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Black Carbon Prepared from Wasted Batteries and its Phosphate Removal Potential

FINAL PROJECT

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Acknowledgments

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Abstract

Nowadays environmental problems have become one of the most severe problems confronted by human beings, and cannot be avoided wherever you are. Protect the earth as well as our shared living space has to be the consensus of the whole human society.

Since the 20th century human beings have been creating unprecedented differentiated materials for the advance of science, technology and societies in general.

But at the same time, resources, environmental pollution, ecological damage and other problems are becoming increasingly outstanding, threatening the development and in the end the survival of human species and our planet as we know it. People have realized that we must change the mindset of "challenging the nature" and the traditional development mode "polluting first and treating later," and try to seek a sustainable development approach in which people, economy, society, environment and resources harmonize with each other.

Two of the many problems human society suffers are the surplus of phosphate in our environment and a specific kind of waste, common batteries that are available in abundance all over the world. This study focuses on giving an alternative use to the no longer needed batteries, using them instead of costly synthetic activated carbon, and to absorb phosphate in water. By reducing and recycling the waste of batteries and decreasing the concentration of phosphate in our water we can solve the corresponding environmental and economic problems at the same time.

1. Introduction

Phosphorus is one of the three essential nutrients for life. It is fundamental for the growth and metabolic reactions of all plants and animals. Along with nitrogen and potassium, phosphorus is can be found in all kind of rocks and soils. In a natural environment, plants metabolize it and return it to the soil in its raw form as part of the lifecycle. The amount of phosphorus can either limit or increase growth.

In aquatic systems, the predominant form of phosphorus is orthophosphate in either the mono- or dipronated forms HPO_4^{2-}, $H_2PO_4^-$ [1] (esters or salts of phosphoric acid). There may also be significant amounts of organic or condensed phosphates present. Filterable Condensed Phosphorus (FCP) is composed of inorganic polyphosphates, metaphosphates, and branched ring structures (Figure 1.1). Filterable Organic Phosphorus (FOP) fraction consists of nucleic acids, phospholipids, inositol, phosphates, phosphoamides, phosphoproteins, sugar phosphates, aminophosphonic acids, phosphorus-containing pesticides, and organic condensed phosphates [2].
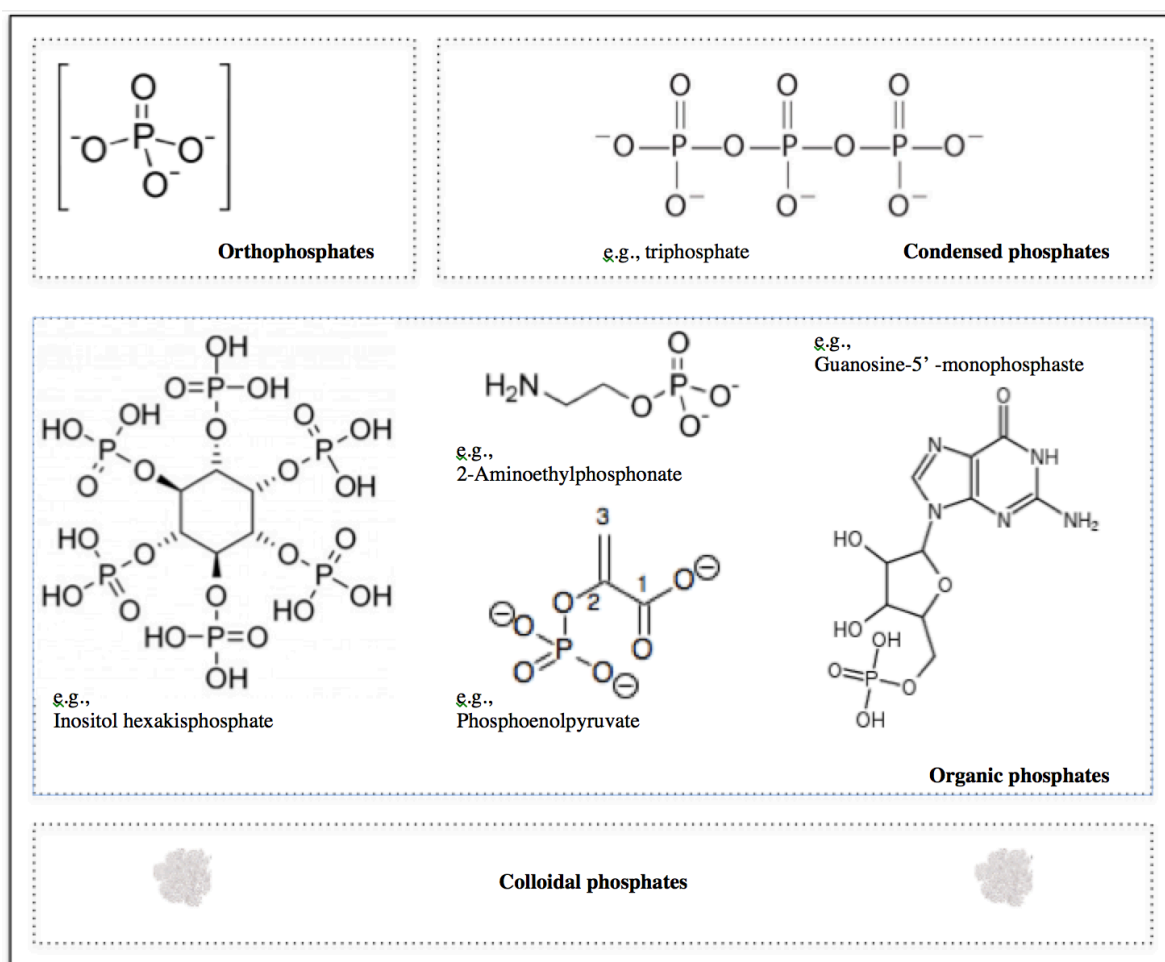

FIGURE 1.1 Forms of phosphorus occurring in water. *Source: Modified from McKelvie, I. D., Peat, D. M., & Worsfold, P. J. (1995). Analytical perspective. Techniques for the quantification and speciation of phosphorus in natural waters. Analytical Proceedings Including Analytical Communications. Royal Society of Chemistry.*

Phosphorus may originate from natural sources such as the mineralization of algae, the dissolution of phosphates minerals, from human and animal waste, from sewage treatment plants, from industrial plants and from the overfertilization of agricultural lands.[3] Because phosphorus is integral to the growth of animals and plants, imbalances in the amount of the naturally occurring phosphorus in the form of phosphates can create detrimental changes to the environment. The human intervention alters the nutrient's natural balance and saturates the soil.

