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Phosphorus and Nitrogen Removal in Modified Biochar Filters

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ABSTRACT

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Onsite wastewater treatment systems in Sweden are getting old and many of them lack sufficient phosphorus, nitrogen and organic carbon reduction. Biochar is a material that has been suggested as an alternative to the common sand or soil used in onsite wastewater treatment systems. The objective of this study was to compare the phosphorus removal capacity between three different modified biochars and one untreated biochar in a batch adsorption and column filter experiment. The modifications included impregnation of ferric chloride ($FeCl_3$), calcium oxide (CaO) and untreated biochar mixed with the commercial phosphorus removal product Polonite. To further study nitrogen removal a filter with one vertical unsaturated section followed by one saturated horizontal flow section was installed.

The batch adsorption experiment showed that CaO impregnated biochar had the highest phosphorus adsorption, i.e. of 0.30 ± 0.03 mg/g in a 3.3 mg/L phosphorus solution. However, the maximum adsorption capacity was calculated to be higher for the $FeCl_3$ impregnated biochar (3.21 ± 0.01 mg/g) than the other biochar types. The pseudo 2nd order kinetic model proved better fit than the pseudo 1st order model for all biochars which suggest that chemical adsorption was important. Phosphorus adsorption to the untreated and $FeCl_3$ impregnated biochar fitted the Langmuir adsorption isotherm model best. This indicates that the adsorption can be modeled as a homogenous monolayer process. The CaO impregnated and Polonite mixed biochars fitted the Freundlich adsorption model best which is an indicative of heterogenic adsorption.

CaO and $FeCl_3$ impregnated biochars had the highest total phosphorus (Tot-P) reduction of 90 ± 8 % and 92 ± 4 % respectively. The Polonite mixed biochar had a Tot-P reduction of 65 ± 14 % and the untreated biochar had a reduction of 43 ± 24 %. However, the effluent of the CaO impregnated biochar filter acquired a red-brown tint and a precipitation that might be an indication of incomplete impregnation of the biochar. The $FeCl_3$ effluent had a very low pH. This can be a problem if the material is to be used in full-scale treatment system together with biological treatment for nitrogen that require a higher pH.

The nitrogen removal filter showed a total nitrogen removal of 62 ± 16 % which is high compared to conventional onsite wastewater treatment systems. Batch adsorption and filter experiment confirms impregnated biochar as a promising replacement or addition to onsite wastewater treatment systems for phosphorus removal. However the removal of organic carbon (as chemical oxygen demand COD) in the filters was lower than expected and further investigation of organic carbon removal needs to be studied to see if these four biochars are suitable in real onsite wastewater treatment systems.

Keywords: biochar, modified biochar, phosphorus filter, wastewater, batch adsorption experiment, nitrogen filter, COD, Tot-P, Tot-N

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REFERAT

Fosfor och kväverening i modifierade biokolsfilter

Ylva Stenström

Många av Sveriges små avloppssystem är gamla och saknar tillräcklig rening av fosfor, kväve och organiskt material. Följden är förorenat grundvatten samt övergödning i hav, sjöar och vattendrag. Lösningar för att förbättra fosfor- och kvävereningen finns på marknaden men många har visat brister i rening och robusthet. Biokol är ett material som har föreslagits som ersättare till jord eller sand i mark och infiltrationsbäddar. Denna studie syftade till att i skak- och kolonnfilterexperiment jämföra fosforreduktion mellan tre modifierade biokol och ett obehandlat biokol. Modifieringen av biokolet innebar impregnering med järnklorid ($FeCl_3$), kalciumoxid (CaO) samt blandning med Polonite som är en kommersiell produkt för fosforrening. För att undersöka förbättring av kväverening installerades även ett filter med obehandlat biokol där en vertikal aerob modul kombinerades med en efterföljande horisontell anaerob modul.

Skakstudien där biokolen skakades i 3.3 mg/L fosforlösning visade att adsorptionen var högst i det CaO-impregnerade biokolet, 0.3 ± 0.03 mg/g. Den maximala potentiella fosforadsorptionen beräknades dock vara högst för biokolet som impregnerats med $FeCl_3$, 3.21 ± 0.01 mg/g. Skakförsöket visade också att fosforadsorptionen var främst kemisk då adsorptionen passade bättre med pseudo andra ordningens modell än pseudo första. Adsorption av fosfor på obehandlat biokol och $FeCl_3$ impregnerat biokol modellerades bäst med Langmuir modellen, vilket tyder på en homogen adsorption. Det Polonite-blandade biokolet och CaO-impregnerade biokolet modellerades bäst med Freundlich modellen vilket är en indikation på en heterogen adsorptionsprocess.

Biokol impregnerat med CaO och $FeCl_3$ gav de högsta totalfosforreduktionerna på 90 ± 8 % respektive 92 ± 4 %. Biokolet som var blandat med Polonite hade en reduktion på 65 ± 14 % och det obehandlade biokolet 43 ± 24 %. Ett problem med filtratet från CaO-filtret var att det fick en rödbrun färg samt en fällning vilket kan ha berott på ofullständig pyrolysering och impregnering. Filtratet från det $FeCl_3$ impregnerade biokolet hade mycket lågt pH vilket kan vara problematiskt om mikrobiologisk tillväxt i filtret för rening av kväve och organiskt material vill uppnås.

Filtret för kväverening gav en total kvävereduktion på 62 ± 16 % vilket är högre än kommersiella system. Resultaten från skak och filterstudien visade på att impregnerade biokol kan ge en förbättrad fosforrening om de skulle användas i små avloppssystem. Rening av organiskt material, kemisk syreförbrukning (COD), var dock låg i alla filter och behöver studeras ytterligare för att avgöra om dessa biokol är lämpliga för småskalig avloppsvattenrening.

Nyckelord: biokol, impregnerat biokol, fosforfilter, avloppsvatten, skakexperiment, kvävefilter, COD, Tot-P, Tot-N

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PREFACE

This project is the final thesis for the Master's Program in Environmental and Water Engineering at Uppsala University (UU) and the Swedish University of Agricultural Science (SLU). It corresponds to 30 ETCS. The project was financed by the Swedish Agency for Marine and Water Management. I would like to give thanks to my supervisor and biochar expert Sahar Dalahmeh, researcher at the Department of Energy and Technology at SLU, for helping me with everything throughout the project. I would also like to thank the subject reviewer Mikael Pell, professor at the Department of Molecular Sciences at SLU for help with the experiments and with thorough reviewing of the report.

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POPULÄRVETENSKAPLIG SAMANFATTNING

Kväve och fosforrening i modifierade biokolsfilter

Ylva Stenström

Till små avloppsanläggningar räknas de anläggningar som renar avloppsvatten för upp till ca 200 personer. De flesta anläggningarna som används idag byggdes på 1970 och 80-talet. Många av dem har börjat tappa funktionen och renar avloppsvattnet allt sämre. De flesta små avlopp är markbaserade där avloppsvatten renas genom att filtreras genom en bädd med sand eller direkt ner i jorden. I marken eller sanden börjar det växa bakterier som konsumerar kväve och organiskt material (COD). Fosfor i avloppsvattnet fastnar också i marken genom bindning till markpartiklarna. Då avloppsanläggningar inte fungerar som avsett släpps kväve, fosfor och COD ut i grundvatten eller ytvatten. Orenat avloppsvatten i grundvatten är inte önskvärt eftersom många hämtar sitt dricksvatten därifrån. Näringsämnen som hamnar i ytvatten skapar övergödning och algblomningar vilket förstör vattenmiljöer, badplatser och förutsättningar för fisk. I Östersjön märks det att de små avloppen har stor påverkan. Även fast bara 10 % av Sveriges befolkning renar sitt avloppsvatten i små avlopp står de för 15 % av det totala fosfortillskottet. Resten av Sveriges befolkning (ca 90 %) som renar sitt vatten i större reningsverk står för endast 18 % av fosforbelastningen. För att förbättra reningen i små avlopp har nya prefabricerade lösningar introducerats på marknaden. Ett problem med dessa är dock att de behöver omfattande tillsyn och underhåll och inte är särskilt robusta.

Ett material som har visat sig vara intressant för avloppsvattensrening är biokol. Biokol är egentligen samma material som grillkol men som tillverkats med miljömässigt eller agronomiskt syfte. Biokol är mest känt för sina jordförbättrande egenskaper inom odling, men materialets stora yta och bindningsförmåga gör det lämpligt för kväve och fosforrening. Om man jämför ett gram biokol med ett gram sand finns det i biokolen 100 gånger så stor yta där fosfor kan fastna. Den större ytan gör även biokol till ett bra material för tillväxt av mikroorganismer. I tidigare studier har det kommit fram att biokol är väldigt bra på att ta bort organiskt material (> 90 % COD borttagning). Dock finns fortfarande brister i fosfor- och kvävereduktion. I denna studie undersöktes därför modifierade biokol för att se om en modifiering kunde öka reningsgraden.

För att undersöka fosforreduktion impregnerades biokol gjort av pilbark med järnklorid och kalciumoxid som är två kemikalier som används för fosforbindning. Ett tredje biokol blandades med det fosforbindande materialet Polonite som innehåller mycket kalk. De impregnerade biokolen och polonitkolet jämfördes med obehandlat pilbarkskol i ett skakförsök. I skakförsöket skakades de i olika koncentrationer av fosforlösningar för att se hur mycket som kunde bindas. Biokolen testades också i ett kolonnförsök där de packades i kolonner för att filtrera riktigt avloppsvatten.

För att undersöka kvävereningsförmågan byggdes ett avloppsvattenfilter med två delar, en del med vertikalt flöde följt av en vattenfylld del med horisontellt flöde. Detta skapade ett filter med en syresatt del följt av en syrefattig vilket är gynnsamt för de bakterier som renar kväve.

Resultatet från skakstudien visade att det kalciumoxidimpregnerade biokolet hade störst kapacitet att avlägsna fosfor. Det framgick också att järnkloridimpregnerat biokol har stor potential att binda fosfor men att bindningen tar längre tid. Från kolonnexperimentet var det klart att de kalciumoxid-och järnkloridimprgnerade biokolen hade högst fosforreduktion på mer än 90 %. Inget av de två kolen visade tecken på minskad fosforreningsförmåga under studien. Ett problem med de impregnerade biokolsfiltrena var att utflödet från det kalciumoxidbehandlade materialet fick en gul-brunaktig färg samt en fällning vilket kan betyda att kolet inte hade blivit helt förkolnat vid tillverkningen. En bättre impregnering av kalciumoxid hade möjligen resulterat i en bättre karaktär på vattnet. Vatten filtrerat i järnkloridfiltret hade väldigt lågt pH vilket kan vara ett problem om man vill använda materialet som fosfor och kvävefilter, då de kvävereducerande bakterierna trivs i ett högre pH. Det polonitblandade biokolet hade en fosforreduktion på ca 65 % medan det obehandlade biokolet bara tog bort ca 43 %. Både Polonite-biokolsfiltret och det obehandlade biokolsfiltret tappade i effektivitet under försökets gång. Kvävefiltret visade hög kvävereningsförmåga på ca 60 %.

Denna studie visar att biokol tillverkat av pilbark inte var bättre att rena avloppsvatten från kväve och fosfor än konventionella små avloppsanläggningar. Men om biokolet modifieras med impregnering kan materialet ses som lovande för fosforrening. Om en syrefri del läggs till i ett biokolsfilter kan kvävereningen också förbättras väsentligt. Dock krävs vidare studier för att undersöka hur biokolfilter bäst kan användas. Intressant var även att alla biokolfilter visade en låg COD borttagningsförmåga jämfört med tidigare studier vilket även det skulle behöva undersökas vidare.

1. INTRODUCTION

It is estimated that there are about 750 000 onsite wastewater treatment systems (OWTSs) in Sweden. Out of these, only 400 000 have a treatment process that goes beyond primary sedimentation. Most existing sites were built in the 1970s and 1980s (Ridderstolpe, 2009), and today many systems are getting old and lack sufficient pollution reduction. This leads to discharge of nitrogen (N) and phosphorus (P) into the environment causing eutrophication in downstream water bodies (Hjelmqvist, 2012; Ejhed et al., 2004; Naturvårdsverket, 2014). Another problem is that drilled drinking water wells risk contamination from nearby malfunctioning OWTSs (Miljömålsrådet, 2010).

P has been suggested as a major concern regarding small wastewater treatment systems (Ridderstolpe, 2009). Only a small fraction (about 10 %) of Sweden's population uses OWTS, yet they represent 15 % of the total net anthropogenic load of P on the Baltic Sea. This can be compared with the load from larger wastewater treatment plants (WWTPs) treating the water of 90 % of the population, but is responsible for only 18 % of the P load (HaV, 2016a). For eutrophication to decrease in Swedish waters the level of P emissions have to decline (Boesch et al., 2006). The N load to the Baltic sea from OWTS is small relative other anthropogenic sources (HaV, 2016a). Nevertheless it is still important that the systems have a sufficient N treatment to prevent eutrophication close to them and inadvertent pollution of ground water reservoirs that are used as drinking water resources.

1.1 ONSITE WASTWATER TREATMENT SYSTEMS

OWTSs are defined as systems treating wastewater for up to 200 population equivalents and most OWTSs in Sweden are built as vertical soil filters. The filters are installed with a septic tank in which heavy particles in the wastewater undergo sedimentation. The water is then either led by gravity or pumped into an infiltration unit. The effluent from infiltration units with closed bottoms is collected and conveyed to a ditch or river. Effluent from infiltration systems with open bottom is discharged directly to the ground water. In the latter the water percolates the underlying natural soil. The vertical distance from the filter bottom to the ground water table is crucial and needs to be at least 1 m (Ridderstolpe, 2009). The recommended hydraulic load for a Swedish OWTS is 30 – 60 L/m^2 and day (Olshammar et al., 2015).

The main mechanism behind P removal in vertical soil filters is adsorption or precipitation to the soil or bed material. The phosphate ions (PO_4^{3+}) adsorbed to the surface of the material can also react with iron (Fe), aluminum (Al) or calcium (Ca) minerals to form strong precipitates or surface complexes. The pH in the soil affects the reaction. At low pH, the phosphate reacts with Fe and Al more easily forming e.g. $FePO_4 \cdot H_2O$. At higher pH the PO_4^{3+} forms complexes with Ca ions more easily, such as $CaHPO_4 \cdot 2H_2O$ and $Ca_4H(PO_4) \cdot 3H_2O$ (US EPA, 2002). Some of the P bound in organic particles can be removed physically by the filtration through the soil. Initially the P reduction can be very high. But the capacity to remove P will successively decrease and at some point the bed material will reach saturation. At this time the efficiency of the P removal will be essentially lowered or even cease (Olshammar et al., 2015). It has also been shown that P may be released (desorbed) from the material in the event of heavy rains (Eveborn et al., 2012). This has made it difficult to estimate the lifetime of P removal in soil infiltration beds.

