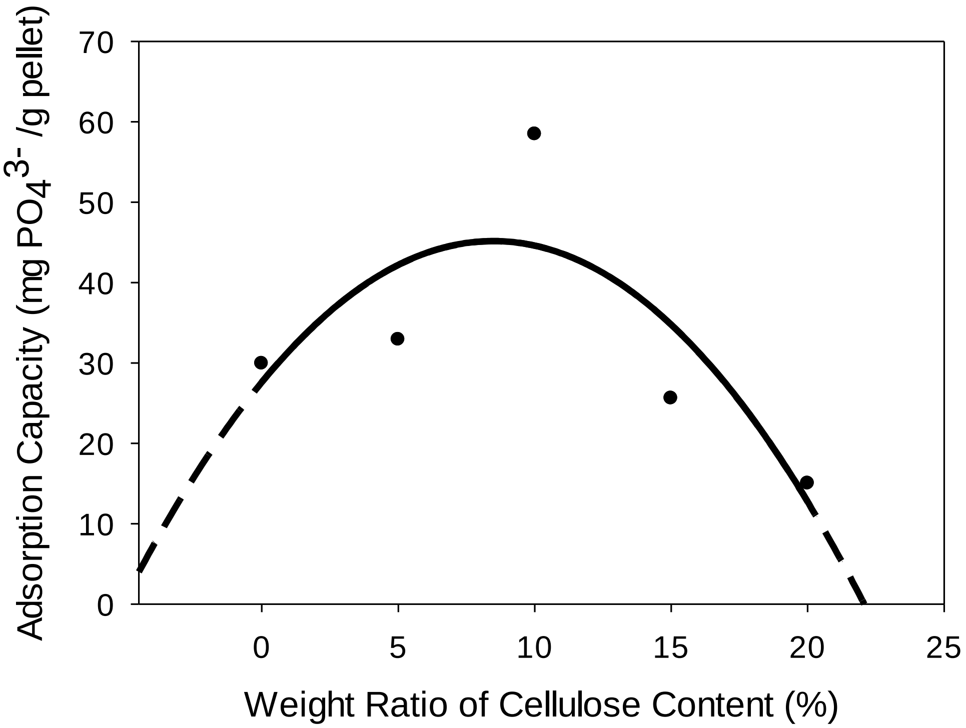


Figure 8 Adsorption capacity for various pellet recipes with varying cellulose content.

This assumption was carried through into developing kinetics and isotherms for only one cure time for each cellulose ratio prepared (0, 5, 10, 15, 20%). One or two hours of calcination at 300 °C were chosen for each cellulose ratio except the pure $MgCO_3$ pellet. The 0% cellulose pellet was used as a baseline for optimizing porosity so the longest oven time was used (overnight for approximately 17 hours). Five different pellet recipes were studied further: 0% cellulose in the oven for 17 hours (0%17), 5% cellulose in the oven for one hour (5%1), 10% cellulose in the oven for two hours (10%2), 15% cellulose in the oven for one hour (15%1), and 20% cellulose in the oven for two hours (20%2).

The buffer study conducted with varying amount of MOPS did not reveal a certain concentration that helped improve the adsorption capacity consistently. The pH was not maintained at 7 even with the highest concentration, 150mM, of MOPS over even just 24 hours. This study revealed that MOPS buffer was not effective at maintaining a pH so all studies conducted after this study did not include buffer. Instead, the pH was adjusted in the original stock solution to 7 and then left to change once the pellets began to influence the solution. The magnesium carbonate pellets generally increased the pH of the solution to 10-11.

An adsorption experiment was conducted to determine the equilibrium time for the phosphate concentration remaining in the solution after pellets had reached adsorption capacity. Figure 9 shows how the phosphate concentration in solution changed with respect to time and suggested an apparent equilibrium time of 600 hours or 25 days. Each recipe removed a different overall percentage of phosphate; 0%17 removed 34%, 5%1 removed 80%, 10%2 removed 72%, 15%1 removed 95% and 20%2 removed 81%.

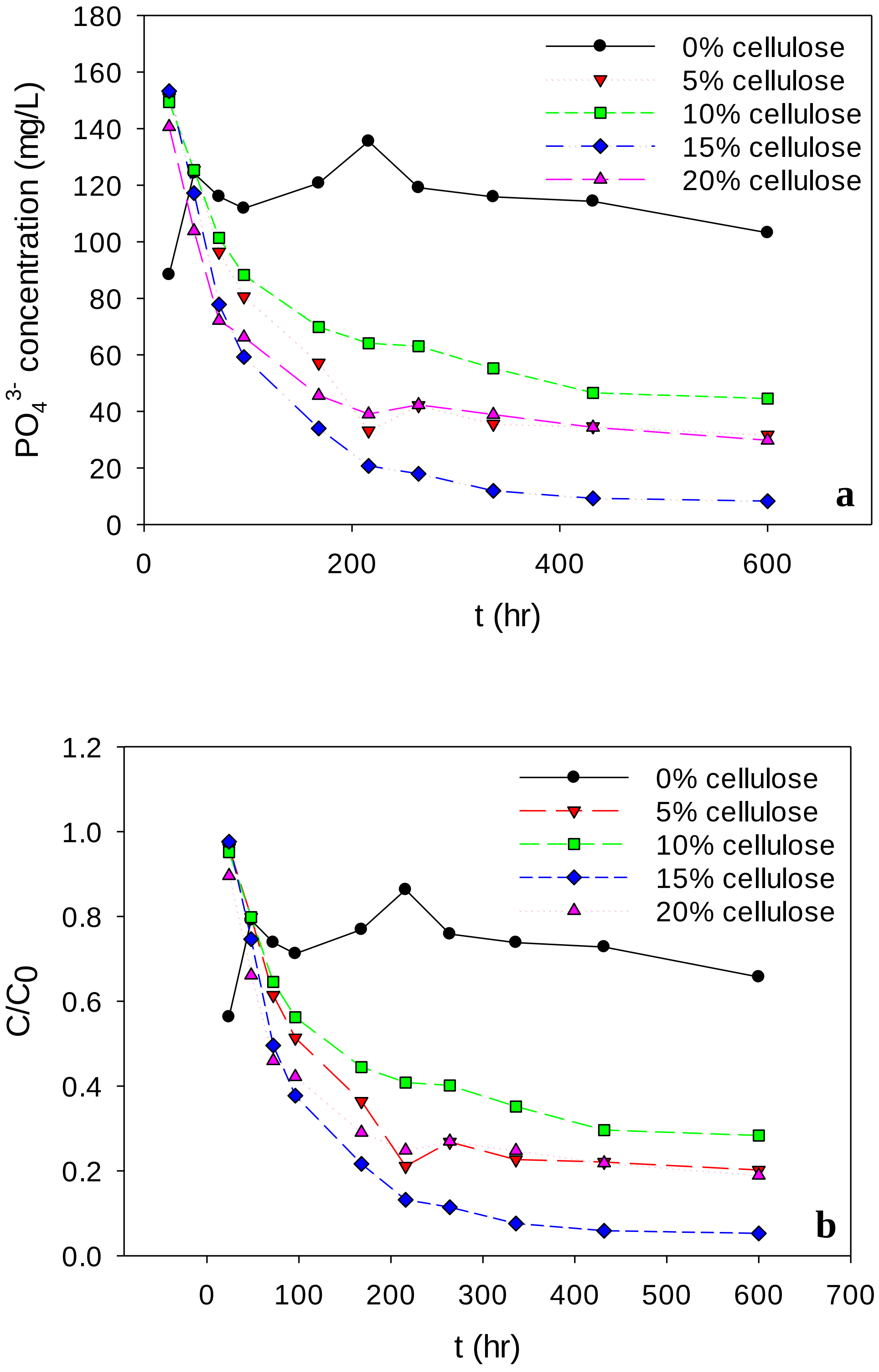


Figure 9 Phosphate concentration (a) remaining in solution over time as the various pellet recipes reach adsorption capacity and (b) concentration changed over time normalized by initial concentration.

3.2.2 Optimum Surface Area

To study the best dimensions for the physical size of the pellet, pellets were studied with the varying surface area of 380 mm^3, 430 mm^3, and 550 mm^3 via cutting the pellets. Although the pellets were cut, the overall mass used was kept consistent. The adsorption experiment was over just four days to investigate the change in adsorption capacity of the three conditions, including the full pellet as a reference baseline. Figure 10 shows the change in adsorption capacity over the four days for each surface area condition for the four pellet recipes.