1.1.　Environmental problems caused by human interference in the phosphate cycle

One of the main environmental problems occur when humans interfere in matter cycles, in this case the phosphate cycle (Figure 1.2). We remove phosphates on certain locations, to apply it on farmland as fertilizers, causing the phosphate concentration of surrounding land-soils and groundwater to rise. Due to the constant addition of phosphates and therfore exceeding the natural concentrations, the cycle is heavily disrupted.
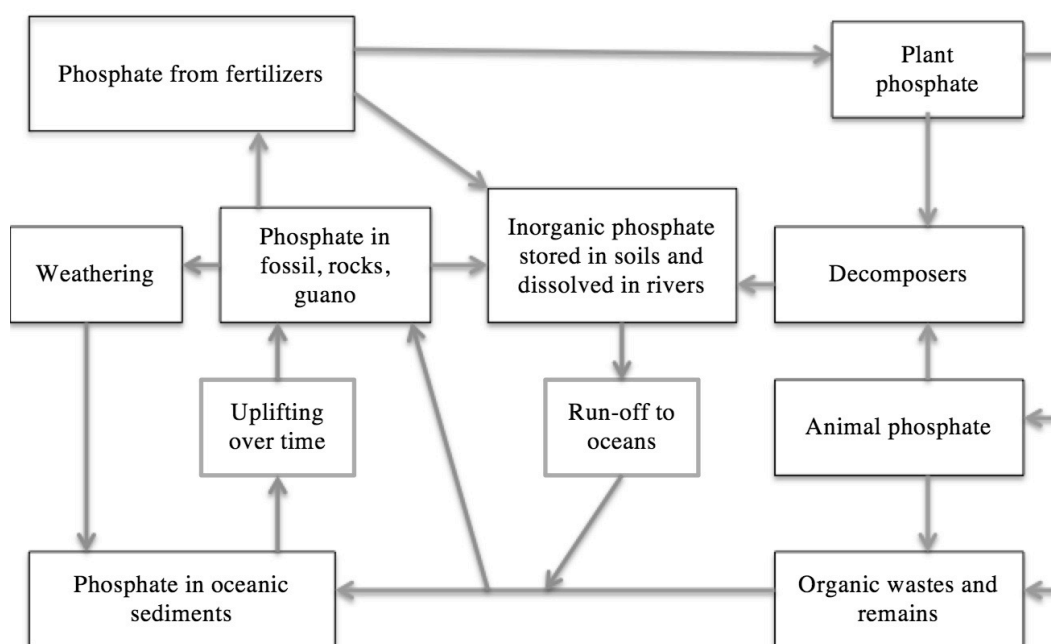
FIGURE 1.2 Phosphate cycle. *(Own source)*

Phosphates have many effects upon organisms. The effects are mainly consequences of emissions of large quantities of phosphate into the environment due to mining and cultivating. During water purification phosphates are often not removed properly, causing a spread of phosphate concentrations over large distances when found on the water surface.

Table 1.1 shows the phosphate levels in fresh water that should be avoided, but are commonly found due to human interference.

TABLE 1.1 Phosphate-phosphorus levels and effects.

Total phosphate/ phosphorus	Effects
0.01-0.03 mg/L	Amount of phosphate-phosphorus in most uncontaminated lakes
0.025 mg/L	Accelerates the eutrophication process in lakes
0.1 mg/L	Recommended maximum for rivers and streams

Source: *Water, Water Everywhere*. HACH Company. Second Edition. 1983.

1.2. Eutrophication

The term "eutrophication" is devrived from the Greek word "eutrophia", meaning "overfed". According to the Organization for Economic Cooperation and Development (OECD) 1982, eutrophication refers to the *excessive nutrients enrichment of water which results in the stimulation of an array of undesirable symptomatic changes, such as nuisance production of algae and other aquatic macrophytes (plants), deterioration of water quality, taste and odour problems and fish kills. Each of these changes significantly interferes with human use of water resources.*

Eutrophication involves the enrichment of waters chiefly by increasing the levels of essential nutrients, such as phosphates, nitrates and silicates[4]. The principal problem is that there are many sources for these nutrients to get into the aquatic ecosystem like, fertilizers, street runoff, animal waste or organic detritus. As a result of this nutrient surpuls algae and duckweed (*Lemnoideae*) begin to form in abundance. If the accumulation of nutrients is severe enough, the algae blooms will cover the entire surface on the water, blocking the sunlight from penetrating the water column with two consequences: 1) preventing photosynthesis below the water surface, lowering the dissolved oxygen concentration, and 2) stopping oxygen transfer through surface aeration[5]. As a consequence the water body becomes extremely depleted of oxygen and sunlight, causing fish and plant life alike to die. When fish and plants begin to die off, decomposing bacteria use the remaining oxygen to break down the dead organic compounds. The result is a body of water packed with algae, lacking aquatic life and oxygen which is essential for a healthy ecosystem.

Eutrophication is a worldwide problem. It is often most severe in shallow lakes which are heavily influenced by large external nutrient loads, frequent sediment resuspension resulting in high turbidity, a highly active sediment-water column nutrient exchange and nutrient regeneration. Consequently, these lakes experience accelerated eutrophication, causing the ecosystem to shift from macrophyte to phytoplankton-dominated conditions, often culminating in summer cyanobacterial blooms.

1.3.   Treatment method

To deal with this big issue chemical treatment methods have been developed for various applications to remove phosphate from aqueous solutions prior to their discharge into runoff and natural water bodies. Because the cost of these treatment technologies are substantial, there is a need to develop more cost effective and high efficiency technologies for phosphate removal. Recently[6] a number of biochars have been identified as effective adsorbents for some common water pollutants, such as organic compounds and heavy metals [7-13]. In this study graphite carbon from battery powder is used with and without modification of its surface to evaluate its usablilty as a phosphate adsorbent.

1.3.1. Adsorption

The term adsorption refers to a process through which a gas or liquid solute accumulates on the surface of a solid or a liquid material (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorption differs from absorption where the substance diffuses into a liquid or solid, forming a solution. However, the term sorption comprehends both processes, whereas desorption represents the reverse process [14].

Depending on the type of bonding formed between the adsorbent and the adsorbate, adsorption is classified as either physisorption or chemisorption. When the adsorbent adheres the adsorbent's surface by weak intermolecular Van der Waals interactions, the process is called physical adsorption, or physisorption, whereas a molecule adhering to a surface through the formation of a chemical bond called chemical adsorption, or chemisorption.

Adsorption is normally described by means of isotherms, the most important of which are the Langmuir isotherm, the Freundlich isotherm and the BET isotherm. An isotherm is a mathematical model showing the amount of adsorbate on the adsorbent and its concentration (if liquid).