N in vertical soil filters is removed partly by adsorption by ammonium (NH_4^+). However, the main removal mechanism is through bacterial mediated processes. Bacterial growth is favored in soils and materials with large pore volume and specific surface area (US EPA, 2002). By consuming organic material (measured as chemical oxygen demand, COD, or biochemical oxygen demand, BOD) in the wastewater, the bacteria will grow and create an active biofilm. Some parts of the biofilm will be exposed to air and other parts will not. Nitrifying bacteria in the biofilm derive their energy from oxidation of NH_4^+ to nitrite (NO_2^-) in a first step and then further to nitrate (NO_3^-). This process called nitrification is aerobic and the bacteria derive their carbon from carbon dioxide fixation. Under anaerobic conditions, another group of bacteria called denitrifying bacteria reduces NO_3^- or other nitrogen oxides to form nitrous oxide (N_2O) and nitrogen gas (N_2) in a process called denitrification. When denitrifying the NO_3^- is used instead of oxygen for respiration. In addition, denitrifying bacteria must be supplied with a readily available energy and carbon source to denitrify. The combined nitrification-denitrification will lower the total content of N (Tot-N) in the water (US EPA, 2002).

The rate of rebuilding and improving older OWTSs is low. Even some newly built systems have shown poor pollutant reduction and do not pass the regulations on nutrient reduction. The Swedish Agency for Marine and Water Management (Havs och Vattenmyndigheten) issued a proposition in 2016 during the time that this thesis was being written. The proposition was to decrease the required total P (Tot-P) removal from 70 % to be 40 % for general sites. However, for areas classified as sensitive to wastewater the required Tot-P reduction was to be increased to 90 % (HaV, 2016b). Furthermore, the reduction of organic material was suggested to be at least 90 % for all sites. It was also suggested that requirements for N reduction should be removed completely for general OWTS. However requirements for N removal was suggested to be put to 50 % if the area is classified as sensitive. A soil based wastewater system built according to present recommendations has the capability to remove 30 ± 10 %, 70 ± 20 % and 80 ± 10 % of influent N, P and COD, respectively (Olshammar et al., 2015). One problem is that many systems today have not been built according to the recommended guidelines. A common mistake is to locate the soil filter too close to the ground water, less than one meter. If the distance is too short the water does not get treated. N and P removal also show large variations depending on soil, placement and load.

To improve the P and N removal in vertical soil filters, alternative solutions and upgrades have become available on the market. An example is precipitation in the septic tank using iron or aluminum salts that significantly improves the P removal rate. Other popular but not as common upgrades are prefabricated treatment systems such as separate phosphor filters. Phosphor filters are commonly made from material with high calcite content and are placed after a closed sand bed to polish the effluent water. They are said to be able to remove up to 90 % of the P (Avloppsguiden, 2009). Polonite is an example of a material used in P filters. It is produced by heating the sedimentary rock opoka that has a high silica and CaO content. Opoka also contains MgO, Al_2O_3 and Fe_2O_3 that helps improve P removal (Brogowski & Renman, 2004). Solutions for improving N removal also exist. They can for instance be compact mini-treatment plants, mimicking large-scale WWTPs. There are many different versions of mini treatment plants but most are built with sedimentation, biological and chemical treatment. All mini-treatment plants use nitrification-denitrification for the reduction of N and can remove around 30 – 60 % of total N. Artificial bed material with large specific surface area is also a method to ensure good microbial development yielding N and BOD removal rates of about 20 – 40 and 90 %, respectively (Avloppsguiden, 2009).

Alternative treatment methods, like the ones mentioned, have shown higher P, N and BOD removal rates than vertical soil filters, but as of today require much supervision and service (HaV, 2016b). A treatment system based on infiltration requires minimal attention and is robust to changes in both load and temperature (Ridderstolpe, 2009). A robust system with high removal capacity is desirable. However, the lack of quality in vertical soil filters makes it necessary to look for new solutions for a secure reduction on P and N.

1.2 BIOCHAR

Char is the product of pyrolysis, where biomass is heated at high temperatures with no access to oxygen. Char is known for its ability to improve soil quality and plant growth. It has also proven itself useful for energy production, climate change mitigation and water treatment. Biochar is defined as char specifically produced for agronomic and environmental management applications (Joseph & Lehman, 2009). The char created after pyrolysis does not degrade over time, but is still a reactive material. The material is similar to activated carbon but does not undergo any activation process, making it a less expensive alternative. Yet biochar has twice the porosity of sand and has a specific surface area more than a 100 times higher than sand or soil with corresponding particle size (Dalahmeh, 2016). This gives biochar an excellent adsorption potential and can create a good environment for microbiological growth which could be beneficial for P, N and COD removal.

P adsorption to biochar is physical and/or chemical. The physical adsorption constitutes weak van der Waals forces between the phosphate ions and the surface. The large pore volume and specific surface area of biochar increases the potential for physical adsorption (Lehmann & Joseph, 2009). What chemical reaction that binds the P depends on the biochar surface and its chemical composition.

A review of several different biochar experiments showed that P removal was not affected much by hydraulic loading rate or particle size (Dalahmeh, 2016). However, to reach an optimal removal of COD and pathogens, a particle size of 1.4 mm and hydraulic load of less than 50 L/m^2 and day was recommended. In the results of the review it was clear that biochar had the capacity to remove 62 – 88 % of the total nitrogen (Tot-N). Biochar also had the capacity to remove 32 – 89 % of the total P (Tot-P), highly depending on its mother material. COD and BOD removal in biochar filters was proven to be high (> 90%) and consistent while it was suggested that the P and N removal processes in biochar filters needed further investigation to reach sufficient and reliable reduction (Dalahmeh, 2016).

1.3 IMPREGNATED BIOCHAR

Recent studies of modified biochar have focused on removal of several different substances; from reduction of heavy metals to carbon dioxide emissions. To impregnate or modify biochar with different elements as a method to improve the removal of specific substances is a growing research field (Rajapaksha et al., 2016). Modifications may occur before or after the biomass undergoes pyrolysis and can include heat treatment, impregnation of different substances and acid or base treatment to change and improve structure and removal properties. Modification of biochar with the objective to remove P has been investigated in a few studies by preforming sorption experiments with P solutions. In a study by Chen et al. (2011), biochar powder for P removal was produced at different temperatures and impregnated with magnetite (Fe_2O_3) with a biochar to Fe ratio of 0.9. The modified biochar showed higher P adsorption (up to 99 % removal) compared to unmodified replicates. Adding iron oxides to the biochar can also have structural benefits producing larger pore volume and specific surface area (Ren et al., 2015). Ferric chloride biochar has been studied by Li et al. (2016) where a Fe to biochar ratio of 0.7 in the biochar resulted in a P adoption as high as 16.58 mg P/g biochar which could be compared to natural sand that can have an adsorption less than 1 mg/g P (Del Bubba et al., 2003). When Liu et al. (2015) tested column filters with Fe modified biochar, 99 % of the Tot-P concentration was removed. Ca modified biochar filters have been studied for the removal of arsenic and chromium (Agrafioti et al., 2014) but is not as common for P removal. However Seo et al. (2005) impregnated and compared construction aggregate quarry with CaO, Al and Fe and found that the CaO impregnated material had superior P removal. Jung et al. (2016) analyzed fine biochar material produced by algae, drained and dried in calcium-alginate beads to investigate P removal and found that the biochar had the capacity to remove 100 mg P/g biochar.

1.4 OBJECTIVES

The overall goal of the project was to investigate the potential of biochar as filter media for removal of wastewater pollutants. Biochar filter materials were tested in a batch adsorption experiment with various phosphate concentrations and in filters for removal of P, N and COD from municipal wastewater. Specific objectives were to:

(i) Evaluate P removal capacity using biochar modified by impregnation with ferric chloride, calcium oxide and biochar mixed with Polonite in a batch adsorption experiment using increasing concentrations of phosphate solutions.

(ii) Evaluate P removal capacity using the same biochar types as in (i) but in a column filters fed with wastewater.

(iii) Investigate N transformation and removal in a biochar filter unit consisting of a vertical flow non-saturated section followed by a horizontal flow saturated section.

2. MATERIALS AND METHOD

2.1 BIOCHAR PREPERATION

Pine bark of particle size of 1 – 7 mm was saturated with solutions of ferric chloride ($FeCl_3$), calcium oxide (CaO) before pyrolysis. $FeCl_3$ and CaO are two common precipitation chemicals used for P removal (US EPA, 2002). After being mixed in the solutions for 24 hours in room temperature, the bark was dried in 100 ºC for another 24 hours. Finally the biochars were pyrolysed in 350 ºC for 3.5 hours. The ratio between ion and biochar was 0.3 for both impregnated biochars. The third biochar type was produced without any impregnation before pyrolysis but also had the pine bark as mother material. After pyrolysis, it was mixed with granular Polonite at a ratio of 0.3. The four different types of modified biochar used in the batch experiment and column filter experiment were named as follows:

UBC – untreated biochar
FBC – biochar impregnated with ferric chloride ($FeCl_3$)
CBC –biochar impregnated with calcium oxide (CaO)
PBC–biochar mixed with Polonite

The biochar used in the N removal filter originated from mixture of hard wood biomass and was obtained from Vildelkol AB (Vindelkol, 2017).

2.2 BATCH ADSORPTION EXPERIMENT

A batch experiment was carried out to assess and compare the adsorption capacity of P for the different types of biochar. One gram of each biochar type was added to 500 mL E-flasks containing 100 mL of phosphate solution of the concentrations 0.5, 3.3, 6.5, 13 and 26 mg PO_4-P/L (labeled C1-C5). The concentration were prepared by diluting 1000 mg PO_4/L stock solution based on monopotassium phosphate (KH_2PO_4) with distilled water (Table 1). The PO_4-P concentrations were selected based on what can be expected in an OWTS and diluted according to Table 1 (Palm et al., 2002). Three replicates (n=3) were prepared for each concentration except for C1 having only one replicate (n=1). The beakers were shaken on a rotary table for 24 hours at 130 rpm and constant room temperature 20 ± 2 ºC. Samples of the adsorbate solution (6 mL) from each of the beakers were extracted after 0 min, 15 min, 75 min, 4 h and 24 h using a pipette. The sorbate samples were filtered through a 0.45 µm filter and their PO_4-P concentration was determined according to method given in Table 2. The pH of the P solutions with biochar was measured during the experiment using pH strips (Table 2). After 24 hours the residual solids were washed with deionized water and then oven dried 80 ºC for 4 hours. The solids were finally stored in plastic bags for later analysis using Scanning Electron Microscopy (SEM) and Fourier Transform- Infrared Spectroscopy (FTIR), but this analysis was not performed during this thesis and was thus not included in the report.

Table 1 Dilution scheme for preparation of different concentrations of P solutions used in biochar adsorption batch experiment. Stock KH_2PO_4 solution of 1000 mg PO_4/L was mixed with distilled water into 100 mL beakers.

Label	PO_4 stock solution (mL)	Volume of beaker (mL)	Final concentration (mg P/L)
C1	0.15	100	0.5
C2	1	100	3.3
C3	2	100	6.5
C4	4	100	13.0
C5	8	100	26.08

2.2.1 Adsorption isotherm

An adsorption isotherm is the relationship between the equilibrium concentration in a solution (Ce) and the amount of adsorbate adsorbed on the surface of the material (Q) at constant temperature. The adsorption of phosphate (Q) from the batch adsorption experiment was calculated using Equation 1:

$$Q = (C_0 - C_e)\frac{V}{m} \qquad (1)$$

where Q is the mass P adsorbed per mass biochar (mg/g), C_0 the initial concentration of the solution (mg/L), C_e the concentration (mg/L) after 24 hours of the batch equilibrium experiment, V the volume of the solution (mL) and m the mass of the adsorbent (g).

The adsorption isotherm is often modelled with a Langmuir or Freundlich equation model (Messing, 2013). Langmuir and Freundlich adsorption isotherms were calculated for each biochar type with data used from the batch adsorption experiment. The Langmuir isotherm (Equation 2) models a monolayer adsorption on a uniform surface, while the Freundlich isotherm (Equation 3) models non-uniform adsorption on a non-uniform surface.

$$Q_e = \frac{k_L Q_m C_e}{1+k_L C_e} \qquad (2)$$

Q_e (mg/g) Equilibrium adsorption capacity
C_e (mg/L) Concentration at equilibrium
k_L (L/mg) Langmuir adsorption constant
Q_m (mg/g) Maximum adsorption capacity

$$Q_e = k_F C_e^{1/n} \qquad (3)$$

k_F (L/g) Freundlich constant
n Dimensionless Freundlich heterogeneity exponent

In order to explore what model best described the batch experimental data, the parameters k_L, Q_m, k_F and n were determined for the models. This was done by linearizing the model Equations (2) and (3). The linear equation of the Langmuir (Equation 4) and Freundlich (Equation 5) was expressed on the form y = kx + m.

$$\frac{C_e}{Q_e} = \frac{Ce}{Q_m} + \frac{1}{k_L Q_m} \qquad (4) \qquad\qquad \ln(Q_e) = \frac{1}{n} lnC_e + \ln(k_F) \qquad (5)$$

Linear plots of the Langmuir Equation (4) were created with Ce as x-axis vs C_e/Q_e as y-axis. This provided the Langmuir parameters Q_m and k_L were $1/k_LQ_m$ is the intercept and $1/Q_m$ as the slope. Graphing Equation (5) with ln(Ce) on the x-axis and $\ln(Q_e)$ on the y-axis provided the Freundlich parameters k_F and n where $\ln(k_F)$ was the intercept and 1/n the slope. This was done for all biochar types.

After obtaining all the parameters, Q_e was calculated for each C_e with the Langmuir and Freundlich Equations (2) and (3). The model that calculated Q_e correlated best with the experimental Q_e was considered the best model to describe the P adsorption on each biochar type.

2.2.2 Kinetic isotherm

A kinetic isotherm describes the adsorption (Q) over time (t). The concentrations analyzed after 0 min, 15 min, 75 min, 4 h and 24 h in the batch adsorption experiment were used to calculate Q_t with Equation (1). The pseudo first (Equation 6) and second (Equation 7) order kinetic models are commonly used to describe the adsorption over time:

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \qquad (6) \qquad\qquad \frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \qquad (7)$$

Q_t (mg/L) Amount adsorbed at time t
k_1 (min^{-1}) Pseudo 1st rate constant
k_2 (g/mg/min) Pseudo 2nd rate constant

In order to see which of pseudo 1st and pseudo 2nd order kinetic models best described the adsorption experiment their linear forms Equation (8) and (9) were used:

$$\ln(Q_e - Q_t) = lnQ_e - k_1 t \qquad (8) \qquad\qquad \frac{t}{Q_t} = \frac{1}{k_2 Q_e} + \frac{t}{Q_e} \qquad (9)$$

The pseudo 1st order equation was graphed on linear form with $\ln(Q_e - Q_t)$ on the y-axis and t on the x-axis. From the linear plot the rate constant k_1 (slope of the graph) and correlation coefficient R^2 was determined. Pseudo 2nd order equation was linearly graphed with t/Q_t on the y-axis and t on the x-axis with the intercept of the graph being $1/k_2Q_e$ and the slope $1/Q_e$. By plotting data this way the k_2 and R^2 for the pseudo 2nd order equation was determined. The linear plot of the two models with the highest correlation coefficient (R^2) was considered the best model to describe the P adsorption of the biochar types over time.