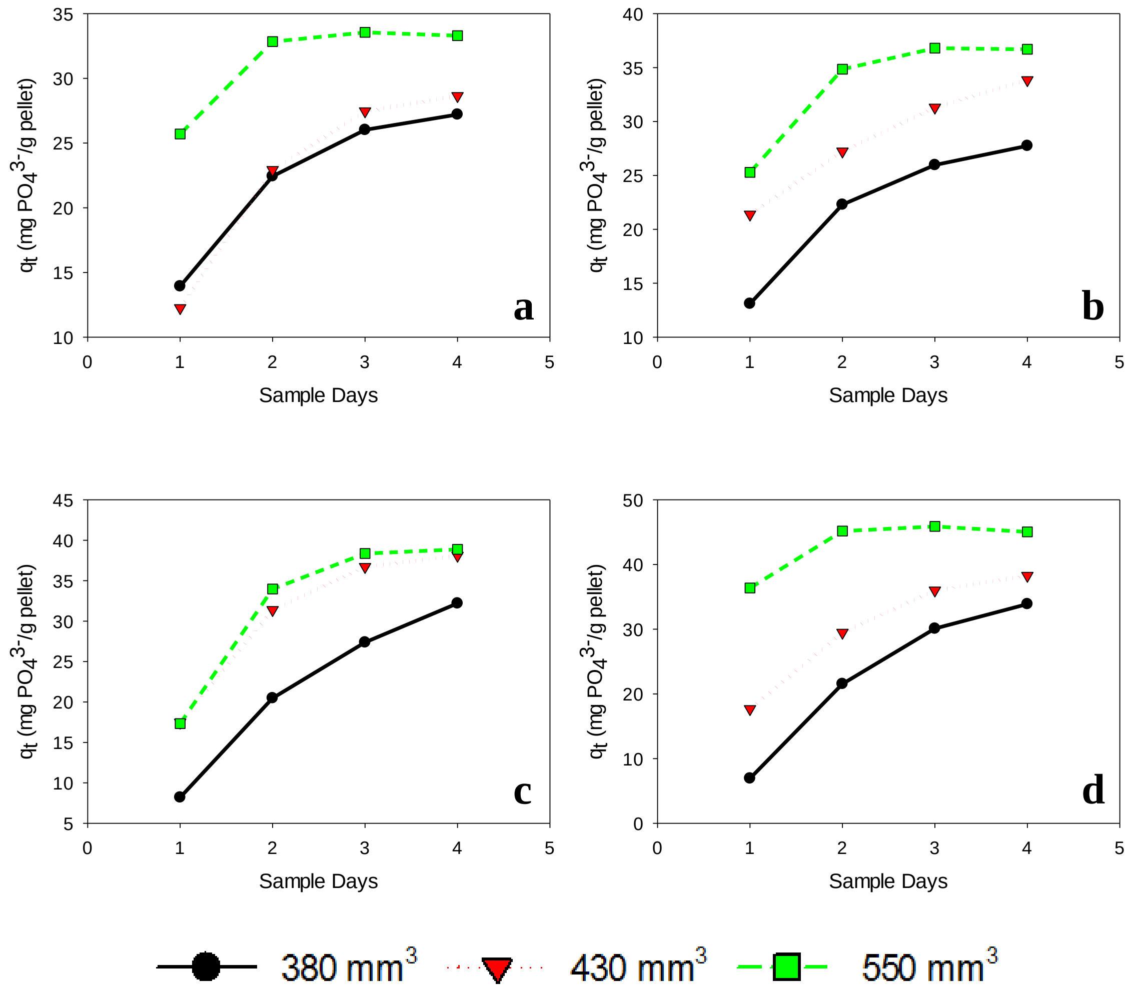


Figure 10 Adsorptive capacity for the three different surface area conditions for (a) 5%1, (b) 10%2, (c) 15%1 and (d) 20%2.

Overall, each pellet recipe had a higher adsorption capacity with the decrease in pellet length. This was expected since cutting the pellet exposed another surface for adsorption and illustrated that adsorption was occurring on the surface of the pellets. Figure 11 illustrates that each variation in surface area still has the same overall trend in adsorption capacity, namely that the capacity increases with the increase in cellulose content.

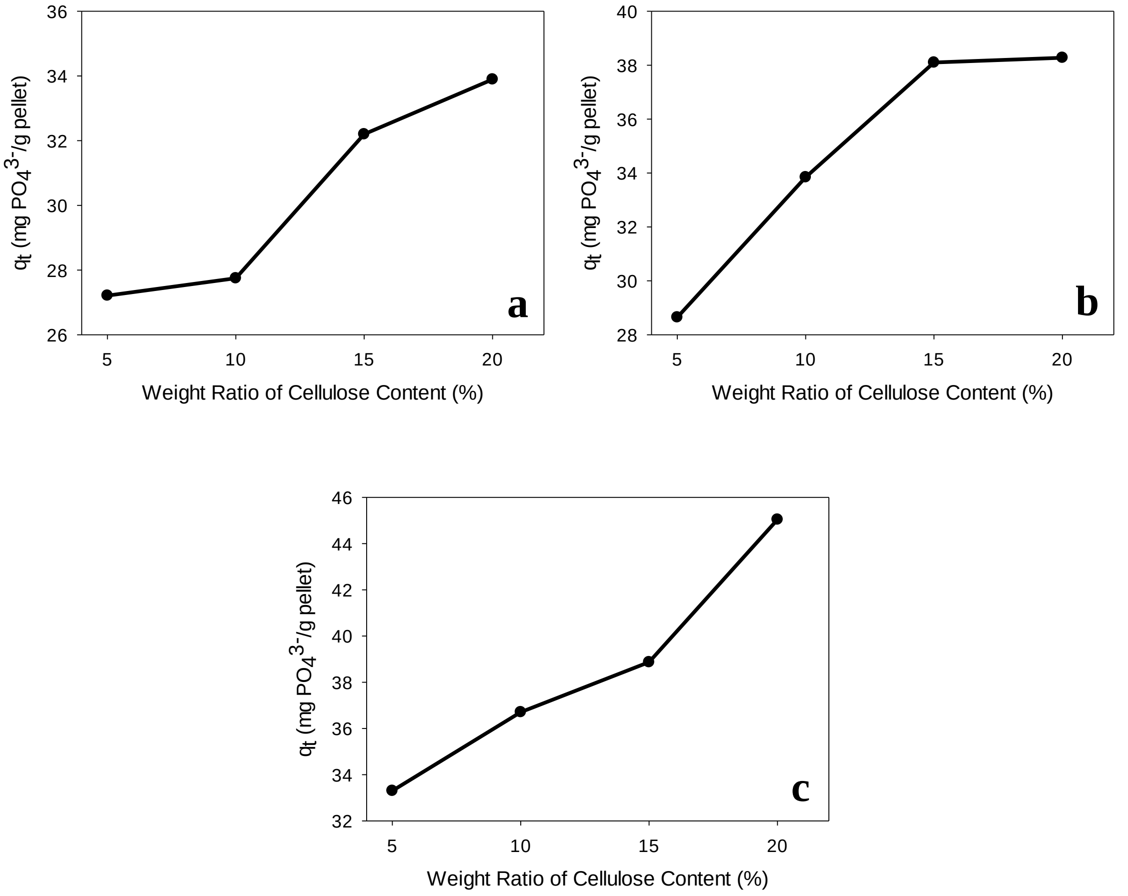


Figure 11 Adsorptive capacity for the three different surface area conditions for (a) 380 mm^3, (b) 430 mm^3, (c) 550 mm^3.

3.2.3 Kinetic Studies

Batch experiments, with one pellet in 125 mL of a solution with target phosphate concentration of 160 mg L^{-1}, were conducted to determine the rate of phosphate adsorption, specifically to find the order of the rate constant. The kinetics of each of the five pellet recipes were studied and compared with the *pseudo*-first order (Figure 12a) and *pseudo*-second order (Figure 12b) kinetics models to find the best fit using a linear regression analysis. The linear forms of the models, the parameters, and how the parameters correlate with each model (R^2) are listed in Table 1. The pellet recipe without cellulose is not included since it is the baseline.

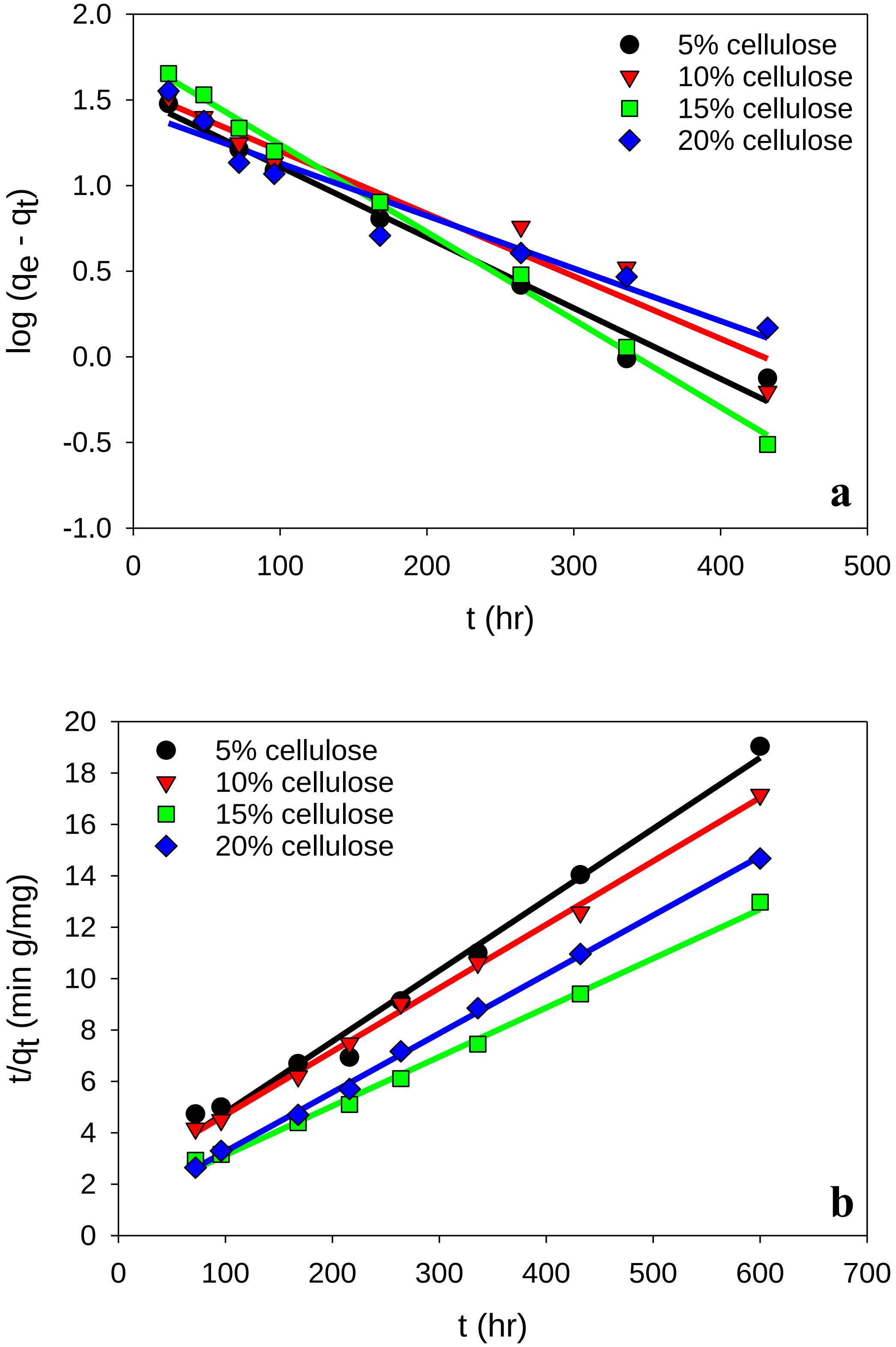


Figure 12 Linearized (a) *pseudo*-first-order kinetics model and (b) *pseudo*-second-order model applied on the four various pellet recipes.

The *pseudo*-first-order model and *pseudo*-second-order model are, respectively, as follows:

$$\log(q_e - q_t) = \log(q_e) - {}^{k_1 t}/_{2.303} \qquad (1)$$

$$^{t}/_{q_t} = {}^{1}/_{k_2 q_e^2} + {}^{t}/_{q_e} \qquad (2)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}) at equilibrium, q_t is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}) at time t, k_1 (hr^{-1}) and k_2 (g mg^{-1} hr^{-1}) are the rate constants for the *pseudo*-first-order model and *pseudo*-second-order model, respectively. The linear forms of the models, the parameters, and how the parameters correlate with each model (R^2) are listed in Table 2. The pellet recipe without cellulose is not included since it is the baseline.