The Langmuir and Freundlich isotherms represent attempts to model adsorption in systems with a limited number of identical adsorptive sites and with certain types of site nonuniformity, respectively. These isotherms are widely used to describe experimental data, although other isotherms are also used and are accepted equally if explaining the observations[15].

An understanding of the molecular-scale processes that control adsorption is invaluable for mechanistic interpretation of adsorption phenomena. However, a complete knowledge of these phenomena is not necessary for designing adsorption-based water treatment processes. The key information needed for such efforts includes the adsorption isotherms for the various constituents of the solutions and knowledge of the adsorption kinetics[15].

1.3.2. Adsorbent

One of the most important and effective factors in an adsorption process is the type of the adsorbent. The adsorbent is a substance on the surface of which the adsorbate adheres and consequently the adsorption process is achieved. An adsorbent should have a high resistance against abrasion, high thermal stability, and small pore diameters. The most essential feature of a good adsorbent is its porous structure that results in a higher surface area. The quality, size and shape of its pores determine the overall adsorption capacity of the adsorbent for a specific substance. Adsorbents are classified according to the diameter of their pores (Table 1-2 Classification of the Pore Size in Adsorbents) [17].

Table 1. 2 Classification of the Pore Size in Adsorbents.

Pore Diameter (d), nm	Type
d > 50	Macropores
$2 \leq d \leq 50$	Mesopores
d < 2	Micropores
d < 0.7	Ultramicropores

Source: Gupta, V.K and Ali, I., J. Colloid Interf. Sci., 271, 321, 2004

Common commercial adsorbents are basically categorized into three groups [18]:

1. Oxygen-based compound: silica gel, zeolites and alumina
2. Carbon-based compounds: activated carbon and graphite
3. Polymeric compounds

These commercial absorbents are expensive and they often need a regeneration process. Therefore lately they are being replaced with other low-cost adsorbents that are also more convenient for the environment.

1.3.3. Activated carbon

Activated carbon is the most popular and oldest adsorbent used in water and wastewater treatment processes due to its high adsorption capacity. Synthetic organic chemicals (SOCs) including pesticides (herbicides and insecticides) do not absorb well on metal hydroides and polymers, meaning that they cannot be taken out easily by coagulation-sedimentation-filtration. Here the application of powdered activated carbon can be the option for a better treatment. Activated carbon can be generated from wide range of materials from charcoal to wood and nuts.

Activated carbon can be made from a variety of carbonaceous raw materials. Processing involves dehydration and carbonization by slow heating of a variety of substances such as battery powder by chemical activation to produce a highly porous structure. Powdered activated

carbon (PAC) is often used in surface water treatment system where it is applied in rapid mix or flocculation and subsequently removed in sedimentation and filtration. Granular Activated Carbon (GAC) is more commonly used, either in the granular filter with sand or configured in a flow-through column as a post-filtration adsorbent. GAC must have good abrasion resistance since it is subject to heat reactivation.

The activation process creates a highly porous surface on the carbon particles with macropores and micropores down to molecular dimensions. Organic contaminants are adsorbed by attraction to and accumulation in pores of appropriate size; thus the pore structure is extremely important in determining adsorptive properties for particular compounds. Activation processes can be modified to produce activated carbons that are targeted for selective removal of particulate organic compounds[15]. In general GAP most commonly absorbs branch-chained high-molecular-weight organic chemicals with low solubility. These include pesticides, volatile organic chemicals, trihalomethanes and NOM (natural organic matter).

Powdered activated carbon is a fine powder applied in a water slurry, which can be added at any location in the treatment process ahead of filtration. At the point of application, the mixing must be adequate to ensure dispersion and the contact time must be long enough for adsorption. Poor adsorption is attributed to short contact time between the carbon particles and the dissolved organic chemicals and interference by adsorption of other organic compounds. Efficiency in removal of SOCs requires a granular activated carbon filter to ensure close contact between the water and carbon for a sufficient time for adsorption to occur.

1.3.4. Adsorption Isotherm

The equilibrium adsorption isotherm is the most fundamental method used to characterize activated carbon for a particular application. This characterization shows the relationship between the adsorbate (contaminant to be removed) and the solid phase concentration of the adsorbate on the adsorbent (activated carbon). The water to be treated should be used when conducting the experiments that lead to the isotherm because it will then contain not only the contaminant but also any interfering substances that might degrade the process [16].

Portions of the water are placed in vials with different concentration of phosphate. After sufficient contact time a equilibrium is established, the carbon is separated from the solution, and the concentration in the water is measured. It is assumed that the reduction of the phosphate concentration in the water is attributed to the adsorption of the adsorbate on the activated carbon, although precautions may be required to prevent volatilization and biodegradation losses.

The solid phase concentration are then calculated:

$$q = \frac{\text{mass of the adsorbate on the activated carbon}}{\text{mass of the activated carbon}} = \frac{(C_0 - C_e)V}{M} \qquad (1)$$

Where,

q = solid phase concentration, mg/g.
C_0 and C_e = concentration of adsorbate in water before adsorption and after equilibrium is attained, respectivey, mg/l.
V = volume of the vial containing the water and activated carbon, liters..
M = mass of activated carbon in the vial, g.

The data can be fit to a variety of models; we apply the frequently used Freundlich model, given by:

$$q = KC_e^b \qquad (2)$$

Where

K and b are coefficients for the model.

1.4. Objectives

As discussed in the previous sections, the high concentration of phosphorus in the water and the generation of waste are environmental problems that nowadays we need to face. To minimize the impact resulting from the residue of used batteries and the surplus of phosphate in our water, the following study is carried out to observe the effectiveness of the battery powder as a phosphate removal. Also we are modifying the structure of the carbon from the batteries through the impregnation of $MgCl_2$ to increase the level of adsorbation.

The specific objectives are:

a) Get familiar with the ESS Method 310.1 to measure and calculate the phosphate concentration in disolutions.
b) Study the reaction of the batterie powder in the adsorption of phosphate in water.
c) Improve the absorbance of the batteries modifying the carbon structure with the impregnation of $MgCl_2$ and pyrolysis.
d) Measure the kinetics and equilibrium isotherm of phosphate adsorption of battery powder.