2.3 COLUMN FILTERS

To investigate the removal of P from real wastewater the four biochar types were tested in a 14 week long column filter experiment. Four 60 cm tall acrylic glass columns with diameter 4.25 cm were filled separately with untreated biochar (UBC), biochar impregnated with calcium oxide (CBC), biochar impregnated with ferric chloride (FBC), and biochar mixed with Polonite (PBC). Underneath and on top of the main biochar layer, 5 cm coarser untreated biochar (8 mm in diameter) was filled to prevent clogging on the very top of the filter and facilitate drainage on the bottom (Figure 1). The filters received 71 mL wastewater per day divided equally between the times 24:00, 08:30 and 16:00 to mimic the load of a real vertical soil infiltration system with 50 L/m^2 and day (Olshammar et al., 2015). Peristaltic pumps regulated with timers were used to feed the filters with wastewater stored in a fridge (2 – 4 ^{o}C). Before feeding, the wastewater was left outside the fridge for 20 minutes to reach room temperature. The wastewater was collected twice a week on Mondays and Thursdays mornings from the municipal wastewater treatment plant in Uppsala (Kungsängsverket). The water was collected directly from the primary sedimentation step of the plant and had to be filtered through a 0.8 mm mesh to remove particles to prevent clogging of the pipe of the pumps.

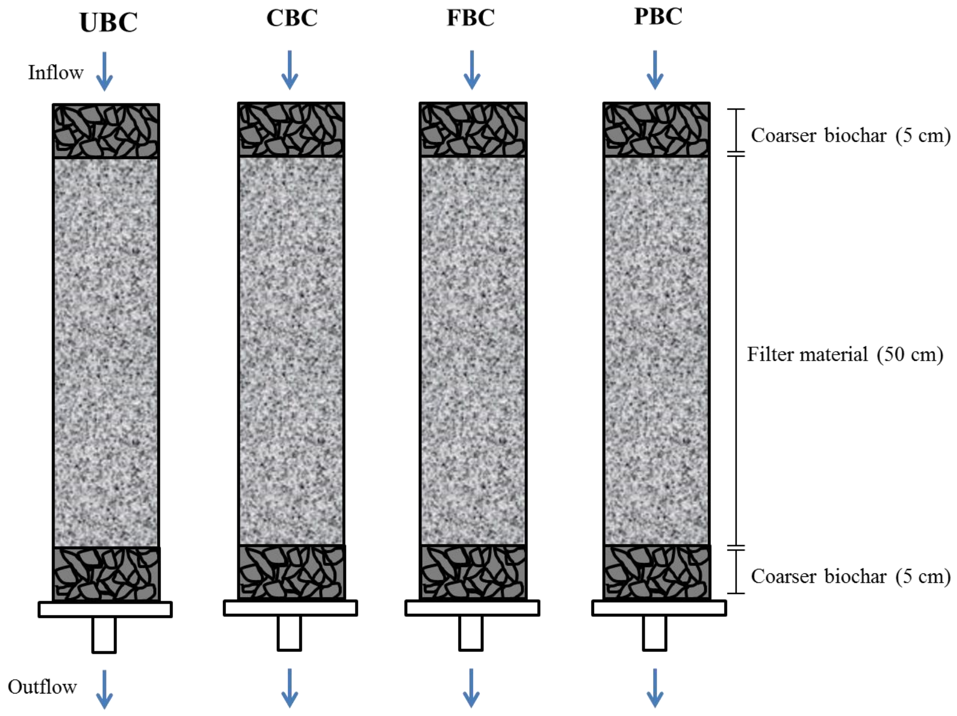


Figure 1 Experimental set-up for column filters filled with untreated biochar (UBC), biochar impregnated with calcium oxide (CBC), biochar impregnated with ferric chloride (FBC) and biochar mixed with Polonite (PBC).

Sampling of the inflow and outflow was done once a week, on Wednesdays, starting on the third week of the experiment. The following parameters were determined weekly: Tot-P, PO_4-P, Tot-N, NO_3-N, NH_4-N and pH and every second week COD was analyzed. The main objective was to investigate P but N measurements took place too. All analysis was conducted using chemical kits (Table 2).

Table 2 Analytical kits, analytical concentration ranges and instruments used for analyzing pollutants in wastewater used in the column filter and lab-scale filter unit experiments.

Substance	**Kit name/Method**	**Range mg/L**	**Instruments**
Tot-N	Spectroquant Crack Set 20 1.14963.0001	0.1-25.0	Spectroquant NOVA 60, VWR International Sverige Thermal reactor TR420, Merck
NH4-N	Spectroquant Ammonium Test 1.00683.0001	2.0-150	Spectroquant NOVA 60 and Aquamate, VWR International Sverige
NO3-N	Spectroquant Nitrate Test 1.09713.0002	0.1-25.0	Spectroquant NOVA 60 and Aquamate, VWR International Sverige
Tot-P	Spectroquant Crack set 10 1.14687.0001	0.0025-5	Spectroquant NOVA 60 and Aquamate, VWR International Sverige Thermal reactor TR420, Merck
PO4-P	Spectroquant Phosphate test 1.14848.0002	0.0025-5	Spectroquant NOVA 60 and Aquamate, VWR International Sverige
COD	Spectroquant COD Cell test 1.09772.0001 and 1.09773.0001	10-100 and 100 - 1500	Spectroquant NOVA 60
pH	pH strips	7-14, 1-7 and 1-14	Papier dosatest, VWR MColorptest, Merck

Removal efficiency was calculated from the difference in concentrations of inflow and outflow of the filters (Equation 10):

$$E = 100\,\frac{C_{in} - C_{out}}{C_{in}} \qquad (10)$$

where E is the removal efficiency (%); C_{in} the concentration of the influent (mg/L); and C_{out} the concentration of the effluent (mg/L).

2.4 NITROGEN REMOVAL FILTER

A biochar filter with an aerobic vertical flow section combined with an anaerobic horizontal flow section was installed at Kungsängsverket and operated for 14 weeks. The biochar used originated from mixture of hard wood biomass and was obtained from Vildelkol AB (Vindelkol, 2017). The horizontal and vertical flow sections were installed using two boxes each with the size of 74×40×29 cm placed on top of each other (Figure 2). In the vertical flow section, a 3 cm drainage layer was prepared with coarse biochar (8 - 16 mm in diameter) at the bottom which had a slope of (1.5: 60; i.e. 2.5%). The section was then filled up to 30 cm with biochar of a particle size that varied between 2.5 and 5 mm. A second 3 cm layer of coarse biochar was placed on the top of the main filter to prevent clogging on the surface.

The horizontal flow biochar section was prepared by filling the box with coarse biochar (25 - 40 mm in diameter) in two 10 cm layers at the inlet and outlet sides. The main 54 cm part of the section was then filled with biochar (1.6 - 2.5 mm in diameter). The depth of the biochar in the horizontal flow section was 30 cm. The outlet of the horizontal flow section was located at a level 4 cm below the inlet level. Before the start of the experiment the filter was gently washed with distilled water. During the experiment, pumps fed the filter with 3 L three times a day, at 9:00, 16:00 and 01:00. This gave a flow of around 42 L/m^2 and day. The wastewater was initially pumped from after primary sedimentation in the plant. However, $FeCl_3$ added directly after the primary sedimentation in the plant interfered with N analysis so the filter with sampling point was relocated in week 7 to a location before the actual $FeCl_3$ dosing in the middle of the primary sedimentation. The water pumped from the primary sedimentation was filtered through a 0.8 mm sieve and the flow was lowered to 1.5 L/day giving a load of 21 L/m^2 to prevent clogging.

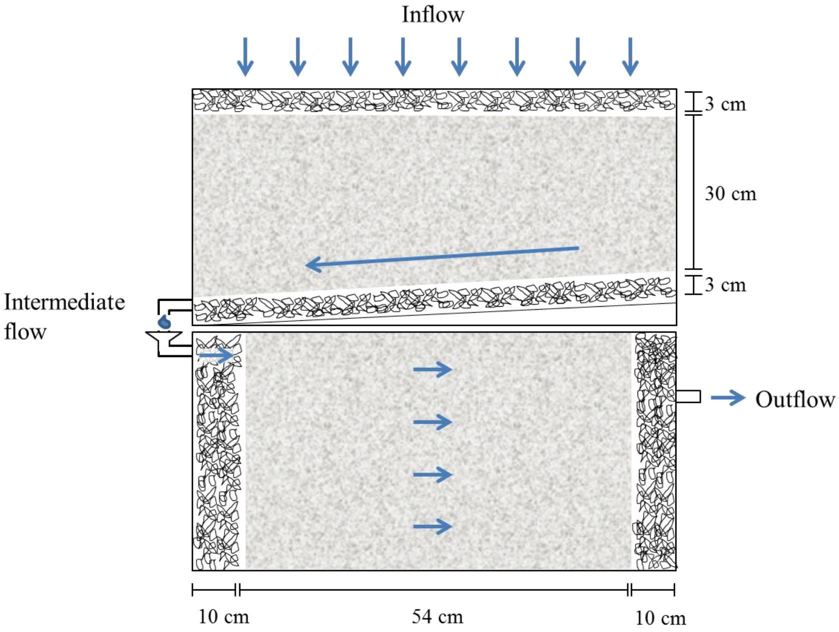


Figure 2 Combined aerobic vertical flow and anaerobic horizontal flow biochar filter unit for wastewater nitrogen removal. The material in the filter was biochar made from hardwood biomass.

Samples were taken from the inflow, intermediate flow and outflow of the filter once a week and N transformation and concentration was measured as Tot-N, NH_4-N and NO_3-N. Even though N was the main investigation objective for this filter P concentrations were also analyzed as Tot-P and PO_4-P. COD concentrations were also analyzed and all analysis was made according to methods given in Table 2. Removal efficiency was calculated according to Equation 10.

3. RESULTS

3.1 BATCH ADSORPTION EXPERIMENT

The mean concentration of P in all solutions (C1 – C5) of the batch adsorption experiment decreased with time for all biochars, except for PBC in C1, where the mean PO_4-P concentrations fluctuated with time and was higher than at start after 24 hours of shaking (Table 3 & Table 10-AI).

The untreated biochar showed low adsorption in the concentration range 0.5 - 13 mg/L (C1-C4) and it was never tested for the highest concentration (26 mg P/L, i.e. C5). The achieved PO_4-P reductions were 16 ± 3 (mean ± standard deviation; n=3) % for UBC, 80 ± 24 % for CBC, 63 ± 22 % for FBC and 50 ± 52 % for PBC after 24 hours of shaking.

Table 3 The average PO_4-P concentrations from shaking experiment where 1 g of untreated biochar (UBC), CaO biochar (CBC), $FeCl_3$ biochar (FBC) and Polonite biochar (PBC) were shaken in five P concentrations C1 – C5 (mg/L) for 24 h.

Biochar	Time	C1	C2	C3	C4	C5
UBC	t_0 (0min)	0.57	3.26	5.87	12.77	X
	t_1 (15min)	0.49	3.25	6.53	12.77	X
	t_2 (1h 15min)	0.53	2.65	5.30	11.59	X
	t_3 (4 h)	0.51	2.90	4.90	10.77	X
	t_4 (24 h)	0.48	2.57	5.00	10.82	X
CBC	t_0 (0min)	0.57	3.48	6.43	13.00	26.30
	t_1 (15min)	0.45	1.27	1.93	8.17	21.80
	t_2 (1h 15min)	0.32	0.48	0.44	1.18	8.66
	t_3 (4 h)	0.33	0.40	0.40	0.81	1.95
	t_4 (24 h)	0.32	0.42	0.50	0.63	0.66
FBC	t_0 (0min)	0.51	3.38	6.72	12.67	25.85
	t_1 (15min)	0.70	2.77	3.78	10.93	23.30
	t_2 (1h 15min)	0.67	2.18	3.07	8.68	20.68
	t_3 (4 h)	0.55	1.75	3.20	6.49	16.79
	t_4 (24 h)	0.36	0.81	1.78	3.52	9.91
PBC	t_0 (0min)	0.46	3.51	6.27	13.07	25.95
	t_1 (15min)	0.67	1.44	2.68	10.37	24.85
	t_2 (1h 15min)	0.49	0.52	0.98	4.82	21.87
	t_3 (4 h)	0.47	0.58	1.10	3.84	16.65
	t_4 (24 h)	0.59	0.74	1.58	3.59	11.06

At the end of the 24 h shaking period the UBC, FBC and PBC biochars were still intact but CBC had disintegrated into fine particles more noticeable than the other biochar types. Beakers with CBC got a red-brown and FBC yellow color while UBC and PBC stayed uncolored.

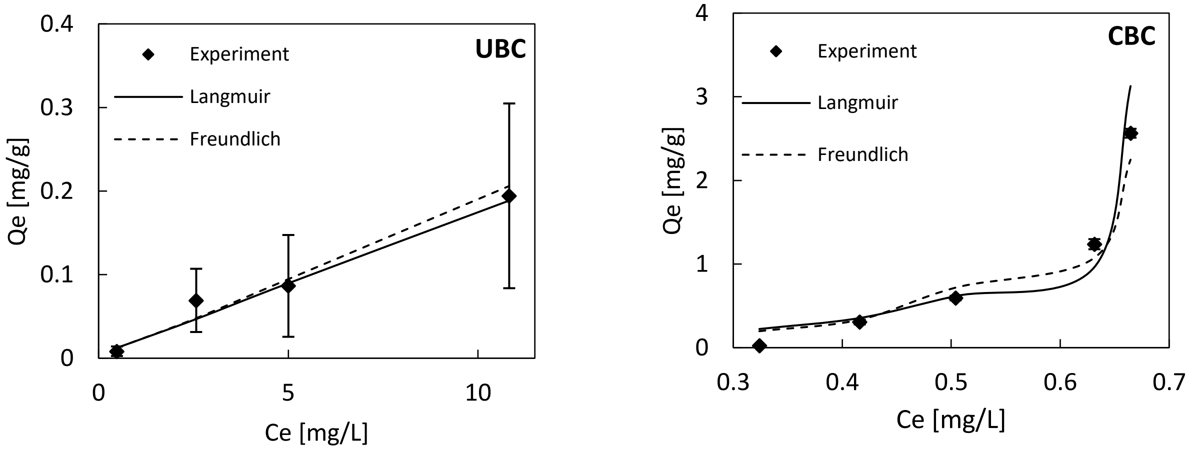
The pH in the PO_4 solution at the start of the shaking (t_0) was 7.0, but it changed with time (Table 4). In the flasks with UBC, CBC and PBC, pH increased to 7.5, 8.5 and 8.8 while the solution with FBC's pH was lowered to 3.0.

Table 4 Mean pH in the different solution concentrations during the batch adsorption experiment for untreated biochar (UBC), calcium oxide impregnated biochar (CBC), ferric chloride impregnated biochar (FBC) and untreated biochar mixed with Polonite (PBC).

Time	UBC	CBC	FBC	PBC
t_0 (0min)	7.0	7.0	7.0	7.0
t_1 (15min)	x	8.7	4.7	9.2
t_2 (1h 15min)	7.0	9.0	4.5	9.5
t_3 (4 h)	7.3	8.8	4.3	9.3
t_4 (24 h)	7.5	8.5	3.0	8.8

3.1.1 Adsorption isotherm

All adsorption isotherm curves show that increasing equilibrium concentrations (C_e) gave an increase in P adsorbed on the surface (Q_e) (Figure 3). The UBC isotherm showed linear behavior, where an increase in concentration (C_e) gave a constant increase in the P concentration on the biochar surface (Q_e). However, the standard deviations of the replicates were high and hence observed trends can only be considered indicative as error bars overlapped to a large extent. Adsorption isotherm curves for FBC and PBC were linear in lower concentrations but at higher equilibrium concentrations, Q_e increased less. CBC showed the opposite with a small increase of Q_e in lower concentrations but higher Q_e when the concentration became higher.