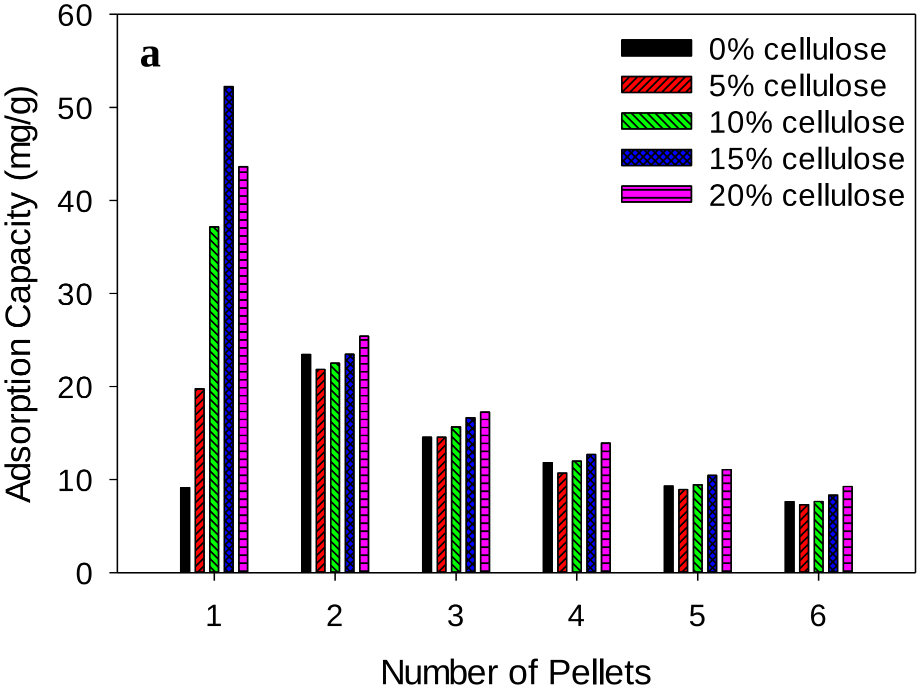
Table 2 Adsorption kinetic models, the corresponding linear forms and parameters of $MgCO_3$ pellets with various amounts of cellulose for 4 different synthesis conditions with initial pH 7 at 23 °C.

Sorbent	***Pseudo*-first-order** $\log(q_e - q_t) = \log(q_e) - {}^{k_1 t}/_{2.303}$			***Pseudo*-second-order** $^{t}/_{q_t} = {}^{1}/_{k_2 q_e^2} + {}^{t}/_{q_e}$		
	q_e (mg g^{-1})	k_1 (hr^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1} hr^{-1})	R^2
5%1	33.34	0.0095	0.9824	36.22	0.0004	0.9880
10%2	36.91	0.0084	0.9497	40.50	0.0003	0.9979
15%1	56.49	0.0118	0.9959	52.25	0.0003	0.9959
20%2	27.48	0.0071	0.9312	43.54	0.0005	0.9988

Overall the best fit model was the *pseudo*-second-order model with $R^2 > 0.98$ for all pellet recipes, but the *pseudo*-first-order model fit all recipes with $R^2 > 0.93$ so both models had strong correlation. The *pseudo*-second-order model indicates that the adsorption that occurred was chemisorption, which assumes monolayer adsorption. The highest model adsorption capacity for both models occurred for the 15%1 pellet; q_e was 56.49 mg g^{-1} for *pseudo*-first-order and 52.25 mg g^{-1} for *pseudo*-second-order. In the *pseudo*-second-order model, $k_2 q_e^2$ represents the initial adsorption rate. The rate for the 5%1, 10%2, 15%1 and 20%2 pellets were as follows: 0.492, 0.449, 0.823 and 1.021 mg g^{-1} hr^{-1}, respectively. This means that although the 15%1 pellet has the highest adsorption capacity, the 20%2 recipe had the fastest initial adsorption rate with 15%1 as a close second.

3.2.4 Sorption Isotherms

Sorption isotherms describe the relationship between the equilibrium adsorbate concentration in the solution and the amount of phosphate adsorbed on the adsorbent. Batch experiments, with one to six pellets in 125 mL of a solution with target phosphate concentrations of 160 mg L^{-1} and 330 mg L^{-1}, were conducted to determine the maximum adsorption capacity of the pellets. The two studies were compared for overall adsorption capacity of phosphate concentration from solution as the adsorbent mass was increased. Figure 13a and 13b represent the two isotherms for overall adsorption capacity on a number of pellets basis.



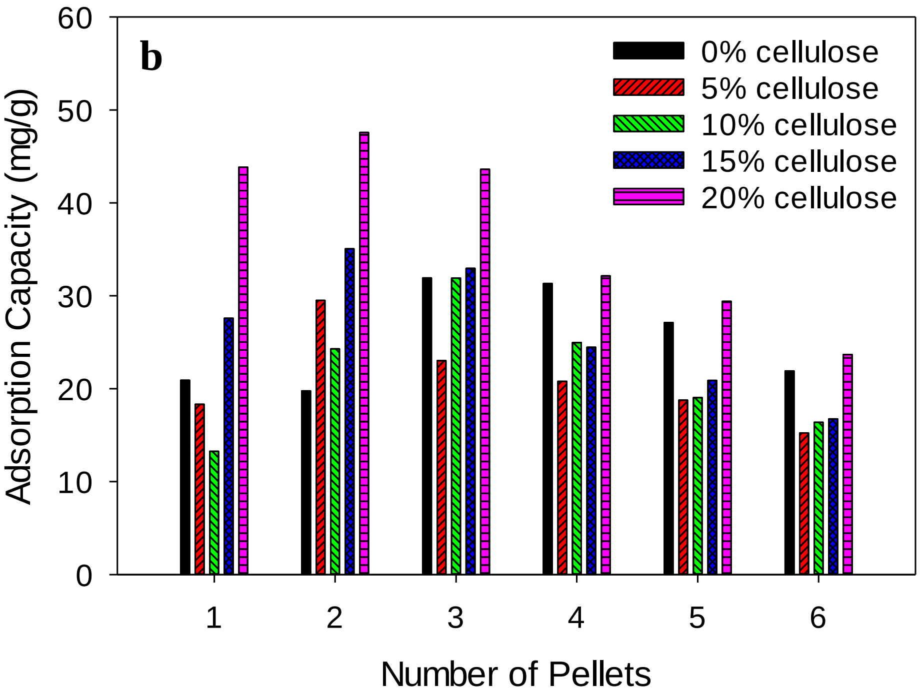


Figure 13 Adsorption capacity comparison with 5 pellet recipes in two isotherm experiments with initial concentration (a) 160 mg L^{-1} and (b) 330 mg L^{-1}.

The lower concentration was more easily removed using multiple pellets than the higher concentration but the adsorption capacities were higher overall in the solution with higher phosphate concentration originally. Since the only option with the pellets was to increase the mass used for the isotherm, the original concentration used in kinetics for one pellet was not high enough to show a removal trend for multiple pellets.

Isotherm data was fitted to both the Langmuir and Freundlich models to determine the best fit using a regression analysis as shown in Figure 14. The linearized Langmuir equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L q_{max}} \qquad (3)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}), C_e is the amount of unadsorbed adsorbate concentration in solution at equilibrium (mg L^{-1}), q_{max} is the maximum amount of adsorbate per unit mass of adsorbent to form a complete monolayer on the surface (mg g^{-1}), and K_L is a constant related to the affinity of the binding sites (L mg^{-1}). Similarly, the linearized Freundlich equation is as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

where K_F is the adsorption capacity of the adsorbent (mg g^{-1} (L $mg^{-1})^{1/n}$) and n indicates sorption favorability.

The lower concentration was difficult to model with Langmuir and Freundlich as seen by Figure 14a and 14c but the results for the 330 mg L^{-1} phosphate concentration modeled better as shown in Figure 14d and 14d, respectively. The parameters found via plotting these linearized equations are shown in Table 3, excluding the 0% cellulose baseline, at the higher phosphate concentration of 330 mg L^{-1}.