2. Materials and methods

2.1. Materials

2.1.1. Reactives

The reactives during the experiment were:

- Sulfuric acid, H_2SO_4, 4.9 N
- Ammonium molybdate $((NH_4)_6 Mo_7O_{24} \cdot 4H_2O)$
- Ascorbic acid $(C_6H_8O_6)$
- Antimony potassium tartrate $((K(SbO)C_4H_4O_6 \cdot 1/2H_2O))$
- Potassium phosphate monobasic (KH_2PO_4)
- Graphite powder
- Magnesium chloride hexahydrate $(MgCl_2 \ 6H_2O)$

2.1.2. Equipment

The equipment was:

- Weighing scale
- Fridge
- Atomic Absorption (U-2800 Spectrophotometer)
- Shaker
- Centrifuge
- Oven
- Furnace

2.1.3. Other materials

Other materials that were also used:

- Pipettes (1ml 5ml)
- Graduated cylinder (10ml, 50ml, 100 ml, 500ml)
- Automatic pipette (1ml)
- Volumetric flask (50ml, 500ml, 1000ml)
- Plastic centrifuge tubes (50ml)

2.2. Methods

2.2.1. Determination of phosphates in water

The phosphate concentrations in the liquid phase samples were determined by the ascorbic acid method (ESS Method 310.1[19]) and a spectrophotometer. The concentrations of phosphate that we used in this method range from 0,002mg/l to 200 mg/l. Phosphate concentrations on the solid phase were calculated with the initial and final aqueous concentrations.

ESS Method is based on the reaction between ammonium molybdate and antimony potassium tartrate in an acid medium with dilute solutions of orthophosphate to form an antimony-phospho-molybdate complex which is reduced to an intensely blue by ascorbic acid. This color is proportional to the phosphorus concentration.

It is necessary to create the following solutions:

a) **Stock Solution A;** Sulfuric acid solution, 4.9 N: Add 136 mL concentrated H_2SO_4 to 800 mL Milli-Q water. Cool and dilute to 1 L with Milli-Q water.

b) **Stock Solution B**; Ammonium molybdate solution: Dissolve 40 g of $((NH_4)_6 Mo_7O_{24} \cdot 4H_2O)$ in 900 mL Milli-Q water and dilute to 1 L. Store at 4°C.

c) **Stock Solution C;** Ascorbic acid: Dissolve 9 g of ascorbic acid ($C_6H_8O_6$) in 400 mL Milli-Q water and dilute to 500 mL. Store at 4°C. Keep well stoppered. Prepared fresh monthly.

d) **Stock Solution D;** Antimony potassium tartrate: Dissolve 3.0 g of $K_2Sb_2(C_4H_2O_6)_2$ in 800 mL Milli-Q water and dilute to 1 L. Store at 4°C.

a) **Combined Color Reagent:** Combine the following solutions in order and mix them after each addition:
   - Stock A (4.9 N H_2SO_4): 50ml
   - Stock B (Ammonium molybdate solution): 15ml
   - Stock C (Ascorbic acid solution): 30ml
   - Stock D (Antimony-tartrate solution): 5ml
   Total volume: 100 ml

b) **Stock Phosphorus Standard:** Dissolve 0.4394 g of Potassium phosphate monobasic (KH_2PO_4) in 900 mL Milli-Q water. Add 2 mL of concentrated H_2SO_4 and dilute to1L.
   1.0mL=0.100mg P (100 mg PO_4^{-3} L^{-1}).

c) **Standard Phosphorus Solution**: Dilute 10.0 mL of stock solution (f) into 1 L.
   1.0 mL = 0.001 mg P (1.0 mg PO_4^{-3} L^{-1})

2.2.2. Calibration line

Once we have the stock A, B, C, D, the color reagent and the Standard Phosphorus Solution 1.0 mg/L, we draw the calibration line.

We did six phosphate dissolutions (from 0.0 mg/L to 0.4 mg/L) from the standard phosphorus solution 1.0 mg/l. We took 10 ml of each dissolution and mixtured it with 1,6 ml of combined color reagent in a 20 ml flask. After 15 minutes we measured with the spectrophotometer (λ: 880 nm) each absorbance.

$$M_1 \cdot V_1 = M_2 \cdot V_2 \tag{3}$$

Where

M_1= Standard phosphorus solution.
V_1= Volume of Standard Phosphorus Solution.
M_2= Dissolution concentration.
V_2= Dissolution volume.

TABLE 2.1 Dissolution for the calibration line.

M_1	V_1	M_2	V_2
1.00	0.00	0.00	100
1.00	0.25	005	100
1.00	0.50	0.10	100
1.00	1.00	0.20	100
1.00	1.25	0.25	100
1.00	1.50	0.30	100
1.00	2.00	0.40	100

The aim is to obtain an equation (4) by least squares adjustment.

$$y = ax + b \tag{4}$$

Where,

x,y = are the coordinates of any point on the line
a = is the slope of the line
b = is the y-intercept (where the line crosses the y-axis)

2.2.3.   Phosphate adsorption by graphite carbon

In our study, first of all we wanted to observe the behavior of the graphite carbon with a phosphate dissolution. For each experiment, the relation was 0.1 g solid per 50 ml phosphate solution, as shown by M. Zhang[20] in the study about the *Synthesis of porous MgO-biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions*. The samples were agitated at 60 rpm in a mechanical shaker for 24 h. The mixtures were centrifuged for 10 min at 4200 rpm to separate the carbon from the liquid and the absorbance was measured without interferences.

Phosphate concentrations on the solid phase were calculated based on the initial and final aqueous concentrations. All the experimental treatments were performed three times.

2.2.4.   Adsorption equilibrium

From the data provided by Yao et. al[21] in her study about *Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings*, the adsorption isotherm is achieved after 24h in the shaker at room temperature.

2.2.5.   Modification of the graphite structure by magnesium chloride hexahydrate

Magnesiumchloride hexahydrate ($MgCl_2$ $6H_2O$) was purchased to prepare a magnesium chloride solution to pretreat the graphite feedstocks. All the solutions used in this work were prepared with distilled (DI) water, which was also used to rinse and clean the samples. The magnesium chloride solution was prepared by dissolving 40 g of $MgCl_2 \cdot 6H_2O$ in 60 mL of distilled water. Each feedstock was immersed into the solution for 2 h. The mixture of graphite and $MgCl_2$ was dried in the oven at 80°C to remove the water. A dry mixture of graphite and $MgCl_2$ was pyrolyzed at different temperatures from 30°C up to 600 °C in the furnace. The graphic 3-1 shows the stages of the pyrolyzed carbon.
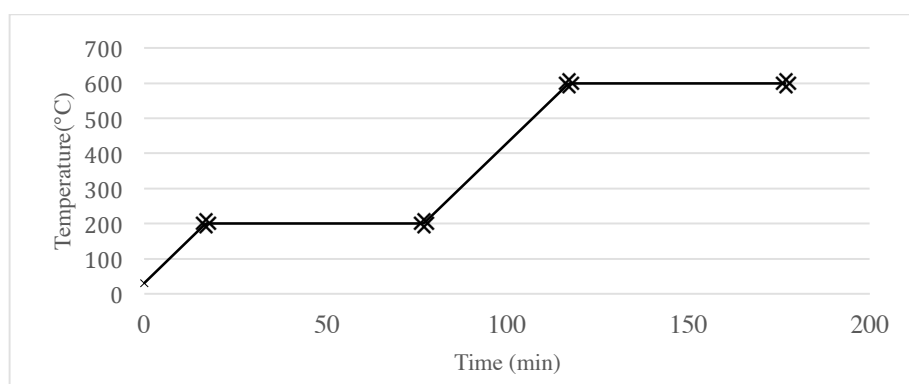
FIGURE 2.1 Furnace stage.