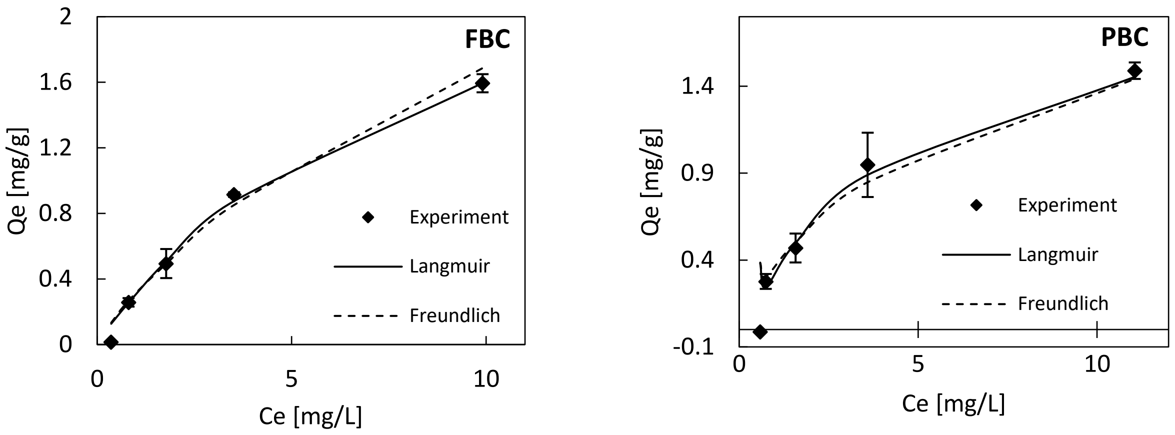


Figure 3 Relation between the concentration of P in the solutions from the batch adsorption experiment at the end of the shaking experiment (C_e) and the concentration of P adsorbed on to the biochar (Qe). Diamond symbols represent measured mean ± standard deviation, n=3.The Langmuir and Freundlish adsorption isotherm models calculated from the data are expressed as solid or dashed lines, respectively. This was done for untreated biochar (UBC), CaO impregnated biochar (CBC), $FeCl_3$ impregnated biochar and untreated biochar mixed with Polonite (PBC) was shaken in initial P solutions of 0.5-26 mg/L.

The correlation coefficients (R^2) were in the range of 0.957 - 0.997 for Langmuir isotherm and 0.960 - 0.993 for Freundlich isotherm for the adsorption of PO_4-P to the biochar types (Table 5). The Langmuir had a higher correlation for UBC and FBC and Freundlich for CBC and PBC. The parameters were calculated from liner plots of the two equations as presented in Figure 11-A2 & Figure 12-A2. FBC had the highest maximum adsorption capacity (Q_m) according the Langmuir (3.21 ± 0.01 mg/g) while Q_m for CBC was negative. CBC also had a negative mean Langmuir adsorption constant k_F. PBC had the highest k_F but also a high standard deviation of 0.21 ± 0.17 L/mg.

Table 5 Model parameters (mean ± standard deviation, n=3) for the Langmuir equation and Freundlich equation calculated from linear plots presented in Figure 11 & Figure 12-A2 for untreated biochar (UBC), CaO impregnated biochar (CBC), $FeCl_3$ impregnated biochar and untreated biochar mixed with Polonite (PBC). A higher R^2 value means a better fit.

Material	**Langmuir model parameters**			**Freundlich model parameters**		
	Q_m (mg/g)	**k_L** (L/mg)	**R^2**	**n**	**k_F** (L/g)	**R^2**
UBC	1.53±2.4	0.004±0.04	0.973±0.48	0.98±0.12	0.02±0.01	0.964±0.17
CBC	-0.41±0.19	-1.18±0.33	0.975±0.48	0.34±0.14	9.04±8.50	0.997±0.49
FBC	3.21±0.01	0.11±0.01	0.997±0.09	1.29±0.13	0.32±0.02	0.993±0.49
PBC	2.42±0.47	0.21±0.17	0.957±0.27	1.68±0.36	0.40±0.13	0.959±0.47

3.1.2 Kinetic isotherms

The UBC reached equilibrium adsorption (Q_e) after 3 hours in all PO_4-P concentrations tested for (Figure 4) with Q_e varying between 0.05 and 0.2 mg/g. This was lower than for the other biochar types. The Q is said to have reached equilibrium when the curve stops increasing and is then named Q_e. The adsorption rate for FBC was faster during the first three hours (240 min) and then slowed down. FBC did however not reach adsorption equilibrium Q in any of the concentrations C2 - C5. PBC reached a stable Q in C2, C3 and C4 but in C5 the biochar never reached equilibrium displaying a final adsorption of around 1.5 mg/g. The CBC reached stable adsorption capacities of 0.3, 0.6 and 1.2 mg/g after 1 hour in C2, C3 and C4 and these were higher than the other biochar types at corresponding concentrations. In C5 the equilibrium occurred first after 3 hours and was around 2.5 mg/g.

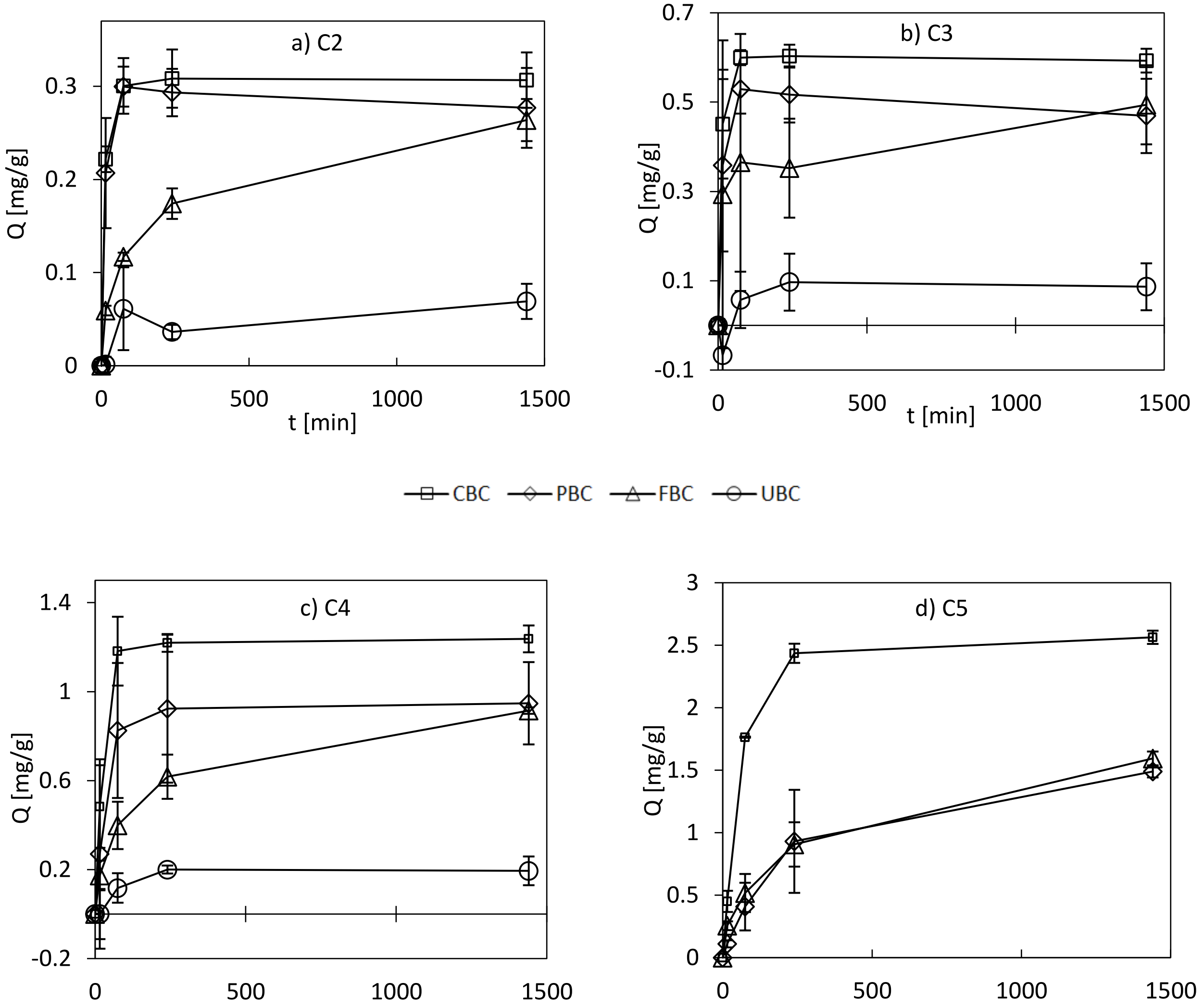


Figure 4 Adsorption of P (Q) onto four biochar types at four P solution concentrations, **a)** 3.3 mg P/L (C2) **b)** 6.5 mg P/L (C3) **c)** 13 mgP/L (C4) and **d)** 26 mg P/L (C5) over 24 hours. Symbols are mean values and error bars the standard deviation.

Higher adsorption capacities were achieved at higher P concentrations for CBC, FBC and PBC (Figure 5). Even if some biochars did not reach equilibrium, their final Q is presented as their equilibrium adsorption Q_e in Figure 5. UBC had the least amount adsorbed P per gram biochar, with around 0.07 - 0.2 mg/g for all concentrations. FBC and PBC displayed similar equilibrium adsorptions of 0.2 and 0.26 mg/g for C2, 0.49 and 0.46 mg/g for C3, 0.91 and 0.95 for C4 and 1.6 and 1.5 mg/g in C5. CBC had the highest equilibrium adsorption in all concentrations with around 0.3 mg/g in C2, 0.6 mg/g in C3, 1.2 mg/g in C4 and 2.6 mg/g in C5. At higher concentrations the gap to the other biochars became wider.

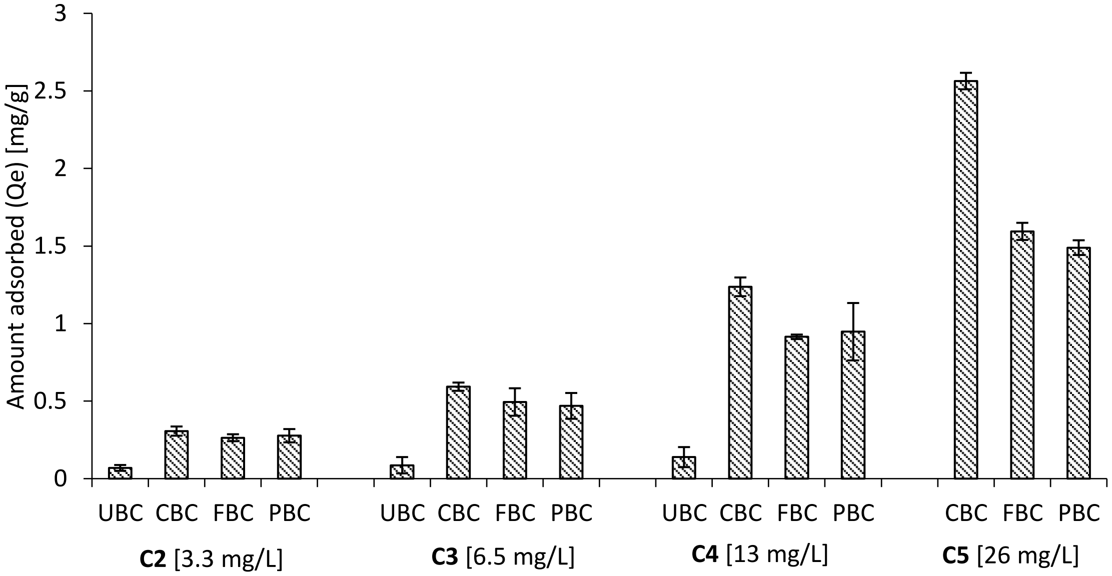


Figure 5 Amount P adsorbed in mg per g biochar after 24 hours of shaking four different biochar types in solutions of 3.3 (C2), 6.5 (C3), 13 (C4) and 26 (C5) mg PO_4^{3-}-P/L. Error bars are mean values ± standard deviations, n =3.

The pseudo 2nd order model had higher R^2 values (0.9102 - 0.9999) than the 1st order model (0.7785 - 0.997) for all biochar types shaken in the PO_4-P concentration 3.3 mg/L (Table 6). This difference was also the case for all other concentrations except for PBC shaken in C5 (26 mg/L) Table 11-A3. Kinetic model parameters for all concentrations and biochars and the linear plots providing the parameters can be found in Table 11-A3 and Figure 13-A3. The Q_e calculated for the 2nd order models were all close to the experimental Q_e. The k_1 value was highest for PBC, 0.097 ± 0.01 min^{-1} and lowest for UBC and PBC, 0.004 min^{-1}. CBC had the highest k_2 at 1.717 ± 1.13 L/mg.

Table 6 Pseudo 1st and pseudo 2nd order model parameters and the experimental value of equilibrium adsorption (Qe) from batch adsorption experiment where four different types of biochar were shaken in 3.3 mg P/L (C2). All parameters are presented as mean ± standard deviation, n=3 and they were calculated by linearization of pseudo 1st and pseudo 2nd order kinetic models (Figure 13-A3).

Material	**Pseudo first order model**			**Pseudo second order model**			**Experimental**
	Q_e [mg/g]	**R^2**	**k_1** [min^{-1}]	**Q_e** [mg/g]	**R^2**	**k_2** [L/mg]	**Q_e** [mg/g]
UBC	0.064±0.03	0.779±0.26	0.004±0.02	0.068±0.02	0.911±0.081	-0.021±0.37	0.069±0.01
CBC	0.156±0.09	0.836±0.14	0.028±0.02	0.307±0.03	0.999±0.0001	1.717±1.13	0.307±0.03
FBC	0.229±0.03	0.919±0.07	0.004±0.00	0.281±0.03	0.997±0.002	0.036±0.01	0.264±0.02
PBC	0.266±0.04	0.997±0.01	0.097±0.05	0.264±0.04	0.999±0.001	-0.499±1.35	0.277±0.04

3.2 COLUMN FILTERS

The concentration of the Tot-P in the influent to the column filters fluctuated between 2.3 and 6.2 mg/L during the experimental period (Figure 6a), with a mean of 3.84 ± 1.14 mg/L (Table 7). The Tot-P concentrations in all effluents were around or below 1 mg/L during the 5 first weeks of the experiment. After week 5 the concentrations in UBC and PBC gradually increased and reached stable effluent concentrations after week 10 of about 2.6 ± 0.1 and 1.5 ± 0.1 mg/L, respectively. Effluent concentrations of CBC and FBC started above 0.5 mg/L but after week 4 they decreased and remained below < 0.5 mg/L until the end of the experiment. The removal efficiencies of UBC and PBC fluctuated and decreased from about 60 and 80 % initially to around 20 and 55 % after week 10. The removal of Tot-P in CBC and FBC filters increased early in the experiment and then remained high at around 90 % (Figure 6b).