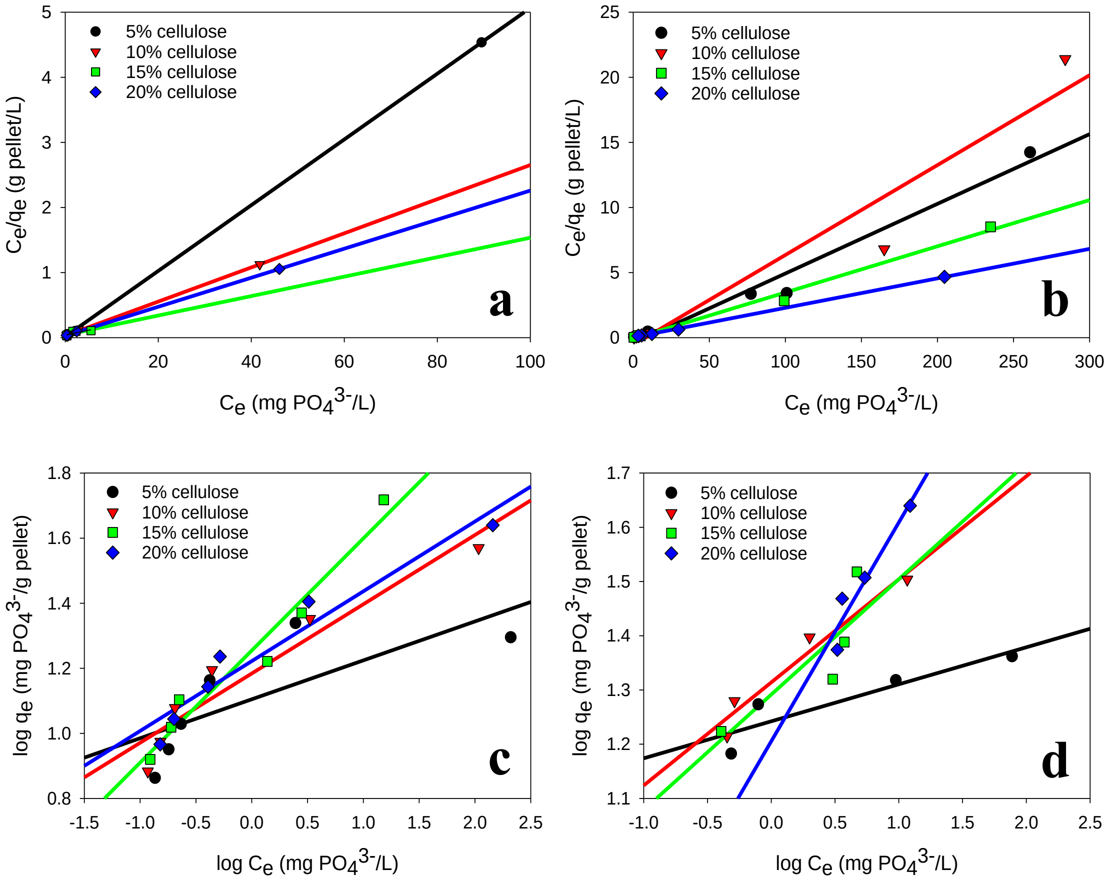


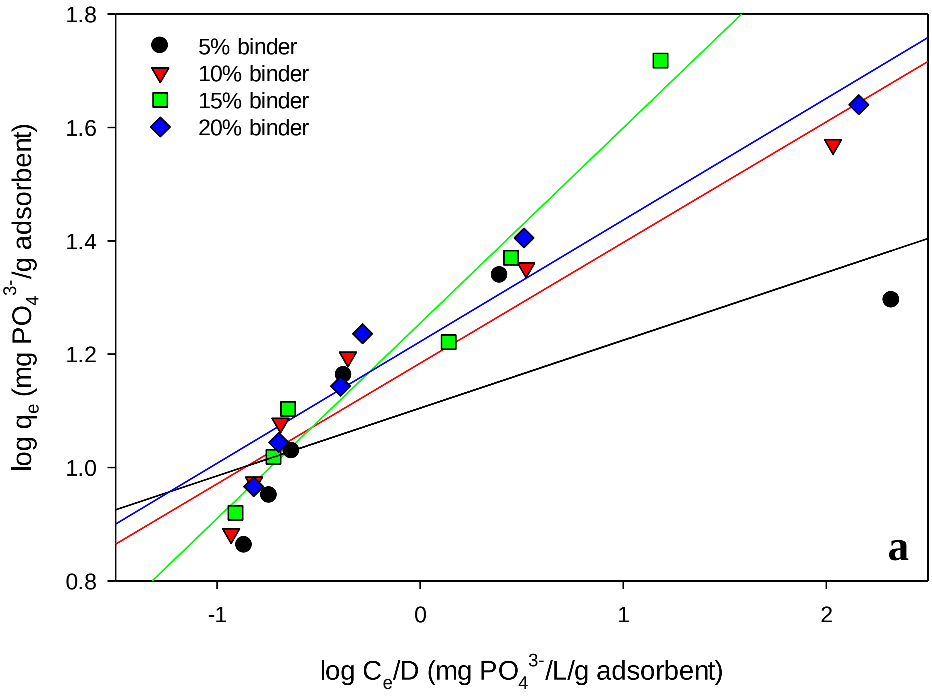
Figure 14 Linearized (a) Langmuir model for 160 mg L^{-1}, (b) Langmuir model for 330 mg L^{-1}, (c) Freundlich model for 160 mg L^{-1} and (d) Freundlich model for 330 mg L^{-1} applied on the four various pellet recipes.

Table 3 Adsorption isotherm models, the corresponding linear forms and parameters of $MgCO_3$ pellets with various amounts of cellulose for 4 different synthesis conditions with initial pH 7 at 23 °C.

Sorbent	**Langmuir isotherm** ${}^{C_e}/_{q_e} = {}^{1}/_{q_{max}}\, C_e + {}^{1}/_{K_L q_{max}}$			**Freundlich isotherm** $\log q_e = \log K_F + {}^{1}/_{n} \log C_e$		
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg g^{-1} (L mg^{-1})$^{1/n}$)	n^{-1}	R^2
5%1	18.69	-0.1264	0.9761	17.47	0.0683	0.8257
10%2	14.47	-0.1247	0.9381	20.61	0.1900	0.9513
15%1	28.17	-0.4517	0.9917	19.57	0.2126	0.7094
20%2	44.25	0.9741	0.9995	16.06	0.4031	0.9124

Based on this analysis, the best fit for the isotherm studies was the Langmuir model revealing that the adsorption occurred in a monolayer fashion. This confirms the findings that the *pseudo*-second-order kinetics model fit best, which also assumes monolayer adsorption. The maximum theoretical adsorption capacities found using the Langmuir model were: 18.7, 14.5, 28.2, and 44.3 mg g^{-1} for 5%1, 10%2, 15%1 and 20%1 pellets, respectively. Here the 20%2 pellet had the highest capacity, but this was the least stable pellet so the results were misleading.

The Freundlich model can be modified to include the adsorbent mass in the log C_e term to normalize for the mass. Figure 15 represents the modified Freundlich model for each of the pellet recipes at both initial phosphate concentration.



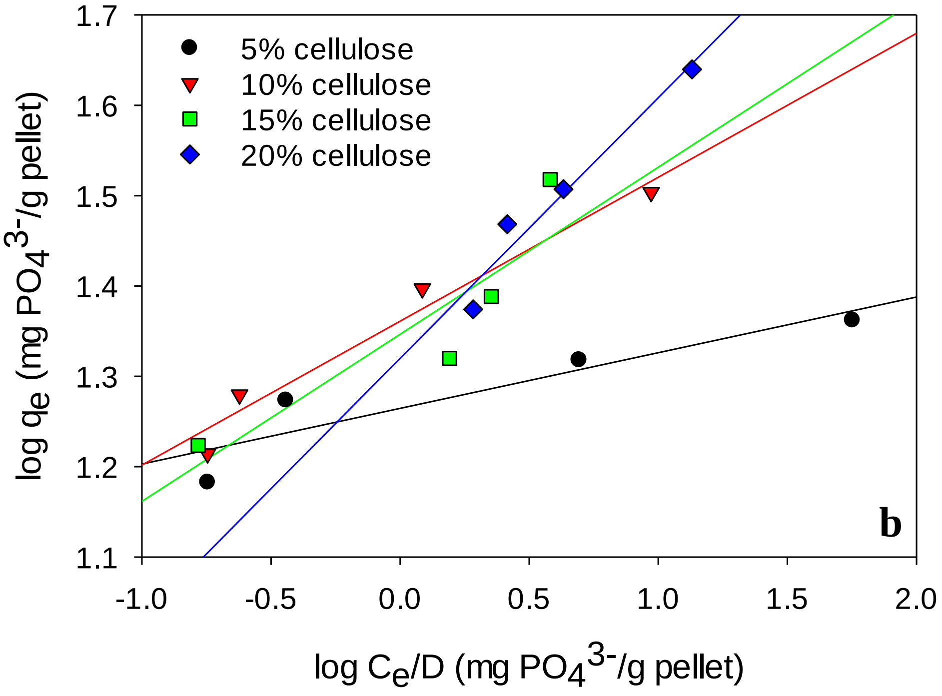


Figure 15 Linearized modified Freundlich applied on the four various pellet recipes for (a) 160 mg L^{-1} and (b) 330 mg L^{-1}.

The final isotherm conducted was completed for the 15%1 pellet in triplicate with the 330 mg L^{-1} solution to find the reproducibility of the adsorption capacity. The results were modeled with the linearized Langmuir and Freundlich models as shown in Figure 16a and b, respectively. The parameters determined from these models are listed in Table 4.

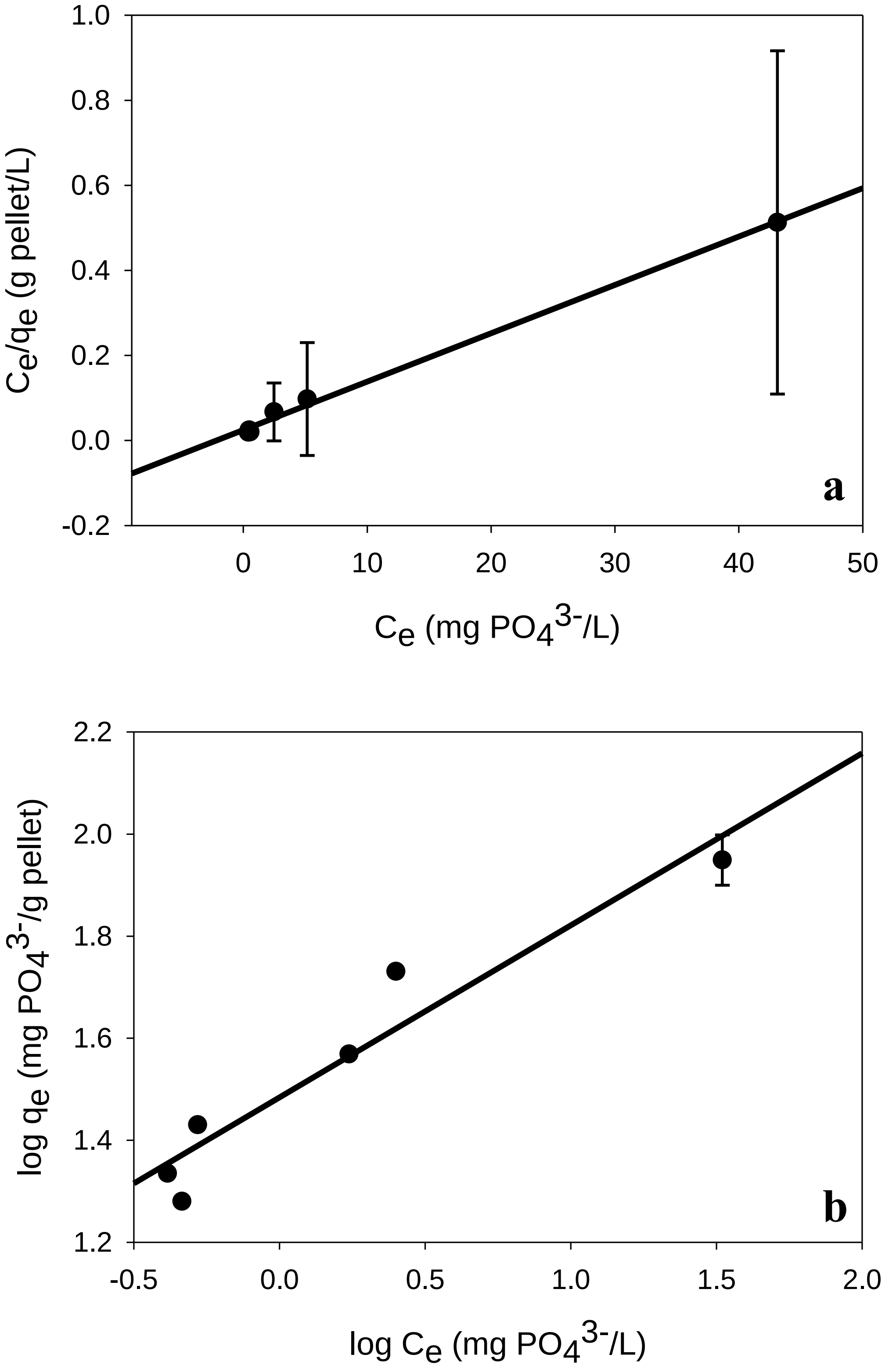


Figure 16 Linearized (a) Langmuir model and (b) Freundlich model applied on the triplicate isotherm experiment with 15%1 pellets.