Two kind of MgO-carbon were prepared,

i.   *MgO-carbon without being washed after the* pyrolysis: We did not wash the graphite after the furnace.

ii. *MgO-carbon being washed after the* pyrolysis: The carbon was washed twice with distilled water to remove possible anions (Cl^-) from the magnesium chloride hexahydrate once it passed the last stage of the furnace (600°C). Afterwards the samples were dried in the oven.

The process can be observed in the Figure 2.2.
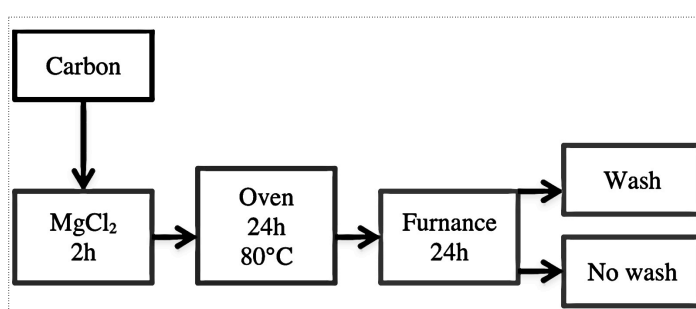
FIGURE 2. 2 Modification process.

2.2.6. Adsorption Isotherms

Adsorption isotherm of phosphate on graphite carbon was determined by mixing 0.1g carbon with 50 mL phosphate solutions of different concentrations ranging from 5 mg/l to 100 mg/l (washed carbon) and 1 mg/l to 1000 (unwashed carbon) in the digestion vessels. Afterwards the vessels were shaken in the mechanical shaker for 24 h at room temperature. This period of time was determined by Yao et al's [21, 22] kinetic experiments as sufficient for the adsorption equilibrium to be established. The samples then were withdrawn and centrifuged to determine adsorbed phosphate concentrations by the same method.

3. Results and discussion

3.1. Calibration line

TABLE 3.1 Phosphate calibration line determind by the ascorbic acid method.

Phosphate concentration (mg/L)	Absorbance (880 nm)
0.05	0.031
0.1	0.067
0.2	0.127
0.25	0.158
0.3	0.186
0.4	0.245
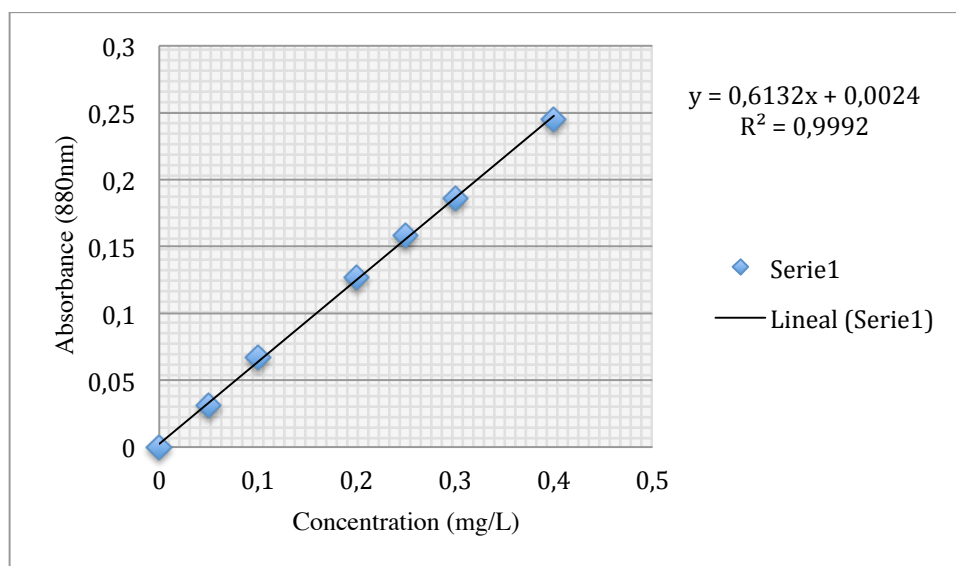
FIGURE 3.1 Calibration line.

The equation to determinate phosphate in a concentration range between 0 and 0,4 mg/l is:

$$y = 0{,}6132\,x + 0{,}0024$$

3.2. Phosphate absorbance by black carbon (graphite).

The first step was to weigh 0,4394 g KH_2PO_4 and putting it into 900 mL of distilled water + 2ml H_2SO_4. Diluting it to 1L in order to obtain 100 mg/L dissolution concentration.

After this solution we prepared another dissolution taking 25ml from the previous solution and putting it into 500 ml flask to obtain a final solution of 5 mg/l

$$100 \text{ mg/l} \cdot V_1 = 5 \text{ mg/l} \cdot 500 \text{ ml} ; V_1 = 25 \text{ mL into 500ml vessel}$$

We took 10 ml of the 5 mg/l solution and mixed it with 1.6 ml of color reagent in a 50 ml volume flask, to calculate the initial concentration. Since our calibration line was between 0,00 - 0,40 ppm we had to dilute the sample to 0.25 mg/L to be inside the range.

$$5 \text{ mg/l} \cdot V_1 = 0,25 \text{ mg/l} \cdot 20 \text{ ml} ; V_1 = 1 \text{ ml into 20 ml vessel.}$$

The absorbance of the sample at 880 nm was 0,156. Once having gained the absorbance (y), we use the formula obtained in the calibration line, achieving the initial concentration (C_0)

$$0.156 = 0.6132x + 0.0024; x = 0.25 mg/L$$

The next step was to weigh the graphite carbon and add it into 50ml of phosphate solution (5,0mg/L). We did three replicas in order to improve our results.

TABLE 3. 2 Grams of black carbon.

Carbon (g)
0,0952
0,1053
0,1013

After 24 hours at room temperature we took the previous three samples from the shaker and put them into the centrifuge for 10 min at 4500 rpm. We diluted it to 0,25 mg/L.

To measure the absorbance, 20 ml were taken from the sample and diluted to another flask with 3,2 ml of color agent. (Phosphate solution : color reagent = 10ml:1.6ml).

TABLE 3. 3 Results of the effectiveness of the activated carbon with the phosphate.