During the whole experiment the UBC and PBC filters had higher mean Tot-P effluent concentrations (2.09 ± 0.74 and 1.25 ± 0.37 mg/L) and lower removal efficiencies (43 ± 24 and 65 ± 14 %) compared to the CBC and PBC filters (Table 7). In contrast CBC and FBC had low outflowing concentration of Tot-P (0.37 ± 0.27 and 0.30 ± 0.18 mg/L) and displayed high removal efficiency (90 ± 8 and 92 ± 4 %).

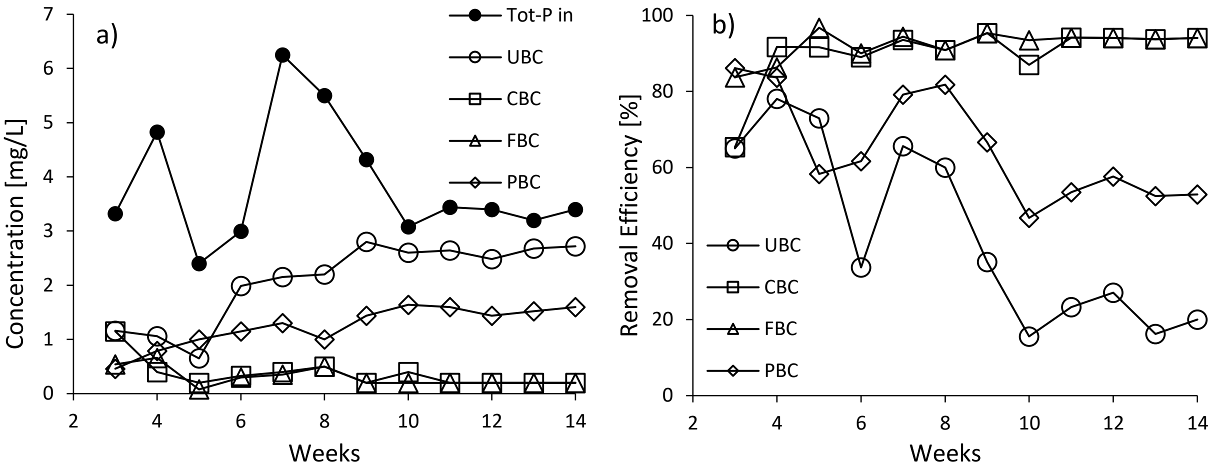


Figure 6 a) The Tot-P concentrations in the influent and in the effluent and **b)** the removal efficiency of the untreated biochar filter (UBC), CaO impregnated biochar filter (CBC), $FeCl_3$ impregnated biochar filter (FBC) and the biochar filter mixed with Polonite (PBC).

The PO_4-P concentration were lower than the Tot-P concentrations and varied in the influent between 1.5 and 5.2 mg/L throughout the experiment with a mean value of 3.18 ± 1.04 mg/L (Figure 7). The concentration and removal efficiency of PO_4-P showed a similar trend to Tot-P. CBC and FBC did however display a higher removal of PO_4-P than Tot-P while UBC and PBC had higher removal efficiency of Tot-P than PO_4-P.

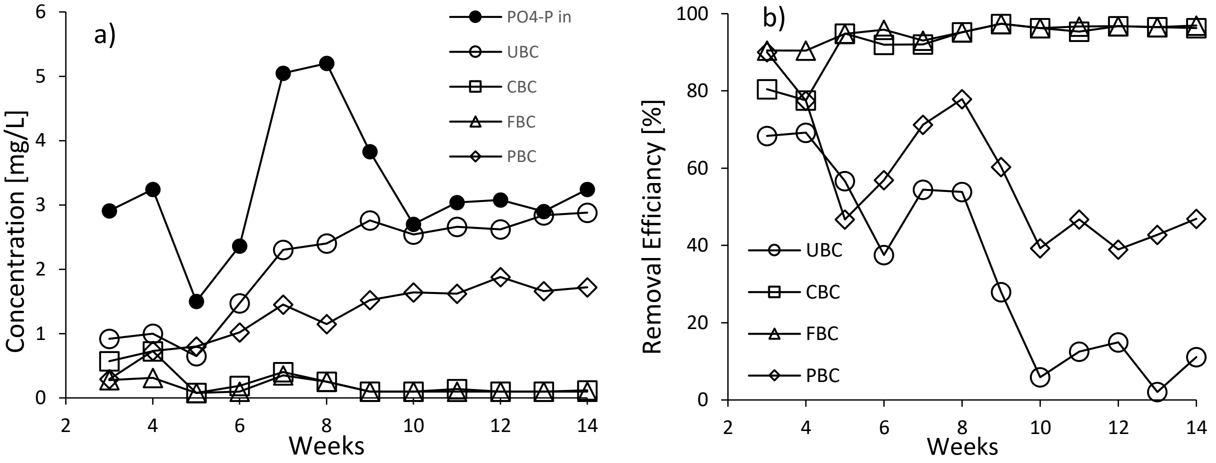


Figure 7 a) The PO_4-P concentrations in the inflow and in the outflow from four different biochar filters and **b)** corresponding PO_4-P removal efficiencies. Untreated biochar filter (UBC), CaO impregnated biochar filter (CBC), $FeCl_3$ impregnated biochar filter (FBC) and the biochar filter mixed with Polonite (PBC).

The COD analysis showed that UBC removed 36 ± 22% of the COD and PBC removed 30 ± 30 %. No clear trend could be red from those data points taken once every second week and the standard deviations were high (Table 7). In average the CBC and FBC had a higher concentration of COD in the effluent than in the influent, resulting in negative removal efficiencies -122 ± 186 % and -100 ± 141 %.

The pH varied in filter effluents. The influent to the filters was neutral with pH 7.1 ± 0.4. The UBC filter effluent was just below neutral (pH 6.7 ± 0.5) while effluents from CBC and PBC discharged an effluent with higher pH (7.8 ± 0.4). The largest pH change was observed for FBC which had an average effluent pH of 2.6 ± 0.9 over the experimental period (Table 7).

The appearance of the effluent from the filters differed from each other and changed over time. Initially the UBC and PBC effluents were turbid and greyish. The CBC effluent had a red-brown color and the FBC effluent was yellow, both turbid. Over time the color and turbidity of UBC, PBC and FBC disappeared but CBC kept its red-brown color. On the surface of the effluent beaker of CBC a precipitate formed and kept forming during the whole experiment**.**

Table 7 The influent and effluent mean concentration (Conc) ± standard deviation and corresponding removal efficiencies (E) of Tot-P, PO_4-P, COD and pH for the untreated biochar filter (UBC), CaO impregnated biochar filter (CBC), $FeCl_3$ impregnated biochar filter (FBC) and the biochar filter mixed with Polonite (PBC).

Type of water	**Tot-P**		**PO_4-P**		**COD**		**pH**
	Conc (mg/L)	**E** (%)	**Conc** (mg/L)	**E** (%)	**Conc** (mg/L)	**E** (%)	
Influent	3.84±1.14	-	3.18±1.04	-	320.8±116.4	-	7.1±0.4
UBC	2.09±0.74	43±24	2.09±0.83	32±25	206.2±113.5	36±22	6.7±0.5
CBC	0.37±0.27	90±8	0.24±0.21	93±7	710.6±480.6	-122±186	7.8±0.4
FBC	0.30±0.18	92±4	0.16±0.10	95±2	641.0±453.5	-100±141	2.6±0.9
PBC	1.25±0.37	65±14	1.29±0.49	58±17	223.4±116.7	30±30	7.8±0.7

The influent Tot-P and PO_4-P displayed a relatively wide variation in concentrations which was also the case for the effluent from the untreated biochar filter (UBC) (Figure 8). Concentrations in the effluent of the PBC filter also fluctuated but varied less than that of the UBC. In contrast CBC and FBC effluent concentrations were low and did not vary much during the experiment.

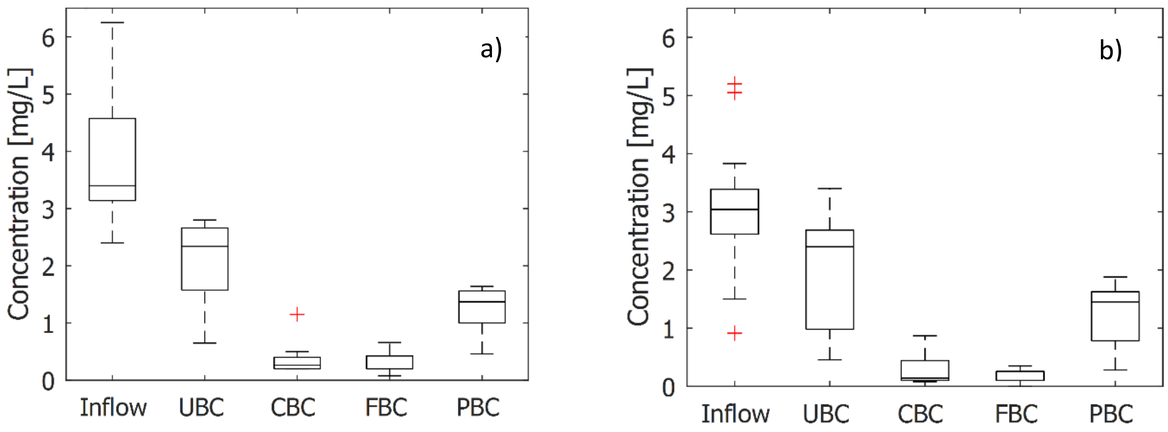


Figure 8 Boxplots of the **a)** Tot-P concentrations and **b)** the PO_4-P concentrations of the untreated biochar filter (UBC), CaO impregnated biochar filter (CBC), $FeCl_3$ impregnated biochar filter (FBC) and the biochar filter mixed with Polonite (PBC). The box is the quartiles of the data set and the medians are shown as a straight line in the box. Max and min values are the whiskers and outliers are shown as red crosses.

3.3 NITROGEN REMOVAL FILTER

The mean concentration of Tot-N in the influent to the vertical aerobic section of the N removal filter was 39.54 ± 8.26 mg/L (Table 8). After the vertical section the effluent concentration of Tot-N had dropped to 21.23 ± 3.36 mg/L. The reduction of Tot-N was stable at around 40 % between week 8 and 14 of the experiment (Figure 9a), resulting in an average removal rate of 42 ± 10 % (Table 8). The influent concentration of Tot-P to the vertical section was stable at 4.62 ± 0.54 mg/L between week 9 and week 14 of the experiment (Table 8). The Tot-P was on average removed by 13 ± 23 % leading to mean concentration in the effluent wastewater of 3.98 ± 0.95 mg/L. The removal of Tot-P in the vertical section was not stable and low points occurred in week 8 and 14 (Figure 9a).

The effluent water from the vertical section became the influent water to the horizontal anaerobic section (Figure 2). The concentration of Tot-N decreased from 21.23 ± 3.36 mg/L in the influent to 12.90 ± 1.45 mg/L in the effluent (Table 8). This corresponded to a reduction of Tot-N of 35 ± 16 %, which was lower than in the vertical section. The Tot-P in the influent to the horizontal filter section, 3.98 ± 0.95 mg/L, decreased to 3.30 ± 0.60 in the effluent. In average, 14 ± 25 % of the Tot-P was removed. Removal rates of Tot-P fluctuated between removal and release during the experiment (Figure 9b).

Together, the two sections removed 62 ± 16 % of Tot-N and 29 ± 8 % of Tot-P during the experiment (Table 8). In week 8, Tot-P concentrations in the effluent was higher than in the influent for both the vertical and horizontal sections (Figure 9a & b). This resulted in large negative removal rates for the total filter during week 8 (Figure 9c). This is why the P results are presented only from week 9 in Table 8.

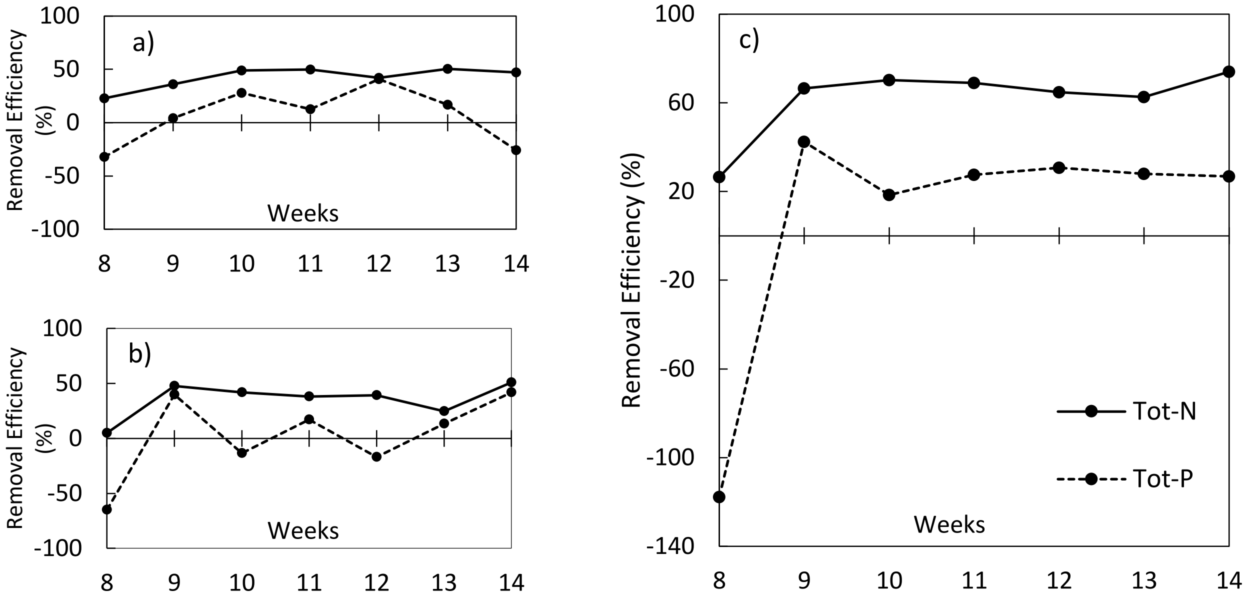


Figure 9 The removal efficiencies of Tot-N and Tot-P in % from **a)** the vertical aerobic section, **b)** the horizontal saturated section and **c)** total nitrogen removal of a two-section biochar filter.

NH_4-N and NO_3-N was also analyzed in the influents and effluents to the vertical and horizontal sections. NH_4-N in the influent to the vertical filter had a higher average concentration than Tot-N (Table 8). It was also clear that NO_3-N concentration increased from 1.60 ± 0.35 mg/L to 6.91 ± 2.23 mg/L while passing the vertical section and thereafter decreased in the horizontal section. The formation of NO_3-N in the vertical section increased between week 8 and 14. This is presented in Figure 14-A4, where the complete dynamics of the N is presented. pH decreased slightly in the whole filter and the two sections removed COD equally well, 30 ± 23 and 30 ± 36 %, respectively. Average removal efficiency of COD was 45 ± 68 % for the entire filter.

Table 8 The average removal efficiencies (%) and concentrations (mg/L) ± standard deviation for all for pollutants measured in the N removal filter. The filter had an aerobic vertical flow section followed by an anaerobic horizontal flow section.