Table 4 Adsorption isotherm models, the corresponding linear forms and parameters of $MgCO_3$ pellets with 15% cellulose with initial pH 7 at 23 °C. Data from triplicate experimental runs.

Sorbent	**Langmuir isotherm** $C_e/q_e = 1/q_{max}\, C_e + 1/K_L q_{max}$			**Freundlich isotherm** $\log q_e = \log K_F + 1/n \log C_e$		
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg g^{-1} (L $mg^{-1})^{1/n}$)	n^{-1}	R^2
15%1	91.74	0.3586	0.9657	28.95	0.2825	0.9457
15%1	116.28	0.5478	0.9785	36.46	0.4531	0.7824
15%1	81.30	0.4786	0.9944	29.89	0.2333	0.7358
Average	96.44 ± 18.0	0.46 ± 0.1		31.76 ± 4.1	0.32 ± 0.1	

The triplicate analysis of the 15%1 pellet resulted in an average q_{max} of 96.4 mg g^{-1} with a standard deviation of 18 mg g^{-1} and relative standard deviation of 18.6% for the experiments. The variation in predicted adsorption capacity from the kinetics and isotherm experiments can be explained by the variation in diffusion and surface area of pellets exposed to the solution. The bottles in the kinetics experiment were moved from the shaker for each sample throughout the experiment whereas the bottles in the isotherm experiment were kept on the table until the full 25 days had passed. During the movement for the kinetics experiment, the pellet may have shifted in the solution and exposed additional surface area for adsorption.

3.4 Desorption Experiment

Since the adsorption of phosphate was proven reasonably successful, pellets from the isotherm were studied for the ability to recover phosphate through desorption. Three different solutions were used to try to achieve this: deionized water (pH ~ 6.6), 0.1 M HCl (pH < 2) and 0.1 M NaOH (pH ~ 12.4). Table 5 shows the percentage of desorption seen after 25 days. This desorbability parameter is defined by the ratio of phosphate desorbed over phosphate adsorbed and provides an indicator for phosphate recovery potential.

Table 5 Desorption of adsorbed phosphate using three different solutions.

Sorbent	**0.1 M HCl**			**0.1 M NaOH**			**DI Water**		
	Adsorbed PO_4^{3-} (mg g^{-1})	Desorbed PO_4^{3-} (mg g^{-1})	Desorption Percentage	Adsorbed PO_4^{3-} (mg g^{-1})	Desorbed PO_4^{3-} (mg g^{-1})	Desorption Percentage	Adsorbed PO_4^{3-} (mg g^{-1})	Desorbed PO_4^{3-} (mg g^{-1})	Desorption Percentage
5%1	7.29	0.26	3.6 %	10.69	0.14	1.3 %	8.93	0.01	0.1 %
10%2	7.65	0.06	0.7 %	11.98	0.23	1.9 %	9.43	0.01	0.1 %
15%1	8.32	0.08	1.0 %	12.69	0.56	**4.4 %**	10.44	0.01	0.1 %
20%2	9.25	0.07	0.8 %	13.91	0.35	2.5 %	11.07	0.01	0.1 %

Based on the results, leaching into water without a desorption aid was negligible. Even with the change in pH, only as much as 4% of phosphate was desorbing. To further investigate what was occurring on the surface of the pellet, XRD analysis was conducted on each pellet after desorption in the acidic and basic solutions (Figure 17a and 17b, respectively).

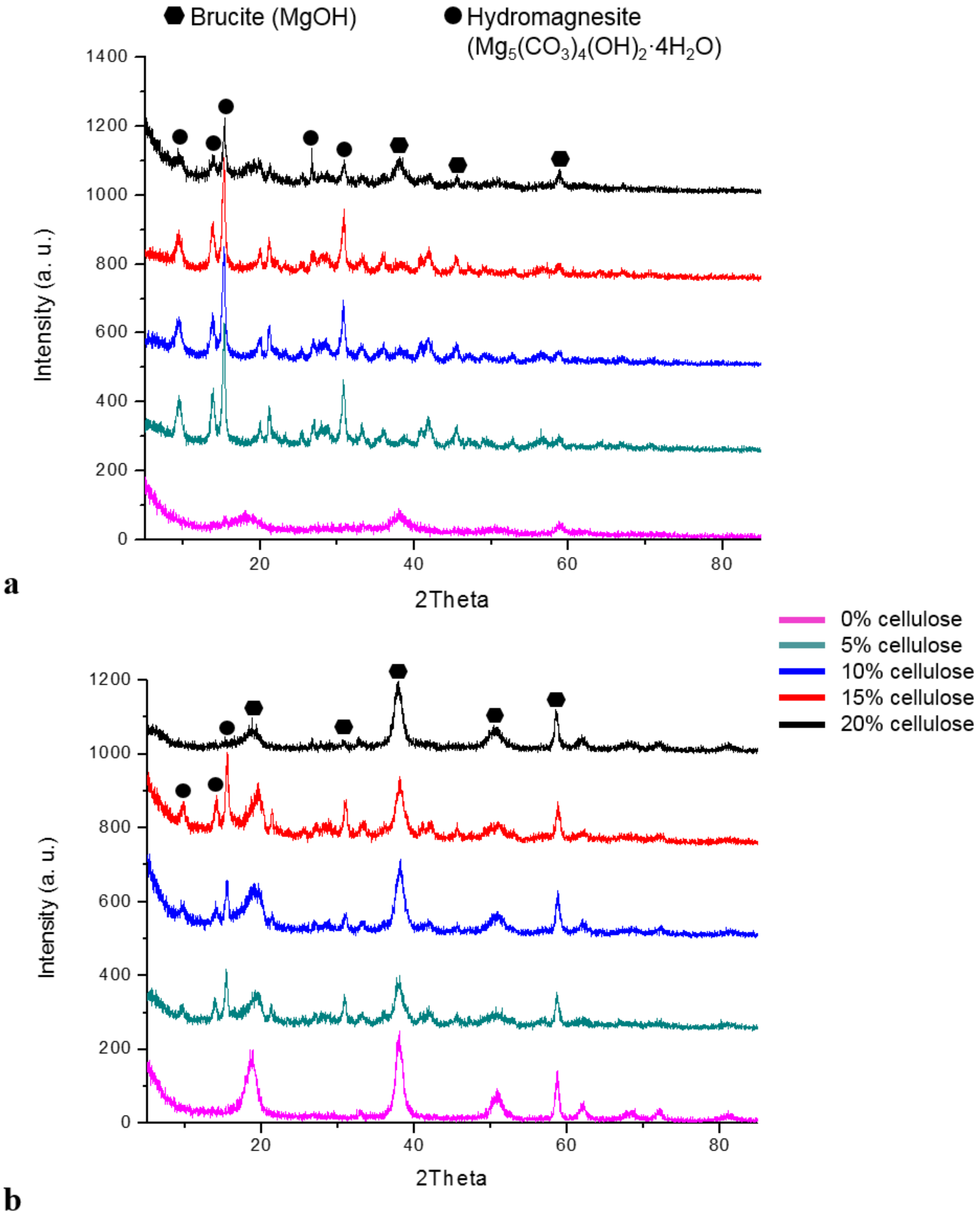


Figure 17 XRD patterns of the various pellets after (a) 0.1M HCl solution and (b) 0.1M NaOH solution desorption experiments were conducted.

From the figure, magnesium phosphate was no longer detected on the pellets after the desorption period (25 days). On closer inspection for the basic solution desorption experiment, the XRD pattern was shifted slightly such that the phosphate compound and hydromagnesite peaks were not differentiable. Overall, the results from XRD were not conclusive enough to determine if phosphate was present on the surface.

Chapter 4: Conclusions

4.1 Summary

Phosphate needs to be recovered from water systems where eutrophication is occurring in order to reduce the supply of phosphate rock mined to keep up with the fertilizer needed to feed a growing population. $MgCO_3$ pellets prepared with varying amounts of cellulose were found to be effective adsorbents for removing phosphate from aqueous suspensions. The calcination of the pellets with higher cellulose ratios proved to result in increased BET surface area until the pellet with 20% cellulose. The highest surface area achieved was 43.1 m^2 g^{-1} for the 15%1 pellet. The increased surface area corresponded to an increased adsorption capacity as seen through the Langmuir models. Although the highest theoretical adsorption capacity was 44.3 mg g^{-1} for the 20%2 pellet from the isotherm, the 15%1 pellet showed the most promise from kinetics experiments and surface area analysis. The 20%2 pellet was the least stable after calcination so the 15%1 pellet would provide adsorption without the stability being lost. From the isotherm experiments conducted for the 15%1 pellet, the adsorption capacity had an average of 96.4 mg g^{-1}. The surface of the pellets changed as phosphate was adsorbed as shown by the SEM and XRD analysis. While enhanced P availability might occur when exposed to the real world, the simple dissolution/desorption experiment suggested quite minimal release. It, of course, says nothing about very slow release.

4.2 Future Work

Further study could be done to improve the understanding of these adsorbents. For example, BET surface area was determined but a porosity as a percentage could be determined to further understand the addition of pores inside the pellet from calcination. The studies conducted were all batch, bench-scale studies. A column experiment could be used for rapid small scale studies to better represent how the pellets would be applied in water treatment. About 10-20 pellets, varying based on pellet dimensions, should be used to create a layer to fill the diameter of the column for analysis on top of sand and gravel. A stainless steel sieve could be placed in the bottom of the column to prevent the media from washing out of the column. The phosphate solution can run through the columns using a Thermo Scientific FH100M Series Peristaltic pump at a rate of 2 mL min^{-1} at room temperature. This type of study would also allow for easier addition of competing ions, like nitrate, sulfate, humic acid and fulvic acid, in addition to phosphate. The goal would be to investigate the effect of competing ions on flow through phosphate adsorption.

Thermally decomposed magnesite has a higher surface area which can slow down struvite production, but this is ideal for adsorption and is what was achieved by making magnesium carbonate pellets with the cellulose binder. Further research could be done to take the pellets with phosphate already adsorbed and attempt to precipitate struvite with the addition of an ammonium source. It has already been shown that thermally decomposed magnesite leads to potentially a 34% reduction in cost compared to conventional $MgCl_2$[48] so this may provide another avenue for research.