C_0 (mg/l)	Carbon (g)	Absorbance (880 nm)	Ce (mg/l)	Elimination %
0.2502	0.0952	0.154	0.246952224	1.30
0.2502	0.1053	0.155	0.248599671	0.64
0.2502	0.1013	0.155	0.248599671	0.4

There was only very little adsorbation by the carbon. As we can observe in the elimination percentage, the maximum elimination was 1.30 %. The carbon didn't work efficiently as a

phosphate adsorbent this time. We had to modify the structure of the carbon with $MgCl_2$ to adsorb more phosphate on the surface of the carbon.

3.3. Analysis of the modificated black carbon (graphite)

3.3.1.   MgO-graphite without being washed after the pyrolysis

The samples, as in previous sections, were performed with the same relation solid/liquid and the same process, but this time the carbon was modified. The sample concentration was 5 mg/l.

TABLE 3. 4 Results from the carbon adsorption (theoretically: 5 mg/l phosphate).

Volume (ml)	Carbon (g)	$C_{0, phosphate}$ (mg/L)	$C_{e, phosphate}$ (mg/L)	Factor	$C_{0, phosphate}$ (mg/L)	$C_{e, phosphate}$ (mg/L)	Elimination %
50	0.1002	0.2502	0.0097	20	4.97	0.25	95,01
50	0.0997	0.2502	0.0064	20	4.97	0.18	96,33
50	0.0998	0.2502	0.0196	20	4.97	0.44	91,08

Once having obtained the results (Table 3.4), we can see that the modified carbon absorbs a great amount of phosphate from the water, reaching values up to 96.33% of elimination. We increased the concentration to 20 mg/l and 100 mg/l (Table 3.5).

TABLE 3. 5 Results from the carbon adsorption (theoretically: 20 mg/l and 100 mg/l).

Volume (ml)	Carbon (g)	$C_{0, phosphate}$ (mg/L)	$C_{f, phosphate}$ (mg/L)	Factor	$C_{0, phosphate}$ (mg/L)	$C_{e, phosphate}$ (mg/L)	Elimination %
50	0.0997	0.2222	0.0180	80	17.82	1.64	90.78
50	0.1010	0.2222	0.0130	80	17.82	1.25	92.97
50	0.1007	0.2222	0.0180	80	17.82	1.64	90.78
50	0.1004	0.247	0.0229	400	98.89	10.18	89.71
50	0.1004	0.247	0.0097	400	98.89	4.96	94.99
50	0.1002	0.247	0.0114	400	98.89	5.61	94.33

It is possible that the excellent absorbance is attributed to the anions (Cl⁻) from the magnesium chloride hexahydrate ($MgCl_2$) instead of the activated carbon. For this reason we discarded the sample and the carbon was washed after the pyrolysis was completed - to remove possible interferences.

3.3.2.   MgO biochar being washed after the pyrolysis

TABLE 3. 6 Results from the Mg-carbon adsorption (theoretically: 20 mg/l, 100 mg/l and 100 mg/l).

Volume (ml)	Carbon (g)	C_0, phosphate (mg/L)	C_e, phosphate (mg/L)	Factor	C_0, phosphate (mg/L)	C_e, phosphate (mg/L)	Elimination %
50	0.1054	0.23	0.1646	80	18.34	13.26	27.74
50	0.1008	0.23	0.2025	80	18.34	16.26	11.38
50	0.1005	0.25	0.0773	400	98.89	31.70	67.94
50	0.1011	0.25	0.0311	400	98.89	13.44	86.41
50	0.1005	0.24	0.2074	4000	1001.96	832.35	16.93
50	0.1011	0.24	0.1662	4000	1001.96	669.28	33.20

TABLE 3. 7 Average results from the Mg-carbon adsorption (theoretically: 20 mg/l , 100 mg/l and 100mg/l).

Volume (ml)	Carbon (g)	C_0, phosphate (mg/L)	$C_{e,\ phosphate}$ (mg/L)	Factor	$C_{0,\ phosphate}$ (mg/L)	$C_{e,\ phosphate}$ (mg/L)	Elimination %
50	0,1031	0,23	0,18355	80	**18,34**	**14,76**	**19,56**
50	0,1008	0,25	0,0542	400	**98,89**	**22,57**	**77,175**
50	0,1008	0,24	0,1868	4000	**1001,96**	**750,815**	**25,065**

The results from the Table 3.7 show that the carbon can absorb part of the phosphate in the solution. For instance in the second sample the solution started with 98.78 mg/l of phosphate and due to the Mg-graphite ended up with 21.68 mg/l., an elimination rate of 77,18%.

The amount of phosphate absorbed is not as big as in the unwashed carbon but at least we can be sure that there are not interferences with anions. After verification the adsorption isotherm was performed.

There is a low percentage of elimination at 20 mg/l due to a possible phenomenon concerning the van der Waals forces between the hydrogen diatomic molecules and the surface of the carbon. These forces exist between molecules and are extremely sensitive to the distance between the carbon surface and the adsorbate molecule. They are also additive, meaning that the adsorption force is the sum of all interactions between all the similar atoms, preventing the phosphate molecules from an easy access to the surface of the carbon. This phenomenon will be explained in the next section.

The amount of phosphate absorbed is not as much as in the unwashed carbon but at least we made sure that there are no interferences with anions. After verifiying that the modified carbon works the adsorption isotherm was performed.

3.3.3.   Adsorption Isotherms

The following tables (Table 3.8 and   Table 3.9) show the results of the equilibrium adsorption isotherm, the most fundamental method to characterize activated carbon. But we found a phenomenon, stated in the previous part, that makes it impossible to incorporate the Langmuir or Freundlich models because of the lack of linear absorbance from the carbon caused by the interference of van der Waals forces.

TABLE 3. 8 Results from the Mg-carbon adsorption (theoretically: 1 mg/l, 5 mg/l, 10 mg/l, 20 mg/l and 30 mg/l).

Volume (ml)	Carbon (g)	$C_{0, phosphate}$ (mg/L)	Factor	$C_{0, phosphate}$ (mg/L)	$C_{e, phosphate}$ (mg/L)	Elimination %
50	0,1005	0,21	4	0,83	0,05	94,04
50	0,1009	0,21	4	0,83	0,12	85,42
50	0,1002	0,21	4	0,83	0,06	93,26
50	0,1007	0,25	20	5,00	0,00	100,26
50	0,1005	0,25	20	5,00	0,02	99,61
50	0,1005	0,25	40	10,00	1,28	87,21
50	0,1001	0,25	40	10,00	1,67	83,30
50	0,1002	0,23	80	18,34	13,39	27,03
50	0,1005	0,23	80	18,34	13,39	27,03
50	0,1005	0,30	100	30,00	1,73	94,24
50	0,1002	0,30	100	30,00	1,57	94,78

TABLE 3. 9 Results from the Mg-carbon adsorption (theoretically: 50 mg/l, 80 mg/l, 200 mg/l, 300 mg/l, 600 mg/l, 1000 mg/l).