Pollutant	**Concertration (mg/L)**			**Removal efficiency (%)**		
	Inflow	**Vertical section effluent**	**Horizontal section effluent**	**Vertical section**	**Horizontal flow section**	**Total Removal efficiency**
pH	7.1±0.1	6.7±0.4	6.8±0.4			
Tot-N	39.54±8.26	21.23±3.36	12.90±1.45	42±10	35±16	62±16
Tot-P*	4.62±0.54	3.98±0.95	3.30±0.60	13±23	14±25	29±8
NH_4-N	42.67±8.55	14.67±2.66	11.00±1.10	65±8	23±17	74±5
NO_3-N	1.60±0.35	6.91±2.23	2.66±0.98	-341±131	58±23	-64±53
PO_4-P*	4.05±0.74	3.79±0.96	2.97±0.56	3±29	19±23	27±10
COD	286.20±116.35	197.80±100.52	152.00±96.43	30±23	30±36	45±68

* Means calculated from week 9

The N removal filter recived wastewater with a verying Tot-N and NH_4-N concentration and more N was removed in the first section than in the second. However, the concentrations in the effluent had smaller variation (Figure 10). The NO_3-N concentration in the intermediate flow varied more than the NO_3-N concentrations in inflow and outflow of the filter. The Tot-P and PO_4-P concentrations in inflow and intermediate flow had a similar variation. The Tot-P concentrations in the outflow was however less varied than the PO_4-P concentraions. COD concentration data had the largest variation of all analyzed pollutants.

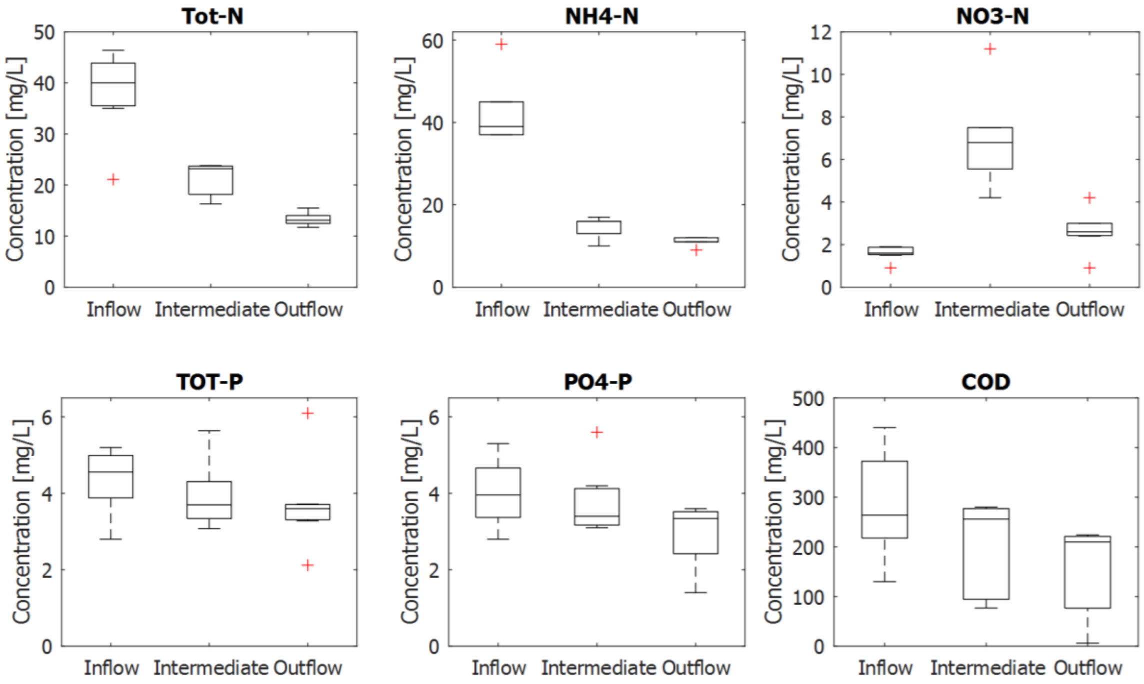


Figure 10 Boxplots showing the change of N and P concentration in the the inflow, intermediate flowand outflow of a two-step biochar filter. The first section of the filter was aerobic and had vertical flow and the second section had horizontal saturated flow.The box is the quartiles with horizontal line in the box showing the median. Max and min values are the whiskers and outliers are presented as red crosses

4. DISCUSSION

4.1 BATCH ADSOPTION EXPERIMENT

In the batch adsorption experiment, four biochar types were shaken with solutions of five different PO_4-P concentrations. CBC had the best P adsorption capacity. PBC and FBC both had a lower but similar adsorption while untreated biochar (UBC) adsorbed the least P. The shape of the adsorption isotherm for CBC (Figure 3) shows that when the equilibrium concentrations are low the increase in equilibrium adsorption was also low. This could indicate dissolved organic compounds being involved in the adsorption at low concentrations (Essington, 2004). The Freundlich model best fitted the PO_4-P adsorption to CBC and PBC biochars which means that the adsorption to these materials was best described as non-uniform. Adsorption to FBC biochar correlated better with the Langmuir adsorption model which indicates that their adsorption can be modeled as homogenous and in a monolayer over the biochar surface. This is in agreement with Li at al. (2016) who found that P removal using wheat straw biochar impregnated with $FeCl_3$ fitted the Langmuir model well. Contrastingly, Chen et al. (2011) reported that P adsorption by untreated and magnetite coated biochar made from orange peel fitted the Freundlich model better. The large standard deviation of the P adsorption on UBC makes it difficult to compare it to the equation models (Figure 3).

The Langmuir adsorption constant k_F was higher for adsorption on PBC than for the other biochar types. This indicates that the affinity between P and PBC was the highest. The Langmuir maximum adsorption Q_m for CBC was negative which is not realistic indicating that this model was not suitable for describing adsorption on CBC (Table 5). FBC had the highest Q_m at 3.2 mg/g but this is still lower than that reported by Liu et al. (2015) who demonstrated an adsorption capacity of 16.58 mg/g for a Fe impregnated biochar made from wheat straw. The biochar in the study by Li et al. (2016) had a smaller diameter than the biochar in this experiment (< 1 mm *vs* 1 - 7 mm) and higher iron to biochar ratio, 0.7 *vs* 0.3, which can explain the difference.

Looking at the Q_e for the kinetic adsorption experiment it is clear that the CBC had the highest equilibrium adsorption at all concentrations tested (Figure 5). In C2 (3.3 mgP/L), i.e. the concentration closest to the average influent wastewater concentration of PO_4-P in the column filters, CBC had the highest Q_e of 0.3 ± 0.03 mg/g after 24 h of shaking. Jung et al. (2016) received a Q_e of 100 mg/g on their Ca modified biochar in a batch sorption experiment. However, the concentration in the experiment by Jung et al. (2016) was 326 mg/L PO_4-P, which makes it inappropriate to compare between the experiments since the concentrations in this study were lower. The higher concentration of P in the solution the more obvious difference between the adsorption characteristics of the different biochar types could be seen (Figure 5). Twenty-four hours was not enough for the FBC biochar to reach an equilibrium adsorption (Figure 4) which means that the Q_e for FBC of 0.264 ± 0.02 mg/g in C2 would most likely be higher and even pass that of PBC (0.277 ± 0.04 mg/g) if longer time would have been given. Alternatively, it could have continued and never reached equilibrium due to a continuous formation of complexes as discussed by Essington (2004). The pseudo second order model was the better fit compared to pseudo first for most biochar types and concentrations (Table 6). This means that the adsorption can be assumed to be mainly chemical as suggested by Ho & McKay (1999 & 1998). The calculated Q_e from the pseudo second order equation was close to the experimental Q_e which implies the accuracy of the model. In previous studies, the second order kinetic model was proven to be the best model for describing P adsorption on magnesium modified biochar. However, $FeCl_3$ modified biochar has shown a better fit for the pseudo first order model by Zhang et al. (2013).

Adsorption and kinetic isotherms behave very different for different types of materials and chemicals, hence, results are difficult to compare. Experimental conditions like beaker size, material properties and preparation, temperature, reaction time etc. have a large influence on the results and these conditions are rarely the same in different studies. Therefore, batch adsorptions experiments are more suitable in comparing adsorption characteristics between materials in the same study (Essington, 2004).

4.2 COLUMN FILTER EXPERIMNET

The inflowing PO_4-P and Tot-P concentrations to the column filters varied considerably as can be seen in Figure 7 and Figure 6 and also in the box plot in Figure 8. The concentration probably varied because the quality of the wastewater from the WWTP differs between days and even changes during the day. These variations can also explain why the average concentration of the inflowing Tot-P, 3.84 mg/L (Table 7) was lower than yearly average of 6 mg/L for WWTP (Kungsängsverket, 2016).

The untreated biochar (UBC) filter had the smallest removal efficiency of Tot-P (43 ± 24 %) of all filters (Table 7). This is lower than what could be expected from a fully functioning vertical soil filter having an estimated Tot-P removal of 70 ± 20 % (Olshammar et al., 2015). The Tot-P reduction in UBC was also in the lower range of what have been shown possible (32 - 89 %) in other filters using untreated biochar (Table 9) (Dalahmeh, 2016). PBC had an average removal of 65 ± 14 % of Tot-P which is comparable of what could be expected from vertical soil filters and also of previously studied biochars. P concentration in the effluent of the UBC and PBC filters continued to increase during the experiment but seemed to become stabilized towards the end. It is difficult to recognize if they would have continued to decrease in efficiency given longer time. The Tot-P removal in CBC and FBC were 90 ± 8 % and 92 ± 4 % respectively and their PO_4-P removal rates were even higher. This is similar to previous batch adsorption studies where Fe modified biochar has been shown to remove of up to 99 % of P (Chen et al., 2011; Liu et al., 2015).

When comparing the Tot-P and PO_4-P removal, both UBC and Polonite biochar removed more Tot-P than PO_4-P (Table 7). The CBC and FBC showed the opposite trend. This means that UBC and PBC removed organic P better while CBC and FBC were more efficient in removing inorganic P. The impregnation in CBC and FBC probably created different surface structures compared to UBC and PBC. PBC should have similar surface to that of UBC since they had the same untreated biochar, which possibly could explain the grouping in the two Tot-P and PO_4-P characteristics.

The initial yellow color of the FBC filter effluent, also seen in the shaking solutions from the batch adsorption experiment, can most likely be explained by $FeCl_3$ treatment that carries a yellow color when dissolved in water. $FeCl_3$ also lowers the pH which can explain the drop in pH seen in the effluent water from the filter and in the PO_4-P solution of the batch adsorption experiment. An average pH of 2.6 ± 0.9 from the FBC filter effluent (Table 7) most likely created unfavorable environment for nitrifying and denitrifying bacteria which must be considered undesirable for wastewater treatment even if low pH favors precipitation reactions between P and iron (US EPA 2002). In contrast, CaO and Polonite increase the pH in aqueous solutions which explains the pH increase in the beakers during the batch sorption experiment (Table 4). The red-brown color of the CBC effluent probably originated from the mother material – willow tree bark. Water that is filtered through bark receives a red-brown color due to the release of organic acids (Dalahmeh et al., 2012). If the color comes from the bark it indicates that the pyrolysis of the biochar was never fully completed as the biochar itself would not release any color. Organic acids present in bark would lower the pH, meaning that the pH might have been even higher in the CBC effluent if the pyrolysis had been complete. Presence of organic acids can explain the shape of CBCs adsorption isotherm and can also be an explanation to the high COD content in the CBC effluent. Ca and Fe ions were most likely released from the CBC and FBC filter materials to the effluents which possibly could explain their high COD contents as calcium and iron compounds can be chemically oxidized in the analysis procedure. To investigate the removal of organic matter it would have been more appropriate to measure biochemical oxygen demand (BOD) or total organic carbon (TOC). TOC sampling occurred but lack of proper equipment and time stopped the analysis. Ca and Fe ions are not likely to affect the COD of PBC and UBC filter effluents to the same extent, yet these filters had lower COD removal rates (36 and 22 %, respectively) than shown in most previous biochar studies (90 %) as reported in Table 9 (Dalahmeh, 2016).

Another problem except for the color of the CBC effluent was the precipitate adding to the effluent beaker surface. It is likely that the precipitate is some calcium phosphate mineral which might lead to problems with clogging in the long run in a full-scale system.

4.3 NITROGEN REMOVAL FILTER

The two sections of the N removal filter removed 62 ± 16 % of the influent N (Figure 9 & Table 9). This was higher than conventional vertical soil filers where removal rates of 30 ± 10 % can be expected (Olshammar et al., 2015) and also higher than alternative OWTP solutions in general (Avloppsguiden, 2009) (Tabel 9). The average total N concentration was lower than that of NH_4-N in the influent which is not realistic. This is likely due to error in analysis during week 11, 12 and 13 (Figure 14c-A4). The increase in NO_3-N concentration in the first and decrease in the second section show that nitrification and denitrification took place (Figure 9a & b). However it was not until the end of the experiment the nitrate removal was high enough to remove almost of the NO_3-N created in the vertical section. The average outflow concentration from the horizontal filer was 2.66 ± 0.98 mg/L. It is likely that the NO_3-N and Tot-N removal capacity would have continued to increase as the biofilm in the filter continued to grow and mature. The P removal in the N removal filter was 29 ± 8 % which was lower than the removal rate observed for UBC in the column experiment and what can be expected from vertical soil filers (Table 9). The relocation of the filter in week 7 seemed to negatively affect the filter performance the following week. When moving the filter some of the water from the lower section had to be emptied and particles were released from the biochar. The disturbance of the microbial community in the biofilm and loose particles was probably the reason why P was released during week 8. After this the removal of Tot-P became more stable (Figure 9c). Moving the filter to the primary sedimentation also meant that the water entering the filter from week 8 was more turbid and contained more particles than before. This could explain why the overall COD removal was relatively low (45 ± 68 %) and varied more compared to vertical soil filters (80 ± 10 %) (Olshammar et al., 2015).

4.4 COMPARING BIOCHARS AND FILTERS

To compare adsorption of P in a batch sorption experiments to a real life systems can be misleading (Brix et al., 2001). Hedstöm (2006) argued that batch sorption experiments may overestimate the P sorption capacity because it is an ideal system with the material saturated in P solutions. Another aspect that was stressed was that biochar pieces can break during the experiment which increases the adsorption surface. Others claim that a shaking experiment severely underestimates the adsorption capacity because it does not take slow reactions of regenerated sorption sites into consideration (USEPA, 2002). In order to fully investigate materials adsorption, a combination between shaking studies and filter studies is recommended (Essington, 2004).

From the shaking experiment it was clear that the CBC had the highest adsorption of P (Table 10). This is in agreement with Seo et al. (2005) who in comparing Fe and Ca treated filter media found that Ca impregnation had the better P removal capacity. However, results from the filter experiment in the present study showed that the CBC is good but not better than FBC (Table 9). One explanation to this can be that the CBC biochar fragmented more than the other biochar types during the batch adsorption experiment. The risk of overestimating adsorption capacity as the biochar is breaking in a batch sorption experiment has been stressed by Hedström (2006). Also if the pyrolysis and impregnation of the CBC biochar was not complete as discussed above, loose CaO particles on the material surfaces might have overestimated the CBC adsorption. If the shaking experiment had been longer the FBC most likely would have reached a higher equilibrium adsorption and the difference in P adsorption capacity between CBC and FBC would have been smaller. It is also difficult to know how the CBC would perform if it had been produced differently.