References

(1) Ashley, K.; Cordell, D.; Mavinic, D. A Brief History of Phosphorus: From the Philosopher's Stone to Nutrient Recovery and Reuse. *Chemosphere* **2011**, *84* (6), 737–746.

(2) Driver, J.; Lijmbach, D.; Steen, I. Why Recover Phosphorus for Recycling, and How? *Environ. Technol.* **1999**, *20* (7), 651–662.

(3) Rhodes, C. J. Peak Phosphorus – Peak Food? The Need to Close the Phosphorus Cycle. *Sci. Prog.* **2013**, *96* (2), 109–152.

(4) Cordell, D.; White, S. Peak Phosphorus: Clarifying the Key Issues of a Vigorous Debate about Long-Term Phosphorus Security. *Sustainability* **2011**, *3* (12), 2027–2049.

(5) Filippelli, G. M. The Global Phosphorus Cycle: Past, Present, and Future. *Elements* **2008**, *4* (2), 89–95.

(6) Dawson, C. J.; Hilton, J. Fertiliser Availability in a Resource-Limited World: Production and Recycling of Nitrogen and Phosphorus. *Food Policy* **2011**, *36*, S14–S22.

(7) Cornel, P.; Schaum, C. Phosphorus Recovery from Wastewater: Needs, Technologies and Costs. *Water Sci. Technol.* **2009**, *59* (6), 1069.

(8) Cordell, D.; Drangert, J.-O.; White, S. The Story of Phosphorus: Global Food Security and Food for Thought. *Glob. Environ. Change* **2009**, *19* (2), 292–305.

(9) Wendling, L. A.; Blomberg, P.; Sarlin, T.; Priha, O.; Arnold, M. Phosphorus Sorption and Recovery Using Mineral-Based Materials: Sorption Mechanisms and Potential Phytoavailability. *Appl. Geochem.* **2013**, *37*, 157–169.

(10) Filippelli, G. M. Phosphate Rock Formation and Marine Phosphorus Geochemistry: The Deep Time Perspective. *Chemosphere* **2011**, *84* (6), 759–766.

(11) Morse, G. K.; Brett, S. W.; Guy, J. A.; Lester, J. N. Review: Phosphorus Removal and Recovery Technologies. *Sci. Total Environ.* **1998**, *212* (1), 69–81.

(12) Withers, P. J. A.; Elser, J. J.; Hilton, J.; Ohtake, H.; Schipper, W. J.; van Dijk, K. C. Greening the Global Phosphorus Cycle: How Green Chemistry Can Help Achieve Planetary P Sustainability. *Green Chem* **2015**, *17* (4), 2087–2099.

(13) Van Vuuren, D. P.; Bouwman, A. F.; Beusen, A. H. W. Phosphorus Demand for the 1970–2100 Period: A Scenario Analysis of Resource Depletion. *Glob. Environ. Change* **2010**, *20* (3), 428–439.

(14) Vaccari, D. A.; Strigul, N. Extrapolating Phosphorus Production to Estimate Resource Reserves. *Chemosphere* **2011**, *84* (6), 792–797.

(15) Elser, J.; Bennett, E. Phosphorus Cycle: A Broken Biogeochemical Cycle. *Nature* **2011**, *478* (7367), 29–31.

(16) Cordell, D.; Rosemarin, A.; Schröder, J. J.; Smit, A. L. Towards Global Phosphorus Security: A Systems Framework for Phosphorus Recovery and Reuse Options. *Chemosphere* **2011**, *84* (6), 747–758.

(17) Steen, I. Phosphorus Availability in the 21st Century Management of a Nonrenewable Resource. *Phosphorus Potassium* **1998**, No. 217, 25–31.

(18) Gilbert, N. The Disappearing Nutrient. *Nature* **2009**, *461* (8), 716–718.

(19) Liu, Y.; Kumar, S.; Kwag, J.-H.; Ra, C. Magnesium Ammonium Phosphate Formation, Recovery and Its Application as Valuable Resources: A Review. *J. Chem. Technol. Biotechnol.* **2013**, *88* (2), 181–189.

(20) Cooper, J.; Lombardi, R.; Boardman, D.; Carliell-Marquet, C. The Future Distribution and Production of Global Phosphate Rock Reserves. *Resour. Conserv. Recycl.* **2011**, *57*, 78–86.

(21) Mayer, B. K.; Baker, L. A.; Boyer, T. H.; Drechsel, P.; Gifford, M.; Hanjra, M. A.; Parameswaran, P.; Stoltzfus, J.; Westerhoff, P.; Rittmann, B. E. Total Value of Phosphorus Recovery. *Environ. Sci. Technol.* **2016**, *50* (13), 6606–6620.

(22) Bradford-Hartke, Z.; Lane, J.; Lant, P.; Leslie, G. Environmental Benefits and Burdens of Phosphorus Recovery from Municipal Wastewater. *Environ. Sci. Technol.* **2015**, *49* (14), 8611–8622.

(23) Dumas, M.; Frossard, E.; Scholz, R. W. Modeling Biogeochemical Processes of Phosphorus for Global Food Supply. *Chemosphere* **2011**, *84* (6), 798–805.

(24) *Water quality and treatment: a handbook of community water supplies*, 5. ed.; Letterman, R. D., American Water Works Association, Eds.; McGraw-Hill: New York, 1999.

(25) Schindler, D. W.; Carpenter, S. R.; Chapra, S. C.; Hecky, R. E.; Orihel, D. M. Reducing Phosphorus to Curb Lake Eutrophication Is a Success. *Environ. Sci. Technol.* **2016**, *50* (17), 8923–8929.

(26) Carpenter, S. R. Phosphorus Control Is Critical to Mitigating Eutrophication. *Proc. Natl. Acad. Sci.* **2008**, *105* (32), 11039–11040.

(27) Correll, D. L. The Role of Phosphorus in the Eutrophication of Receiving Waters: A Review. *J. Environ. Qual.* **1998**, *27* (2), 261–266.

(28) Rittmann, B. E.; Mayer, B.; Westerhoff, P.; Edwards, M. Capturing the Lost Phosphorus. *Chemosphere* **2011**, *84* (6), 846–853.

(29) Diaz, R. J.; Rosenberg, R. Spreading Dead Zones and Consequences for Marine Ecosystems. *Science* **2008**, *321* (5891), 926–929.

(30) Schindler, D. W. Recent Advances in the Understanding and Management of Eutrophication. *Limnol. Oceanogr.* **2006**, *51* (1), 356–363.

(31) Paerl, H. W.; Otten, T. G. Harmful Cyanobacterial Blooms: Causes, Consequences, and Controls. *Microb. Ecol.* **2013**, *65* (4), 995–1010.

(32) Qin, B.; Gao, G.; Zhu, G.; Zhang, Y.; Song, Y.; Tang, X.; Xu, H.; Deng, J. Lake Eutrophication and Its Ecosystem Response. *Chin. Sci. Bull.* **2013**, *58* (9), 961–970.

(33) Heisler, J.; Glibert, P. M.; Burkholder, J. M.; Anderson, D. M.; Cochlan, W.; Dennison, W. C.; Dortch, Q.; Gobler, C. J.; Heil, C. A.; Humphries, E.; et al. Eutrophication and Harmful Algal Blooms: A Scientific Consensus. *Harmful Algae* **2008**, *8* (1), 3–13.

(34) Conley, D. J.; Paerl, H. W.; Howarth, R. W.; Boesch, D. F.; Seitzinger, S. P.; Havens, K. E.; Lancelot, C.; Likens, G. E.; others. Controlling Eutrophication: Nitrogen and Phosphorus. *Science* **2009**, *323* (5917), 1014–1015.

(35) Ramasahayam, S. K.; Guzman, L.; Gunawan, G.; Viswanathan, T. A Comprehensive Review of Phosphorus Removal Technologies and Processes. *J. Macromol. Sci. Part A* **2014**, *51* (6), 538–545.

(36) Parry, R. Agricultural Phosphorus and Water Quality. *J. Environ. Qual.* **1998**, *27* (2), 258–261.

(37) Dodds, W. K.; Bouska, W. W.; Eitzmann, J. L.; Pilger, T. J.; Pitts, K. L.; Riley, A. J.; Schloesser, J. T.; Thornbrugh, D. J. Eutrophication of U.S. Freshwaters: Analysis of Potential Economic Damages. *Environ. Sci. Technol.* **2009**, *43* (1), 12–19.

(38) Kleinman, P. J. A.; Sharpley, A. N.; McDowell, R. W.; Flaten, D. N.; Buda, A. R.; Tao, L.; Bergstrom, L.; Zhu, Q. Managing Agricultural Phosphorus for Water Quality Protection: Principles for Progress. *Plant Soil* **2011**, *349* (1–2), 169–182.

(39) Schröder, J. J.; Smit, A. L.; Cordell, D.; Rosemarin, A. Improved Phosphorus Use Efficiency in Agriculture: A Key Requirement for Its Sustainable Use. *Chemosphere* **2011**, *84* (6), 822–831.

(40) Suh, S.; Yee, S. Phosphorus Use-Efficiency of Agriculture and Food System in the US. *Chemosphere* **2011**, *84* (6), 806–813.

(41) Sharpley, A.; Jarvie, H. P.; Buda, A.; May, L.; Spears, B.; Kleinman, P. Phosphorus Legacy: Overcoming the Effects of Past Management Practices to Mitigate Future Water Quality Impairment. *J. Environ. Qual.* **2013**, *42* (5), 1308.

(42) Mino, T.; Van Loosdrecht, M. C. M.; Heijnen, J. J. Microbiology and Biochemistry of the Enhanced Biological Phosphate Removal Process. *Water Res.* **1998**, *32* (11), 3193–3207.

(43) de-Bashan, L. E.; Bashan, Y. Recent Advances in Removing Phosphorus from Wastewater and Its Future Use as Fertilizer (1997–2003). *Water Res.* **2004**, *38* (19), 4222–4246.

(44) Barat, R.; Montoya, T.; Seco, A.; Ferrer, J. The Role of Potassium, Magnesium and Calcium in the Enhanced Biological Phosphorus Removal Treatment Plants. *Environ. Technol.* **2005**, *26* (9), 983–992.

(45) Booker, N. A.; Priestley, A. J.; Fraser, I. H. Struvite Formation in Wastewater Treatment Plants: Opportunities for Nutrient Recovery. *Environ. Technol.* **1999**, *20* (7), 777–782.