Volume (ml)	Carbon (g)	$C_{0, phosphate}$ (mg/L)	Factor	$C_{0, phosphate}$ (mg/L)	$C_{e, phosphate}$ (mg/L)	Elimination %
50	0,1008	0,25	200	49,45	11,61	76,52
50	0,1002	0,25	200	49,45	16,50	66,62
50	0,1002	0,25	200	49,45	11,61	76,52
50	0,1005	0,25	320	80,00	9,71	87,87
50	0,1002	0,25	320	80,00	15,97	80,04
50	0,1002	0,30	6667	200,00	68,06	65,97
50	0,1007	0,30	6667	200,00	94,15	52,92
50	0,1007	0,28	1000	283,11	123,29	56,45
50	0,1001	0,28	1000	283,11	131,44	53,57
50	0,1002	0,28	1000	283,11	141,23	50,12
50	0,1005	0,30	2000	602,09	507,50	15,71
50	0,1007	0,30	2000	602,09	419,44	30,34
50	0,1011	0,25	4000	1001,96	832,35	16,93
50	0,1015	0,25	4000	1001,96	669,28	33,20

The Table 3.10 was realized with the average results from Table 3.8 and Table 3.9, to analyze the results. The point 49,45 mg/l was deleted because there was an experimental mistake.

TABLE 3. 10 Average results from the Mg-carbon adsorption (theoretically: 1 mg/l, 5 mg/l, 10 mg/l, 20 mg/l, 30 mg/l, 50 mg/l, 80 mg/l, 200 mg/l, 300 mg/l, 600 mg/l, 1000 mg/l).

Volume (ml)	Carbon (g)	$C_{0, phosphate}$ (mg/L)	Factor	$C_{0, phosphate}$ (mg/L)	$C_{e, phosphate}$ (mg/L)	Elimination %
50	0,1005	0,21	4	0,83	0,08	91
50	0,1006	0,25	20	5,00	0,01	100
50	0,1003	0,25	40	10,00	1,47	85
50	0,1004	0,23	80	18,34	13,39	27
50	0,1004	0,30	100	30,00	1,65	95
~~50~~	~~0,1004~~	~~0,25~~	~~200~~	~~49,45~~	~~13,24~~	~~73~~
50	0,1004	0,25	320	80,00	12,84	84
50	0,1005	0,30	667	200,00	81,10	59
50	0,1003	0,28	1000	283,11	131,99	53
50	0,1006	0,30	2000	602,09	463,47	23
~~50~~	~~0,1013~~	~~0,25~~	~~4000~~	~~1000.96~~	~~750,82~~	~~25~~

The point 49.45 mg/l was deleted since it is an experimental mistake. There is a small mistake in the 1001.96 mg/l point, also related to an experimental mistake.

The percentage of this point (1001.96 mg/l) should not increase but decrease, because in high concentrations the carbon has less empty spaces on its surface, resulting in a higher saturation of phosphate.

The previous results (Table 3.10) are expressed in the next figure (Figure 3.1), without the 49,45 mg/l point. The point 20mg/l was repeated 7 times to confirm it.

FIGURE 3.1. Elimination percentage with initial phosphate concentration.

As we can observe in the Figure 3.2, a low concentration of phosphate (1 mg/l and 5 mg/l) results in a high absorption from the activated carbon because the carbon has a lot of empty places on its surface and the molecules of the hydrogen and the phosphate have the same chance to be linked to the carbon. But at the same time the electrical forces of the phosphate are stronger and the small amount of phosphate dissolved in the water create bonds with the activated carbon. When the concentration is exeeding 20 mg/l the elimination starts to decrease. We think this could be due to the formation of hydrogen bonds on the surface of the carbon. These bonds are difficult to create and easy to break. However in low concentrations of phosphate the molecular distance between the phosphate and the carbon is big and the chance of the hydrogen molecules to create bonds is higher than the phosphate molecules due to the higher concentration of hydrogen. The electric power of the phosphate molecules is not enough to break the van der Waals bonds and the surface of the carbon is packed with hydrogen molecules. This could be the reason that the elimination percentage decreases from this point on. Once the concentration of phosphate increases a bit more, enough for the phosphate to have less distance with the solid carbon particles and a higher chance to create bonds with its surface, the hydrogen bonds cannot be formed because the electrical power gains the empty spaces and the elimination percentage increases again.

When the concentration increases, the removal of phosphate decreases because there is more phosphate to absorb and less empty spaces in the surface of the activated carbon.
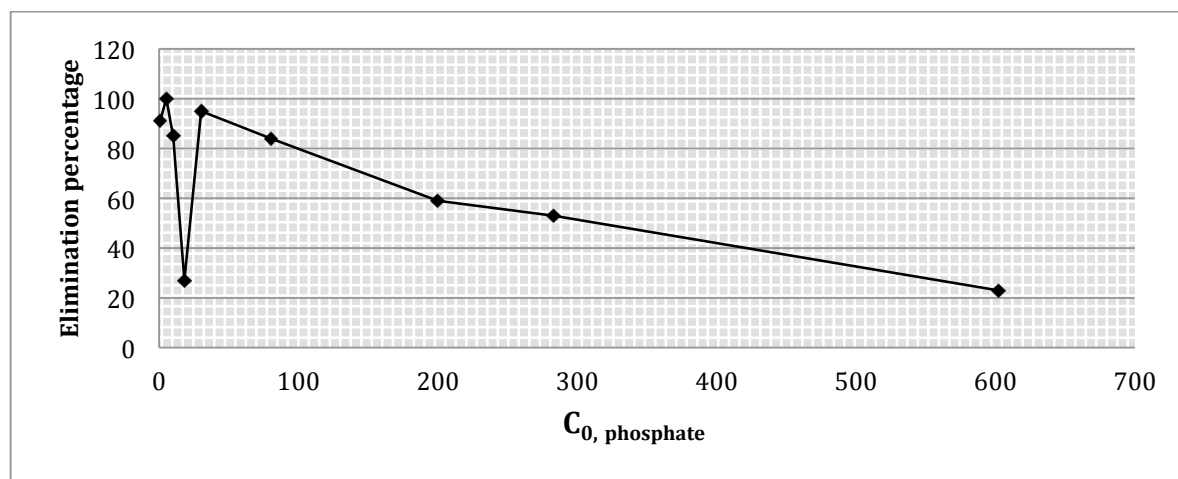

FIGURE 3.2. Elimination percentage with initial phosphate concentration without 1000mg/l point.