Both the filter experiment and the batch adsorption experiment concordantly showed that PBC had a better P removal than UBC. The filter experiment showed that by mixing untreated biochar with Polonite, the Tot-P removal became 1.5 times higher compared to the mother material. Batch sorption experiment also showed that the PBC had three times higher P removal than UBC.

Table 9 Comparison between the results of pollutant removal (%) from filter experiments and literature for biochar filters Dalahmeh (2016)* and vertical soil filters Olshammar et al., (2015)** (mean ± standard deviation). The filter experiments comprised column with untreated biochar (UBC), biochar impregnated with calcium oxide (CBC) or ferric chloride (FBC) and untreated biochar mixed with Polonite (PBC). The N removal filter was constructed with a vertical unsaturated flow section followed by a vertical saturated flow section.

Chemical	**Results**					**Literature**	
	UBC	**CBC**	**FBC**	**PBC**	**N-Removal filter**	**Removal in Biochar Filters***	**Removal in Vertical Soil Filters ****
COD	36 ± 22	-122 ± 186	-100 ± 141	30 ± 30	45 ± 68	> 90	80 ± 10
Tot-P	43 ± 24	90 ± 8	92 ± 4	65 ± 14	29 ± 8	32 – 66	70 ± 20
Tot-N					62 ± 16	62 – 88	30 ± 10

A factor that affects the P and N removal is the volume and depth of the filters. The column filters were 50 cm tall which is similar to the 55 and 60 cm biochar filters compared with (Dalahmeh, 2016). The unsaturated filter section in the N removal filter was 30 cm deep which is smaller than the vertical soil filters (Olshammar et al., 2015). It is possible that a larger N removal filter might have had a better N removal.

If for instance the CBC or FBC would be used in real-scale filters the amount of filter material do not need to be high since the removal efficiency is high. It is possible that impregnated biochar in a filter would be more suitable as a separate P filter module connected to a larger system such as the N removal filter. To use the N filter in larger scale would require some planning on where to locate the filter. Alternately the unsaturated section or the whole filter system could be installed on top of a soil profile with a pump feeding the filter with wastewater from a septic tank.

4.4 POSSIBLE SUORCES OF EXPERIMENTAL ERROR

In the second week of the column experiment large hydrophobic (dry) areas in the column filters were observed and the filters were therefore washed with distilled water which enabled wastewater to flow through the entire filter volume. It could not be excluded that the washing could have removed some of the impregnation on FBC and CBC lowering their removal capacity.

The N removal filter was relocated due to interference of $FeCl_3$ on the N samples. After that the N removal filter had been relocated analysis results became more stable. However it is possible that some residual $FeCl_3$, used as P precipitation chemical, from the wastewater got adsorbed and stayed in the filter and further influenced the analysis. Initially, N parameters were also measured in the influent and effluent of the column filters. However, it soon became clear that ions and high COD from the filters themselves interfered with the kits for chemical analyses, giving unrealistic and highly fluctuating results. It was therefore decided to stop the N measurements in week 5 and to only present P data as the analysis kit for P was not as affected by high COD. In conclusion, there is a risk that some of the results in this report might be affected by intrinsic COD and ions from the filter materials. In future studies, when sampling water from impregnated filters, it is important to consider the potential problems the impregnation itself might cause on the analysis.

5. CONCLUSIONS

The batch adsorption and filter experiments in this study demonstrates that modification of biochar made from hard wood bark can improve phosphorus removal capacity. Especially modification by impregnation before pyrolysis can improve the phosphorus removal compared to unmodified biochar or biochar mixed with Polonite. These materials are promising replacements or additions to vertical soil filters.

The column filters with biochar impregnated with ferric chloride and calcium oxide showed phosphorus removal rates of 93 ± 7 % and 95 ± 2 % which was higher than untreated biochar and biochar mixed with Polonite which removed 32 ± 25 % and 58 ± 17 %, respectively.

The Freundlich adsorption model best fitted the P adsorption onto CaO impregnated and Polonite mixed biochar. Adsorption to untreated and $FeCl_3$ biochar correlated better with the Langmuir adsorption model. The adsorption over time for all biochar types was best described by pseudo 2^{nd} order kinetic model.

The effluent from ferric chloride impregnated biochar had low pH. The effluent from the calcium oxide impregnated biochar had some precipitation in it and a brown-red color and the biochar was probably not completely prepared. The low pH, color and precipitation can be a problem if the materials are to be used in full-scale treatment system.

Biochar filter consisting of a vertical flow aerobic section followed by a horizontal section with saturated flow reached a high total nitrogen removal rate of 62 ± 16 %, a removal rate higher than that of conventional vertical soil filters as well as most alternative onsite wastewater treatment systems.

5.1 SUGGESTIONS FOR FURTHER EXPERIMENTS

For further studies it would be interesting to see how impregnated biochar filters and N removal units will perform in a long-term column study. Improved filtration or sedimentation of the inflowing wastewater to the N removal filter would make a more realistic set up and possible better COD treatment. Clogging effects, not investigated in this study, and changes in flow patterns through the filters caused by clogging would be another important area to investigate in order to evaluate the life time of filter materials. It would be worth considering redoing the calcium oxide impregnation of the biochar to see if the observed color and precipitation effects would disappear. It would also be interesting to expose calcium oxide biochar to higher P concentration in a batch adsorption experiment to see if the adsorption isotherm will show signs of a decreasing equilibrium adsorption (Q_e). A longer batch adsorption experiment to investigate the $FeCl_3$ equilibrium adsorption would also be interesting.

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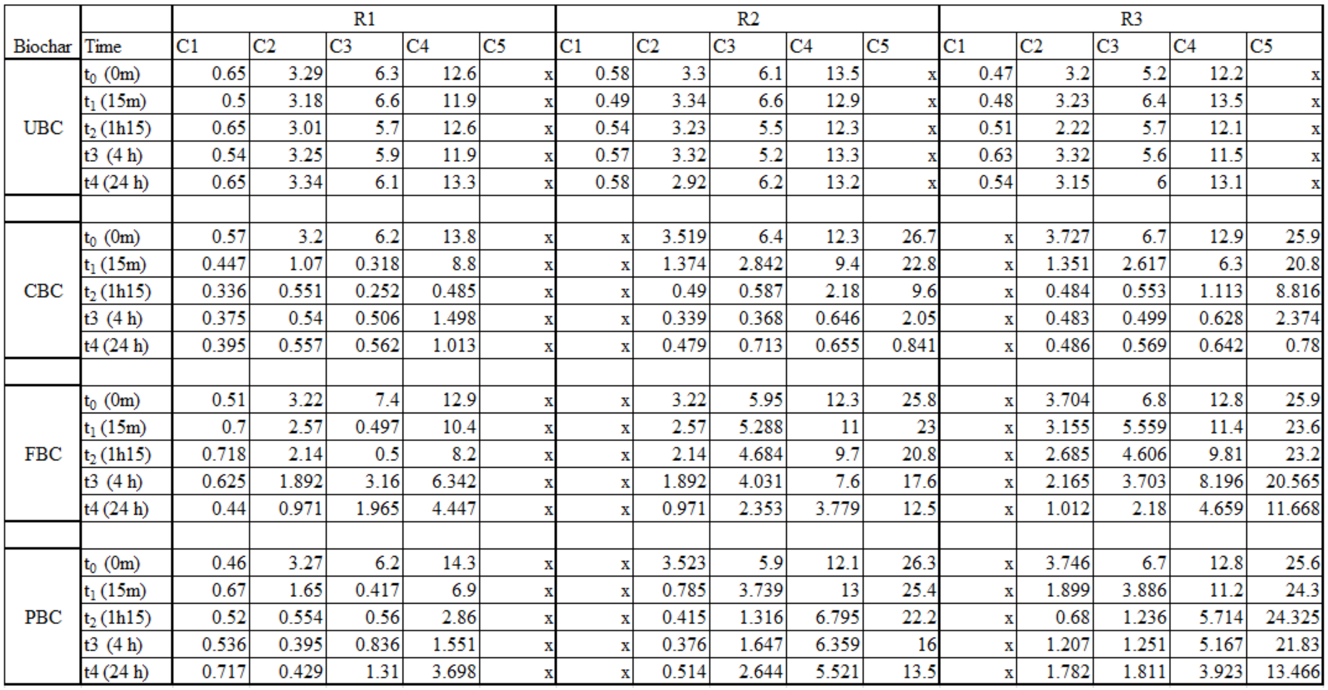
7. APPENDIX

APPENDIX I - Shaking experiment

All the data from the shaking experiment can be seen in Table 8. The concentrations in this table were then adjusted for the volume chance of the beakers when sampling took place. The mean concentrations adjusted for the volume change can be found in Table 3 in the Result section. The UBC did not get exposed or C5 because it showed little adsorption. CBC, FBC and PBC did not get more than one replicate for C1 because the concentration were considered too low to give interesting data.

Table 10 Results from the shaking experiment with all replicated (R1-R3), concentrations (mg/L) (C1-C5) and biochar types UBC, CBC, FBC and PBC. The concentrations in the table have not been adjusted for the change of volume that took place at each sampling time.



		R1					R2					R3				
Biochar	Time	C1	C2	C3	C4	C5	C1	C2	C3	C4	C5	C1	C2	C3	C4	C5
UBC	t_0 (0m)	0.65	3.29	6.3	12.6	x	0.58	3.3	6.1	13.5	x	0.47	3.2	5.2	12.2	x
	t_1 (15m)	0.5	3.18	6.6	11.9	x	0.49	3.34	6.6	12.9	x	0.48	3.23	6.4	13.5	x
	t_2 (1h15)	0.65	3.01	5.7	12.6	x	0.54	3.23	5.5	12.3	x	0.51	2.22	5.7	12.1	x
	t3 (4 h)	0.54	3.25	5.9	11.9	x	0.57	3.32	5.2	13.3	x	0.63	3.32	5.6	11.5	x
	t4 (24 h)	0.65	3.34	6.1	13.3	x	0.58	2.92	6.2	13.2	x	0.54	3.15	6	13.1	x
CBC	t_0 (0m)	0.57	3.2	6.2	13.8	x	x	3.519	6.4	12.3	26.7	x	3.727	6.7	12.9	25.9
	t_1 (15m)	0.447	1.07	0.318	8.8	x	x	1.374	2.842	9.4	22.8	x	1.351	2.617	6.3	20.8
	t_2 (1h15)	0.336	0.551	0.252	0.485	x	x	0.49	0.587	2.18	9.6	x	0.484	0.553	1.113	8.816
	t3 (4 h)	0.375	0.54	0.506	1.498	x	x	0.339	0.368	0.646	2.05	x	0.483	0.499	0.628	2.374
	t4 (24 h)	0.395	0.557	0.562	1.013	x	x	0.479	0.713	0.655	0.841	x	0.486	0.569	0.642	0.78
FBC	t_0 (0m)	0.51	3.22	7.4	12.9	x	x	3.22	5.95	12.3	25.8	x	3.704	6.8	12.8	25.9
	t_1 (15m)	0.7	2.57	0.497	10.4	x	x	2.57	5.288	11	23	x	3.155	5.559	11.4	23.6
	t_2 (1h15)	0.718	2.14	0.5	8.2	x	x	2.14	4.684	9.7	20.8	x	2.685	4.606	9.81	23.2
	t3 (4 h)	0.625	1.892	3.16	6.342	x	x	1.892	4.031	7.6	17.6	x	2.165	3.703	8.196	20.565
	t4 (24 h)	0.44	0.971	1.965	4.447	x	x	0.971	2.353	3.779	12.5	x	1.012	2.18	4.659	11.668
PBC	t_0 (0m)	0.46	3.27	6.2	14.3	x	x	3.523	5.9	12.1	26.3	x	3.746	6.7	12.8	25.6
	t_1 (15m)	0.67	1.65	0.417	6.9	x	x	0.785	3.739	13	25.4	x	1.899	3.886	11.2	24.3
	t_2 (1h15)	0.52	0.554	0.56	2.86	x	x	0.415	1.316	6.795	22.2	x	0.68	1.236	5.714	24.325
	t3 (4 h)	0.536	0.395	0.836	1.551	x	x	0.376	1.647	6.359	16	x	1.207	1.251	5.167	21.83
	t4 (24 h)	0.717	0.429	1.31	3.698	x	x	0.514	2.644	5.521	13.5	x	1.782	1.811	3.923	13.466

APPENDIX II - Adsorption isotherms

The graphs that provided all Langmuir and Freundlich parameters are shown in Figure 12 & Figure 13. The linear equation of Langmuir model (Equation 4) is Ce plotted vs Ce/Qe. The linear plot provided the parameters Q_m and k_L where the slope was $1/Q_m$ and the intercept $1/Q_mk_L$ and they are presented in Table 5.

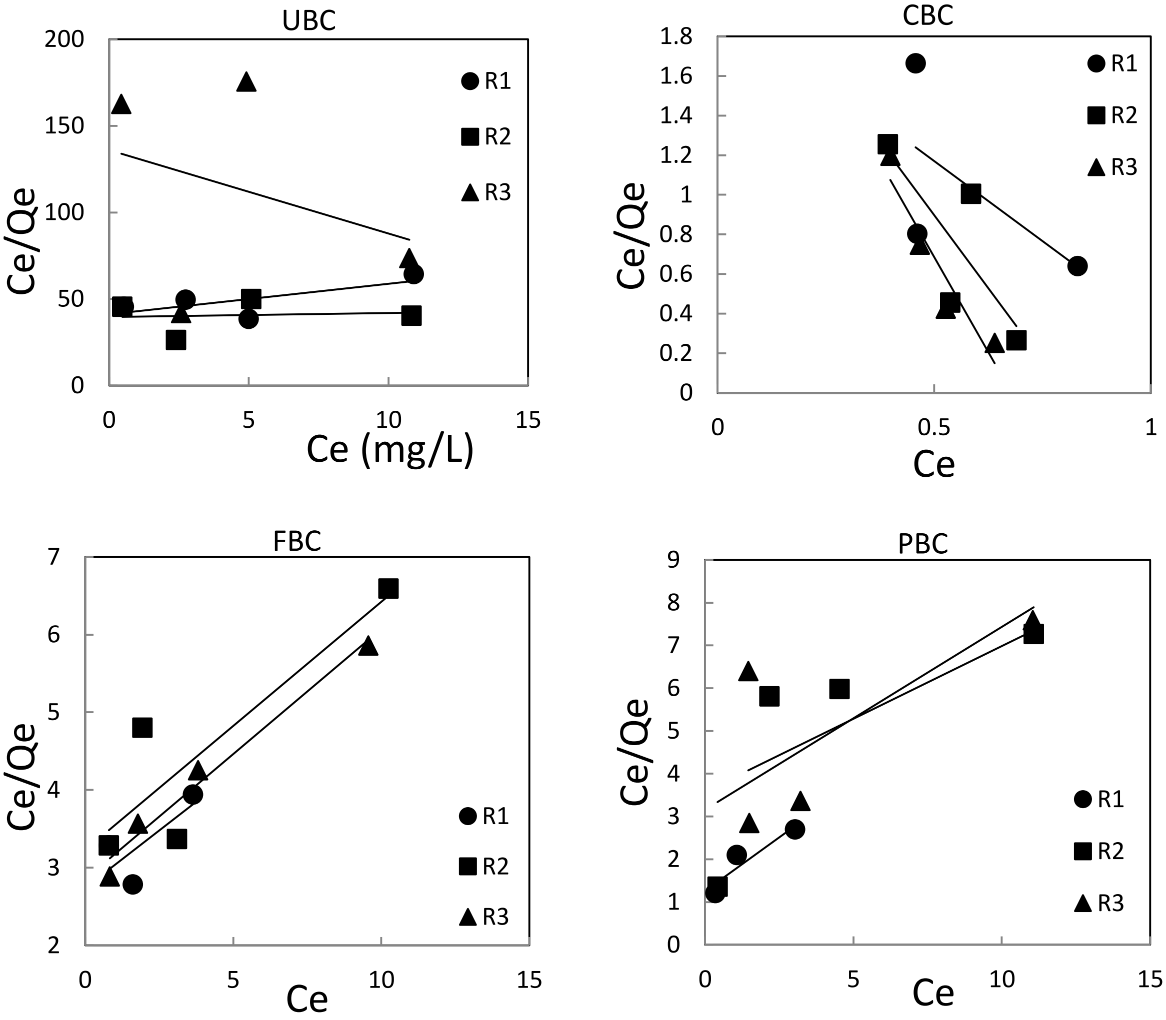


Figure 11 Linear plots of the linearization of the Langmuir equation.