(46) Jaffer, Y.; Clark, T. A.; Pearce, P.; Parsons, S. A. Potential Phosphorus Recovery by Struvite Formation. *Water Res.* **2002**, *36* (7), 1834–1842.

(47) Doyle, J. D.; Parsons, S. A. Struvite Formation, Control and Recovery. *Water Res.* **2002**, *36* (16), 3925–3940.

(48) Kataki, S.; West, H.; Clarke, M.; Baruah, D. C. Phosphorus Recovery as Struvite: Recent Concerns for Use of Seed, Alternative Mg Source, Nitrogen Conservation and Fertilizer Potential. *Resour. Conserv. Recycl.* **2016**, *107*, 142–156.

(49) Su, C.-C.; Dulfo, L. D.; Dalida, M. L. P.; Lu, M.-C. Magnesium Phosphate Crystallization in a Fluidized-Bed Reactor: Effects of pH, Mg:P Molar Ratio and Seed. *Sep. Purif. Technol.* **2014**, *125*, 90–96.

(50) Shu, L.; Schneider, P.; Jegatheesan, V.; Johnson, J. An Economic Evaluation of Phosphorus Recovery as Struvite from Digester Supernatant. *Bioresour. Technol.* **2006**, *97* (17), 2211–2216.

(51) Hao, X.; Wang, C.; van Loosdrecht, M. C. M.; Hu, Y. Looking Beyond Struvite for P-Recovery. *Environ. Sci. Technol.* **2013**, *47* (10), 4965–4966.

(52) Talboys, P. J.; Heppell, J.; Roose, T.; Healey, J. R.; Jones, D. L.; Withers, P. J. A. Struvite: A Slow-Release Fertiliser for Sustainable Phosphorus Management? *Plant Soil* **2016**, *401* (1–2), 109–123.

(53) Johnston A.E.*; Richards, I. R. Effectiveness of Different Precipitated Phosphates as Phosphorus Sources for Plants. *Soil Use Manag.* **2003**, *19* (1), 45–49.

(54) Barat, R.; Bouzas, A.; Martí, N.; Ferrer, J.; Seco, A. Precipitation Assessment in Wastewater Treatment Plants Operated for Biological Nutrient Removal: A Case Study in Murcia, Spain. *J. Environ. Manage.* **2009**, *90* (2), 850–857.

(55) Egle, L.; Rechberger, H.; Krampe, J.; Zessner, M. Phosphorus Recovery from Municipal Wastewater: An Integrated Comparative Technological, Environmental and Economic Assessment of P Recovery Technologies. *Sci. Total Environ.* **2016**.

(56) Rouquerol, F.; Rouquerol, J.; Sing, K. S. W.; Maurin, G.; Llewellyn, P. Introduction. In *Adsorption by Powders and Porous Solids*; Elsevier, 2014; pp 1–24.

(57) Foo, K. Y.; Hameed, B. H. Insights into the Modeling of Adsorption Isotherm Systems. *Chem. Eng. J.* **2010**, *156* (1), 2–10.

(58) Moharami, S.; Jalali, M. Removal of Phosphorus from Aqueous Solution by Iranian Natural Adsorbents. *Chem. Eng. J.* **2013**, *223*, 328–339.

(59) Hamdi, N.; Srasra, E. Removal of Phosphate Ions from Aqueous Solution Using Tunisian Clays Minerals and Synthetic Zeolite. *J. Environ. Sci.* **2012**, *24* (4), 617–623.

(60) Yang, S.; Zhao, Y.; Chen, R.; Feng, C.; Zhang, Z.; Lei, Z.; Yang, Y. A Novel Tablet Porous Material Developed as Adsorbent for Phosphate Removal and Recycling. *J. Colloid Interface Sci.* **2013**, *396*, 197–204.

(61) Yang, S.; Zhao, Y.; Ding, D.; Wang, Y.; Feng, C.; Lei, Z.; Yang, Y.; Zhang, Z. An Electrochemically Modified Novel Tablet Porous Material Developed as Adsorbent for Phosphate Removal from Aqueous Solution. *Chem. Eng. J.* **2013**, *220*, 367–374.

(62) Liu, S.; Li, J.; Yang, Y.; Wang, J.; Ding, H. Influence of Environmental Factors on the Phosphorus Adsorption of Lanthanum-Modified Bentonite in Eutrophic Water and Sediment. *Environ. Sci. Pollut. Res.* **2016**, *23* (3), 2487–2494.

(63) Tian, S.; Jiang, P.; Ning, P.; Su, Y. Enhanced Adsorption Removal of Phosphate from Water by Mixed Lanthanum/Aluminum Pillared Montmorillonite. *Chem. Eng. J.* **2009**, *151* (1–3), 141–148.

(64) Haghseresht, F.; Wang, S.; Do, D. D. A Novel Lanthanum-Modified Bentonite, Phoslock, for Phosphate Removal from Wastewaters. *Appl. Clay Sci.* **2009**, *46* (4), 369–375.

(65) Zamparas, M.; Gianni, A.; Stathi, P.; Deligiannakis, Y.; Zacharias, I. Removal of Phosphate from Natural Waters Using Innovative Modified Bentonites. *Appl. Clay Sci.* **2012**, *62–63*, 101–106.

(66) Cai, P.; Zheng, H.; Wang, C.; Ma, H.; Hu, J.; Pu, Y.; Liang, P. Competitive Adsorption Characteristics of Fluoride and Phosphate on Calcined Mg–Al–CO3 Layered Double Hydroxides. *J. Hazard. Mater.* **2012**, *213–214*, 100–108.

(67) Peleka, E. N.; Deliyanni, E. A. Adsorptive Removal of Phosphates from Aqueous Solutions. *Desalination* **2009**, *245* (1–3), 357–371.
(68) Cheng, X.; Huang, X.; Wang, X.; Sun, D. Influence of Calcination on the Adsorptive Removal of Phosphate by Zn–Al Layered Double Hydroxides from Excess Sludge Liquor. *J. Hazard. Mater.* **2010**, *177* (1–3), 516–523.
(69) Chitrakar, R.; Tezuka, S.; Sonoda, A.; Sakane, K.; Ooi, K.; Hirotsu, T. Adsorption of Phosphate from Seawater on Calcined MgMn-Layered Double Hydroxides. *J. Colloid Interface Sci.* **2005**, *290* (1), 45–51.
(70) Hosni, K.; Srasra, E. Evaluation of Phosphate Removal from Water by Calcined-LDH Synthesized from the Dolomite. *Colloid J.* **2010**, *72* (3), 423–431.
(71) Kuzawa, K.; Jung, Y.-J.; Kiso, Y.; Yamada, T.; Nagai, M.; Lee, T.-G. Phosphate Removal and Recovery with a Synthetic Hydrotalcite as an Adsorbent. *Chemosphere* **2006**, *62* (1), 45–52.
(72) Halajnia, A.; Oustan, S.; Najafi, N.; Khataee, A. R.; Lakzian, A. Adsorption–desorption Characteristics of Nitrate, Phosphate and Sulfate on Mg–Al Layered Double Hydroxide. *Appl. Clay Sci.* **2013**, *80–81*, 305–312.
(73) Guaya, D.; Valderrama, C.; Farran, A.; Armijos, C.; Cortina, J. L. Simultaneous Phosphate and Ammonium Removal from Aqueous Solution by a Hydrated Aluminum Oxide Modified Natural Zeolite. *Chem. Eng. J.* **2015**, *271*, 204–213.
(74) Xie, J.; Wang, Z.; Fang, D.; Li, C.; Wu, D. Green Synthesis of a Novel Hybrid Sorbent of Zeolite/Lanthanum Hydroxide and Its Application in the Removal and Recovery of Phosphate from Water. *J. Colloid Interface Sci.* **2014**, *423*, 13–19.
(75) Meng, S.; Li, Y.; Zhang, T.; Chen, J.; Xu, P.; Song, C.; Fan, L.; Qiu, L. Influences of Environmental Factors on Lanthanum/Aluminum-Modified Zeolite Adsorbent (La/Al-ZA) for Phosphorus Adsorption from Wastewater. *Water. Air. Soil Pollut.* **2013**, *224* (6).
(76) Onyango, M. S.; Kuchar, D.; Kubota, M.; Matsuda, H. Adsorptive Removal of Phosphate Ions from Aqueous Solution Using Synthetic Zeolite. *Ind. Eng. Chem. Res.* **2007**, *46* (3), 894–900.
(77) Chen, J.; Kong, H.; Wu, D.; Hu, Z.; Wang, Z.; Wang, Y. Removal of Phosphate from Aqueous Solution by Zeolite Synthesized from Fly Ash. *J. Colloid Interface Sci.* **2006**, *300* (2), 491–497.
(78) Zhang, L.; Zhou, Q.; Liu, J.; Chang, N.; Wan, L.; Chen, J. Phosphate Adsorption on Lanthanum Hydroxide-Doped Activated Carbon Fiber. *Chem. Eng. J.* **2012**, *185–186*, 160–167.
(79) Xie, J.; Wang, Z.; Lu, S.; Wu, D.; Zhang, Z.; Kong, H. Removal and Recovery of Phosphate from Water by Lanthanum Hydroxide Materials. *Chem. Eng. J.* **2014**, *254*, 163–170.
(80) Zhang, J.; Shen, Z.; Shan, W.; Chen, Z.; Mei, Z.; Lei, Y.; Wang, W. Adsorption Behavior of Phosphate on Lanthanum(III) Doped Mesoporous Silicates Material. *J. Environ. Sci.* **2010**, *22* (4), 507–511.
(81) Li, H.; Ru, J.; Yin, W.; Liu, X.; Wang, J.; Zhang, W. Removal of Phosphate from Polluted Water by Lanthanum Doped Vesuvianite. *J. Hazard. Mater.* **2009**, *168* (1), 326–330.
(82) Huang, W.-Y.; Li, D.; Liu, Z.-Q.; Tao, Q.; Zhu, Y.; Yang, J.; Zhang, Y.-M. Kinetics, Isotherm, Thermodynamic, and Adsorption Mechanism Studies of La(OH)3-Modified Exfoliated Vermiculites as Highly Efficient Phosphate Adsorbents. *Chem. Eng. J.* **2014**, *236*, 191–201.
(83) Chen, N.; Feng, C.; Zhang, Z.; Liu, R.; Gao, Y.; Li, M.; Sugiura, N. Preparation and Characterization of lanthanum(III) Loaded Granular Ceramic for Phosphorus Adsorption from Aqueous Solution. *J. Taiwan Inst. Chem. Eng.* **2012**, *43* (5), 783–789.
(84) Yagi, S.; Fukushi, K. Removal of Phosphate from Solution by Adsorption and Precipitation of Calcium Phosphate onto Monohydrocalcite. *J. Colloid Interface Sci.* **2012**, *384* (1), 128–136.
(85) Köse, T. E.; Kıvanç, B. Adsorption of Phosphate from Aqueous Solutions Using Calcined Waste Eggshell. *Chem. Eng. J.* **2011**, *178*, 34–39.
(86) Xiong, J.; Qin, Y.; Islam, E.; Yue, M.; Wang, W. Phosphate Removal from Solution Using Powdered Freshwater Mussel Shells. *Desalination* **2011**, *276* (1–3), 317–321.
(87) Yeom, S. H.; Jung, K.-Y. Recycling Wasted Scallop Shell as an Adsorbent for the Removal of Phosphate. *J. Ind. Eng. Chem.* **2009**, *15* (1), 40–44.