Using the following isotherm results (Co and Ce) of the Table 3.11, the solid phase concentration were calculated (q_e) for each individual isotherm vials contained in 50 ml of water. The initial concentration was 0,83 mg/l; 5 mg/l; 10 mg/l; 18,34 mg/l; 30 mg/l; 80 mg/l; 283,11 mg/l and 602,09 mg/l.

TABLE 3. 11 Average results from the Mg-carbon adsorption with q_e and concentration of carbon.

Volume (ml)	Carbon g/5l	Carbon (g)	$C_{0,\,phosphate}$ (mg/L)	$C_{e,\,phosphate}$ (mg/L)	Elimination %	q_e mg/l
50	2,01	0,1005	0,83	0,08	91	0,40
50	2,012	0,1006	5	0,01	100	2,49
50	2,006	0,1003	10	1,47	85	4,97
50	2,008	0,1004	18,34	13,39	27	9,05
50	2,008	0,1004	30	1,65	95	14,93
50	2,008	0,1004	80	12,84	84	39,82
50	2,01	0,1005	200	81,10	59	99,44
50	2,006	0,1003	283,11	131,99	53	141,07
50	2,012	0,1006	602,09	463,47	23	299,14

4. Conclusions

Black carbon (graphite) prepared from wasted batteries as activated carbon can be used as an alternative instead of the expensive commercial ones. They can be found in industrial/urban waste. The main advantages of battery powder compared to the commercial absorbent are that they are cheap, abundant, easily available, disposable without regeneration and are usable after the simple magnesium chloride hexahydrate impregnation, without the need for complex thermal or chemical processes. Graphite is not only cheap but also could be more effective in some cases. They contribute considerably to the protection of the environment, minimizing the waste of batteries and prolonging their lifespan, converting them to cheap, activated carbon that can be used to remove phosphate from aquatic systems, reducing eutrophication problems.

The solution for the isothermal adsorption model would be to create a new mathematical model according to our experimental outcomes, since the Langmuir and Freundlich model (as well as others) fail to explain our results.

5. References

[1]Matthiensen, A., Galvfio, J. A., & Oetterer, M. (2013). Phosphates in Aquatic Systems. *Handbook of Water Analysis*, 327.

[2]McKelvie, I. D. (2005). Separation, preconcentration and speciation of organic phosphorus in environmental samples. *Organic phosphorus in the environment*, 1-20.

[3]Mesquita, R. B., Ferreira, M., Tóth, I. V., Bordalo, A. A., McKelvie, I. D., & Rangel, A. O. (2011). Development of a flow method for the determination of phosphate in estuarine and freshwaters—Comparison of flow cells in spectrophotometric sequential injection analysis. *Analytica chimica acta*, *701*(1), 15-22.

[4]Lee, G. F., Jones, R., & Rast, W. (1980). Availability of phosphorus to phytoplankton and its implications for phosphorus management strategies. *Ch*, *11*, 259-308.

[5]Ghosh, T., & Mondal, D. Journal of Today's Biological Sciences: Research & Review (JTBSRR) Accepted Article for Publication Eutrophication: Causative factors and remedial measures.

[6]Zhang, M., Gao, B., Yao, Y., Xue, Y., & Inyang, M. (2012). Synthesis of porous MgO-biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions. *Chemical Engineering Journal*, *210*, 26-32.

[7]Qin, H., Liu, Y., Li, L., Pan, G., Zhang, X., & Zheng, J. (2012). Adsorption of cadmium in solution by biochar from household biowaste. *J Ecol Rural Environ*, *28*, 181-186.

[8]Xu, T., Lou, L., Luo, L., Cao, R., Duan, D., & Chen, Y. (2012). Effect of bamboo biochar on pentachlorophenol leachability and bioavailability in agricultural soil. *Science of the Total Environment*, *414*, 727-731.

[9]Hale, S., Hanley, K., Lehmann, J., Zimmerman, A., & Cornelissen, G. (2011). Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar. *Environmental science & technology*, *45*(24), 10445-10453.

[10]Teixidó, M., Pignatello, J. J., Beltrán, J. L., Granados, M., & Peccia, J. (2011). Speciation of the ionizable antibiotic sulfamethazine on black carbon (biochar). *Environmental science & technology*, *45*(23), 10020-10027.

[11]Kong, H., He, J., Gao, Y., Wu, H., & Zhu, X. (2011). Cosorption of phenanthrene and mercury (II) from aqueous solution by soybean stalk-based biochar. *Journal of agricultural and food chemistry*, *59*(22), 12116-12123.

[12]Ni, J., Pignatello, J. J., & Xing, B. (2011). Adsorption of aromatic carboxylate ions to black carbon (biochar) is accompanied by proton exchange with water. *Environmental science & technology*, *45*(21), 9240-9248.

[13]Lin, Y., Munroe, P., Joseph, S., Henderson, R., & Ziolkowski, A. (2012). Water extractable organic carbon in untreated and chemical treated biochars. *Chemosphere*, *87*(2), 151-157.

[14]Inglezakis, V., & Poulopoulos, S. (2006, August 23). *Adsorption, ion exchange and catalysis: design of operations and environmental applications* (Vol. 3). Elsevier.

[15]Benjamin, M. M., & Lawler, D. F. (2013, August 13). *Water quality engineering: physical/chemical treatment processes*. John Wiley & Sons.

[16]Viessman, W., Hammer, M. J., Perez, E. M., & P. A (2009). *Water supply and pollution control*. (Pearson New International Edition, 2014)

[17]Gupta, V. K., & Ali, I. (2004). Removal of lead and chromium from wastewater using bagasse fly ash—a sugar industry waste. *Journal of colloid and interface science*, *271*(2), 321-328.

[18] Eslamian, S. (2014, March 21). *Handbook of Engineering Hydrology: Environmental Hydrology and Water Management* (S. Eslamian). CRC Press.

[19]USEPA, ESS Method 310.1: Ortho-phosphorus, Dissolved Automated, AscorbicAcid, Environmental Sciences Section Inorganic Chemistry Unit, Wisconsin State Lab of Hygiene, 1992

[20] Zhang, M., Gao, B., Yao, Y., Xue, Y., & Inyang, M. (2012). Synthesis of porous MgO-biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions. *Chemical Engineering Journal*, *210*, 26-32.

[21]Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P., et al. (2011). Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. *Journal of hazardous materials*, *190*(1), 501-507.

[22]Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P., et al. (2011). Biochar derived from anaerobically digested sugar beet tailings: characterization and phosphate removal potential. *Bioresource technology*, *102*(10), 6273-6278.