The linear equation of the Freundlich model (Equation 5) is expressed as $\ln Q_e$ vs $\ln C_e$. The slope is 1/n and intercepts in $\ln k_F$. The parameters are all presented in Table 5 in the result section.

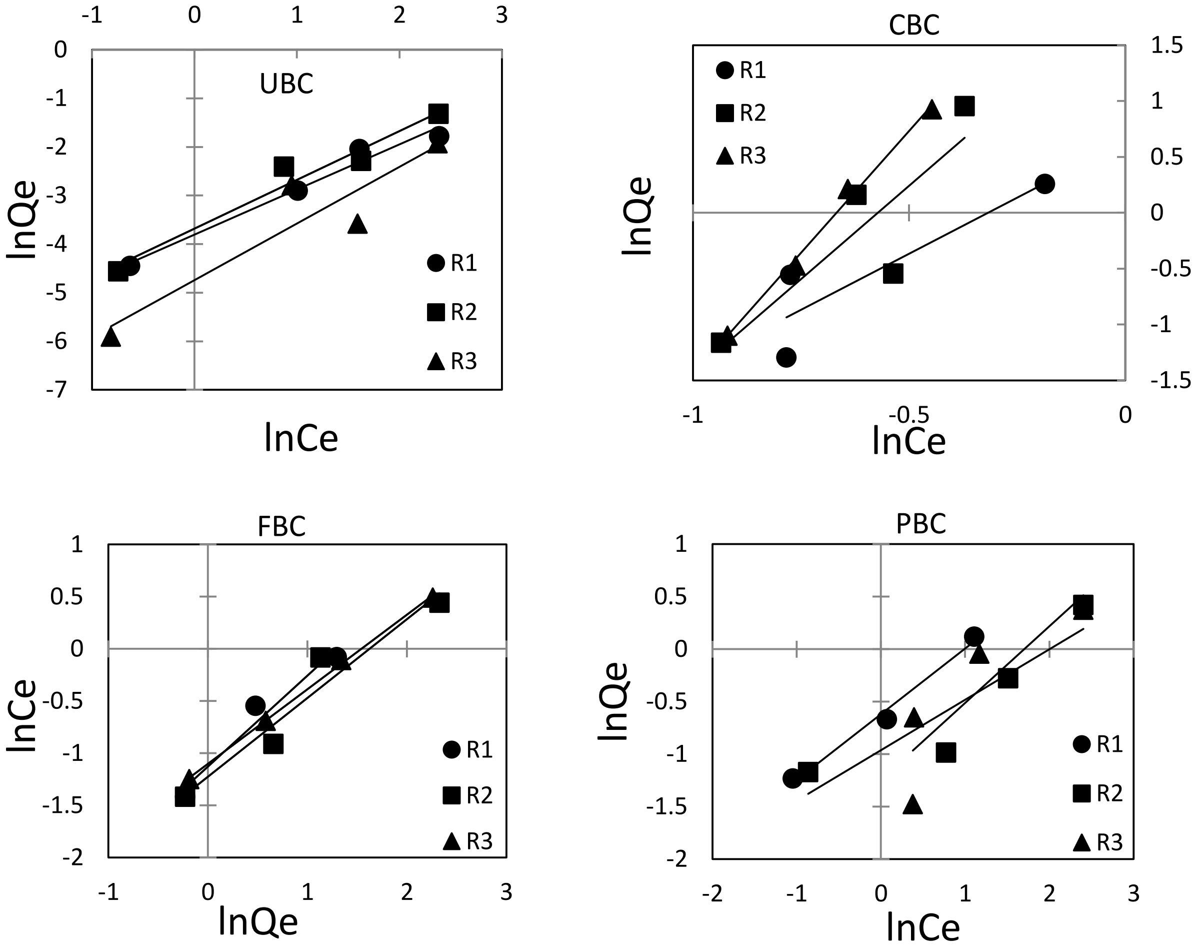


Figure 12 Plots of the linear version of Freundlich model for all biochar types.

APPENDIX III - Kinetic isotherms

Model parameters derived from calculated pseudo first and second order equation 6 & 7 (Table 11).

Table 11 All the calculated parameters for the kinetic isotherms

Concentration	**Biochar type**	**Pseudo 1st order model parameters**			**Pseudo 2nd order model parameters**			**Experimental**
		Q_e (mg/g)	R^2	k_1 (min^{-1})	Q_e (mg/g)	R^2	k_2 (g/mg/min)	Qe (mg/g)
C2	**UBC**	0.064	0.77850	0.004	0.068	0.9107	-0.021	0.069
	CBC	0.156	0.83597	0.028	0.307	1.0000	1.717	0.307
	FBC	0.229	0.91907	0.004	0.281	0.9965	0.036	0.264
	PBC	0.266	0.99700	0.097	0.264	0.9998	-0.499	0.277
C3	**UBC**	0.123	0.85430	0.021	0.085	0.9913	-0.593	0.086
	CBC	0.586	0.99970	0.063	0.594	1.0000	1.657	0.593
	FBC	0.456	0.95767	0.005	0.516	0.9970	0.055	0.494
	PBC	0.385	0.99700	0.049	0.468	0.9995	-0.496	0.469
C4	**UBC**	0.182	0.55703	0.664	0.199	0.9940	-0.081	0.194
	CBC	1.015	0.98263	0.021	1.250	0.9997	0.075	1.237
	FBC	0.815	0.95843	0.005	0.916	0.9978	0.014	0.914
	PBC	0.847	0.87223	0.029	0.950	0.9951	-0.047	0.947
C5	**UBC**	-	-	-	-	-	-	-
	CBC	2.409	0.99200	0.013	2.654	0.9988	0.008	2.564
	FBC	1.467	0.96665	0.003	1.774	0.9887	0.004	1.594
	PBC	1.494	0.99450	0.005	1.756	0.9814	0.002	1.489

Linearization of pseudo 2^{nd} order equation gave liner plots with t/Q as y-axis and t as x-axis (Figure 13a-d). The plots have the slope $1/Q_e$ and intercept $1/k_2Qe$ and the parameters Q_e, k_2 and correlation R^2 are presented in Table 6 in and Table 11. Pseudo 2^{nd} had the best fit for all biochar and concentrations except for PBC and C5 (Figure 13e). Pseudo 1^{st} equation gave a linear plot with $\ln(Q_e\text{-}Q_t)$ as y-axis. The slope is k_1 and intercept $\ln(Q_e)$ and k_1 and Q_e are presented in Table 6 in the Result section and in Table 11.

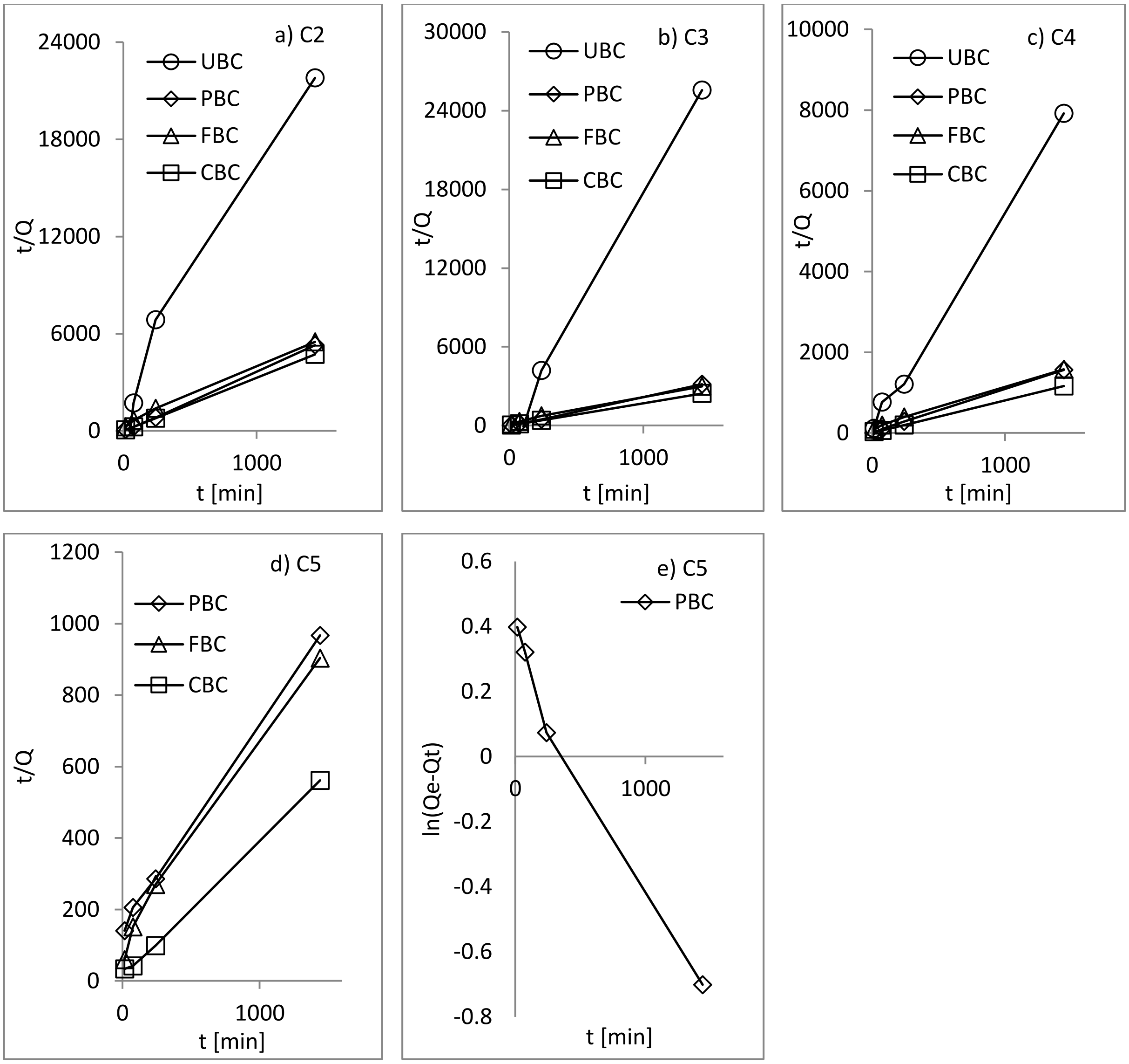


Figure 13 a-d) The linear plots of pseudo 2nd order kinetic model for C1, C2, C3, C4 and C5 where t/Q has the unit min/mg/g. **e)** The pseudo 1st order kinetic model linear plot for C5 and Polonite (PBC) with y-axis ln(Qe-Qt) (mg/g).

APPENDIX VI - Filter experiments

The removal efficiency of NH_4-N in the vertical section of the N removal filter was stable around 50 % from week 9 to 14 of the experiment (Figure 14a). In the same filter section, NO_3-N was not removed but created. As the experiment proceeded higher NO_3-N were measures in the outflow of the vertical filter section. In the Horizontal section, the NH_4-N removal varied more than in the previous section but had an average removal around 40 % (Figure 14b). The NO_3-N removal was not stable and increased during the experiment (Figure 14b). In the whole filter (Figure 14c), NH_4-N and Tot-N displayed stable removal whereas the filter had an increasing removal of NO_3-N. Tot-N removal is also presented in the result section (Figure 9).

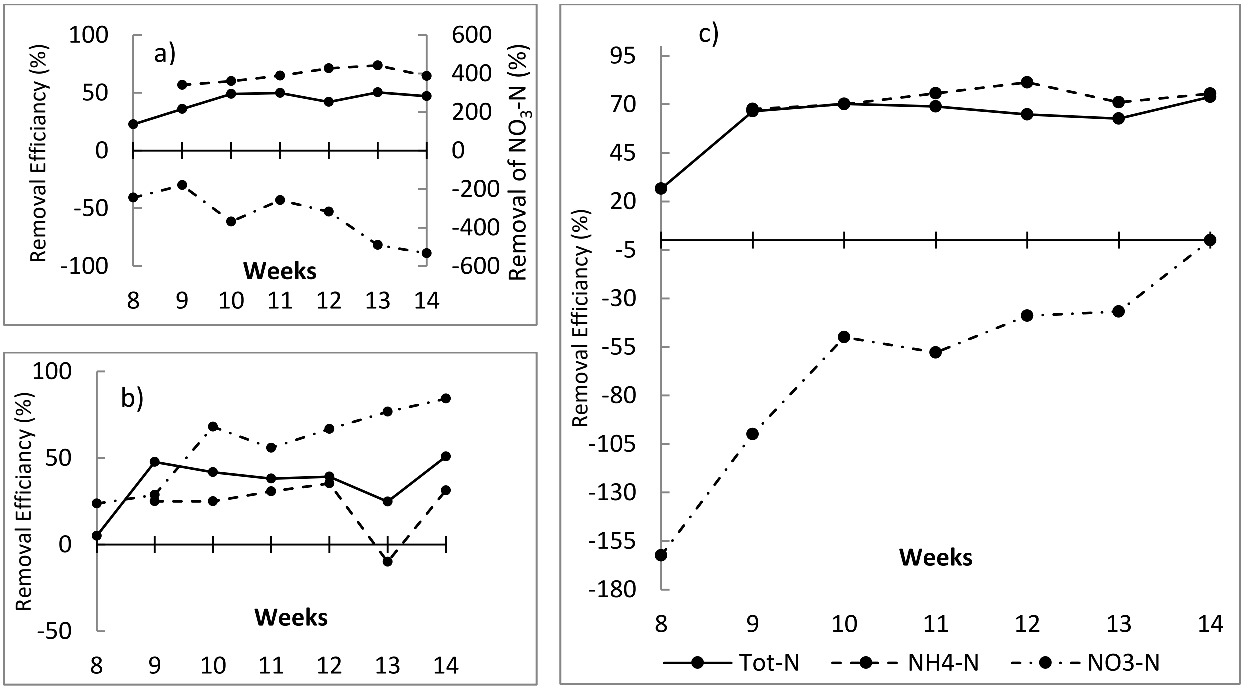


Figure 14 The variation of the removal of NH_4-N, NO_3-N and Tot-N in the nitrogen removal filters **a)** First unsaturated section with vertical flow, **b)** second saturated section with horizontal flow and **c)** total filter with both sections combined.