(88) Jeon, D. J.; Yeom, S. H. Recycling Wasted Biomaterial, Crab Shells, as an Adsorbent for the Removal of High Concentration of Phosphate. *Bioresour. Technol.* **2009**, *100* (9), 2646–2649.

(89) Millero, F.; Huang, F.; Zhu, X.; Liu, X.; Zhang, J.-Z. Adsorption and Desorption of Phosphate on Calcite and Aragonite in Seawater. *Aquat. Geochem.* **2001**, *7* (1), 33–56.

(90) Oguz, E.; Gurses, A.; Yalcin, M. Removal of Phosphate from Waste Waters by Adsorption. *Water. Air. Soil Pollut.* **2003**, *148* (1–4), 279–287.

(91) Xie, F.; Wu, F.; Liu, G.; Mu, Y.; Feng, C.; Wang, H.; Giesy, J. P. Removal of Phosphate from Eutrophic Lakes through Adsorption by in Situ Formation of Magnesium Hydroxide from Diatomite. *Environ. Sci. Technol.* **2014**, *48* (1), 582–590.

(92) Zhou, J.; Yang, S.; Yu, J. Facile Fabrication of Mesoporous MgO Microspheres and Their Enhanced Adsorption Performance for Phosphate from Aqueous Solutions. *Colloids Surf. Physicochem. Eng. Asp.* **2011**, *379* (1–3), 102–108.

(93) Ye, H.; Chen, F.; Sheng, Y.; Sheng, G.; Fu, J. Adsorption of Phosphate from Aqueous Solution onto Modified Palygorskites. *Sep. Purif. Technol.* **2006**, *50* (3), 283–290.

(94) Gan, F.; Zhou, J.; Wang, H.; Du, C.; Chen, X. Removal of Phosphate from Aqueous Solution by Thermally Treated Natural Palygorskite. *Water Res.* **2009**, *43* (11), 2907–2915.

(95) Fang, C.; Zhang, T.; Li, P.; Jiang, R.; Wang, Y. Application of Magnesium Modified Corn Biochar for Phosphorus Removal and Recovery from Swine Wastewater. *Int. J. Environ. Res. Public. Health* **2014**, *11* (9), 9217–9237.

(96) Xu, N.; Li, Y.; Zheng, L.; Gao, Y.; Yin, H.; Zhao, J.; Chen, Z.; Chen, J.; Chen, M. Synthesis and Application of Magnesium Amorphous Calcium Carbonate for Removal of High Concentration of Phosphate. *Chem. Eng. J.* **2014**, *251*, 102–110.

(97) Fang, C.; Zhang, T.; Li, P.; Jiang, R.; Wu, S.; Nie, H.; Wang, Y. Phosphorus Recovery from Biogas Fermentation Liquid by Ca–Mg Loaded Biochar. *J. Environ. Sci.* **2015**, *29*, 106–114.

(98) Yin, H.; Kong, M. Simultaneous Removal of Ammonium and Phosphate from Eutrophic Waters Using Natural Calcium-Rich Attapulgite-Based Versatile Adsorbent. *Desalination* **2014**, *351*, 128–137.

(99) Roques, H.; Nugroho-Jeudy, L.; Lebugle, A. Phosphorus Removal from Wastewater by Half-Burned Dolomite. *Water Res.* **1991**, *25* (8), 959–965.

(100) Karaca, S.; Gurses, A.; Ejder, M.; Acikyildiz, M. Adsorptive Removal of Phosphate from Aqueous Solutions Using Raw and Calcinated Dolomite. *J. Hazard. Mater.* **2006**, *128* (2–3), 273–279.

(101) Lalley, J.; Han, C.; Li, X.; Dionysiou, D. D.; Nadagouda, M. N. Phosphate Adsorption Using Modified Iron Oxide-Based Sorbents in Lake Water: Kinetics, Equilibrium, and Column Tests. *Chem. Eng. J.* **2016**, *284*, 1386–1396.

(102) Zeng, L.; Li, X.; Liu, J. Adsorptive Removal of Phosphate from Aqueous Solutions Using Iron Oxide Tailings. *Water Res.* **2004**, *38* (5), 1318–1326.

(103) Nur, T.; Johir, M. A. H.; Loganathan, P.; Nguyen, T.; Vigneswaran, S.; Kandasamy, J. Phosphate Removal from Water Using an Iron Oxide Impregnated Strong Base Anion Exchange Resin. *J. Ind. Eng. Chem.* **2014**, *20* (4), 1301–1307.

(104) Wang, Z.; Fang, W.; Xing, M.; Wu, D. A Bench-Scale Study on the Removal and Recovery of Phosphate by Hydrous Zirconia-Coated Magnetite Nanoparticles. *J. Magn. Magn. Mater.* **2017**, *424*, 213–220.

(105) Long, F.; Gong, J.-L.; Zeng, G.-M.; Chen, L.; Wang, X.-Y.; Deng, J.-H.; Niu, Q.-Y.; Zhang, H.-Y.; Zhang, X.-R. Removal of Phosphate from Aqueous Solution by Magnetic Fe–Zr Binary Oxide. *Chem. Eng. J.* **2011**, *171* (2), 448–455.

(106) Chardon, W. J.; Groenenberg, J. E.; Temminghoff, E. J. M.; Koopmans, G. F. Use of Reactive Materials to Bind Phosphorus. *J. Environ. Qual.* **2012**, *41* (3), 636.

(107) Liu, H.; Sun, X.; Yin, C.; Hu, C. Removal of Phosphate by Mesoporous ZrO2. *J. Hazard. Mater.* **2008**, *151* (2–3), 616–622.

(108) Wang, M. k.; Tzou, Y. M. Phosphate Sorption by Calcite, and Iron-Rich Calcareous Soils. *Geoderma* **1994**, *65*, 249–261.

(109) Lai, L.; Xie, Q.; Chi, L.; Gu, W.; Wu, D. Adsorption of Phosphate from Water by Easily Separable Fe3O4@SiO2 Core/Shell Magnetic Nanoparticles Functionalized with Hydrous Lanthanum Oxide. *J. Colloid Interface Sci.* **2016**, *465*, 76–82.

(110) Bellier, N.; Chazarenc, F.; Comeau, Y. Phosphorus Removal from Wastewater by Mineral Apatite. *Water Res.* **2006**, *40* (15), 2965–2971.

(111) Shin, E. W.; Han, J. S.; Jang, M.; Min, S.-H.; Park, J. K.; Rowell, R. M. Phosphate Adsorption on Aluminum-Impregnated Mesoporous Silicates: Surface Structure and Behavior of Adsorbents. *Environ. Sci. Technol.* **2004**, *38* (3), 912–917.

(112) Yang, Y.; Zhao, Y.; Babatunde, A.; Wang, L.; Ren, Y.; Han, Y. Characteristics and Mechanisms of Phosphate Adsorption on Dewatered Alum Sludge. *Sep. Purif. Technol.* **2006**, *51* (2), 193–200.

(113) Bhardwaj, D.; Sharma, P.; Sharma, M.; Tomar, R. Removal and Slow Release Studies of Phosphate on Surfactant Loaded Hydrothermally Synthesized Silicate Nanoparticles. *J. Taiwan Inst. Chem. Eng.* **2014**, *45* (5), 2649–2658.

(114) Yan, Y.; Sun, X.; Ma, F.; Li, J.; Shen, J.; Han, W.; Liu, X.; Wang, L. Removal of Phosphate from Wastewater Using Alkaline Residue. *J. Environ. Sci.* **2014**, *26* (5), 970–980.

(115) Liu, X.; Zhang, L. Removal of Phosphate Anions Using the Modified Chitosan Beads: Adsorption Kinetic, Isotherm and Mechanism Studies. *Powder Technol.* **2015**, *277*, 112–119.

(116) Bai, L.; Wang, C.; He, L.; Pei, Y. Influence of the Inherent Properties of Drinking Water Treatment Residuals on Their Phosphorus Adsorption Capacities. *J. Environ. Sci.* **2014**, *26* (12), 2397–2405.

(117) Wajima, T.; Rakovan, J. F. Removal Behavior of Phosphate from Aqueous Solution by Calcined Paper Sludge. *Colloids Surf. Physicochem. Eng. Asp.* **2013**, *435*, 132–138.

(118) Agyei, N. M.; Strydom, C. A.; Potgieter, J. H. The Removal of Phosphate Ions from Aqueous Solution by Fly Ash, Slag, Ordinary Portland Cement and Related Blends. *Cem. Concr. Res.* **2002**, *32*, 1889–1897.

(119) Hutchison, A. J.; Wilkie, M. Use of Magnesium as a Drug in Chronic Kidney Disease. *Clin. Kidney J.* **2012**, *5* (Suppl 1), i62–i70.

(120) de Francisco, Á. L.; Belmar, L.; Piñera, C.; Kislikova, M.; Seras, M.; Serrano, M.; Albines, Z.; Sango, C.; Arias, M. Effect of Calcium Acetate/Magnesium Carbonate in the Treatment of Hyperphosphataemia in Dialysis Patients in Real Clinical Practice. One Year Follow up. *Nefrologia* **2014**, *34* (5), 617–27.

(121) Freitag, F.; Kleinebudde, P. How Do Roll Compaction/Dry Granulation Affect the Tableting Behaviour of Inorganic Materials? Comparison of Four Magnesium Carbonates. *Eur. J. Pharm. Sci.* **2003**, *19* (4), 281–289.

(122) Maguire, M. E.; Cowan, J. A. Preface–Introduction–Magnesium in the New Millenium. *BioMetals* **2002**, *15* (3), 201–201.

(123) White, P. J.; Greenwood, D. J. Properties and Management of Cationic Elements for Crop Growth. In *Soil Conditions and Plant Growth*; Blackwell Publishing Ltd., 2013; pp 160–194.