Parameters Affecting Phosphate Sorption from Sludge Liquors by Hybrid Anion Sorbents

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M.Sc. Yinan Tang

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by
M.Sc. Yinan Tang
born in Nantong, China

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Supervisor: em. Prof. Dr.-Ing. E.h. Hermann H. Hahn, Ph.D
Co-supervisor: Prof. Dr. rer. nat. habil. Josef Winter

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Korreferent: Prof. Dr. rer. nat. habil. Josef Winter, Karlsruhe

Yinan Tang

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Vorwort des Herausgebers

Die Autorin dieses Bandes hat eine Fragestellung aufgegriffen, die zum einen von den Forschungsinstitutionen seit geraumer Zeit intensiv bearbeitet wird aber zum anderen auch berufsständische und regelsetzende Vereinigung (z.B. Deutsche Vereinigung für Wasser, Abwasser und Abfall, oder auch Klärschlammnutzungsinstitutionen) behandeln. Dies macht deutlich, dass sich die Autorin dieser Dissertationsschrift mit einem wichtigen Thema befasst und auch einem, das an der Front technisch-wissenschaftlicher Entwicklung steht.

Die Einführung in die Thematik und spiegelbildlich dazu die abschließende Zusammenfassung sind sehr kondensiert verfasst; dies wirkt in einem allzu verbalen Zeitalter erholsam. – In vielen wissenschaftlichen Arbeiten, nicht nur in hoch kompetitiven Prestigepublikationen, ist dem sog. Stand von Technik und Wissenschaft ein bedeutender Raum zugestanden, nicht zuletzt auch um zu zeigen, wo der eigene Beitrag anzusiedeln ist, wo der eigene Beitrag eine entscheidende Lücke zu schließen vermag. Dies geschieht im zweiten Kapitel. So werden z.B. die in der Abwassertechnik weithin bekannten Grundlagen der generellen P-Elimination etc. oder auch der Adsorptionsthermodynamik breit(er) dargestellt, und die neueren und eventuell „konkurrierenden" Arbeiten zur dielektrischen oder auch an „Organika-adsorbierenden" Phosphoreliminierung knapp beschrieben.

Nun zu den wichtigsten Ergebnissen: Mittels sog. ESEM Bildern zeigt die Autorin, dass die von ihr ausgewählte und untersuchte Adsorptionsmatrix (Layne RT) unterschiedliche Oberflächen zeigt, ob sie in einer nicht modifizierten Form oder mit Hydroxidionen aktiviert oder mit Phosphat Ionen belegt ist oder gar in Wechselwirkung mit Schlammwasser getreten ist. Weiterhin untersucht und berichtet sie den Einfluss des pH-Wertes des Mediums, in dem die Adsorbate gelöst sind, auf die Adsorption. Wie zu erwarten, ist dieser Einfluss signifikant. Über die Darstellung der Adsorptionsisothermen in Form der zeitlichen Aufnahme des Adsorbates an die Adsorbentien für die verschiedensten Anfangskonzentrationen von Adsorbat einerseits und Adsorbenz andererseits wird geklärt, dass der jeweilige Prozess in etwa 30 bis 60 Minuten eine Art Gleichgewicht erreicht und dass Adsorptionsmodelle wie von Langmuir, Freundlich, oder Redlich-Peterson erkennen lassen, dass es sich nicht um eine einfache Einschichten-Adsorption handeln kann. In einer ganzen Serie von sog. Batchversuchen, werden zu erwartende oder zu befürchtende Konkurrenzreaktionen.

Für die Anwendung sind Durchflusssysteme eher von Bedeutung; die Autorin untersucht also den von ihr propagierten Prozess in einer filterartigen Versuchsapparatur, deren Geometrie allerdings im Hinblick auf mögliche Randeffekte nicht diskutiert wurde. Sie stellt fest, dass bei (sehr) hohen Durchflussraten einen gewissen Einfluss auf den Durchbruchspunkt gibt, dass allerdings dann bei zwei niedrigeren untersuchten Durchsatzraten der Einfluss kaum mehr beobachtbar ist. Der Durchbruch erfolgt interessanterweise erst nach dem Durchfluss von etwa 40 Bettvolumina und die Säulenbelegung ist akzeptabel hoch. Sehr wichtig und interessant ist die Beobachtung, dass der CSB-„Durchbruch“ schon sehr früh erfolgt, also die gelösten organischen Stoffe wohl doch wenig zurückgehalten werden. Die sich logischerweise anschließenden Untersuchungen zur Regeneration der Adsorptionsmatrix werden ebenfalls in Batch- und dazugehörigen Durchflusssystemen untersucht. Es zeigt sich, dass bei bis zu viermaligen Regenerationszyklen (im Batchbetrieb und Durchflussuntersuchungen) keine signifikante Verminderung des P-Rückhaltes eintritt.

Die von der Autorin aufgegriffene Fragestellung ist von großer Bedeutung für eine, vor allem auch für den praktischen Einsatz in der Abwasser- und Schlammtechnologie wichtige, Zusatzstufe. Sie ist wissenschaftlich in dieser Konfiguration sicherlich als Neuland zu bezeichnen. Es ist aber auch eine technische Fragestellung, die geklärt werden muss, bevor eine solche Prozessstufe konzeptionell einbezogen wird. Insofern ist diese Schrift für den Bereich der Siedlungswasserwirtschaft, insbesondere für die Phosphorrückgewinnung von großem Interesse und sicherlich auch von großer Bedeutung.

Im Februar 2015 Hermann H. Hahn

Kurzfassung

Phosphor (P) ist nicht nur ein wesentliches Element für Landwirtschaft und Industrie, sondern eine generell knappe Ressource in der Natur. Über moderne kommunale Systeme gelangt Phosphor nach menschlichem Verzehr als Abwasser in Kläranlagen und reichert sich dann im Klärschlamm an. Die Phosphorrückgewinnung aus Klärschlamm stellt nicht nur eine Ergänzung der P-Versorgung dar, sondern auch gleichzeitig eine Verringerung der P-Belastung der Rückbelastungswässer. In dieser Arbeit wird eine Zwei-Phasen-Technologie, bestehend aus Sorption und Elektrodialyse, für P-Rückgewinnung untersucht. Die selektive Sorption von Phosphat-Ionen aus P-reichen Wässern ist ein kritischer Schritt für das Gesamtsystem, das die Qualität des Endproduktes und die Leistungsfähigkeit der Technologie bestimmt.

In dieser Arbeit wurde ein Hybrid-Anion Sorptionsmittel, genannt LayneRT eingesetzt, um Phosphat-Ionen aus Schlammwasser zu eliminieren. Batch-Experimente wurden durchgeführt, um das Sorbens zu charakterisieren und die optimalen Randbedingungen für die maximale Sorptionskapazität zu bestimmen. Isothermen Tests zeigten ein günstiges Gleichgewicht bei Phosphat Kapazitäten um 20 mg PO_4^{3-}/g bei Ein-Komponenten-Modell-Lösungen. Der optimale pH-Wert für eine hohe Sorptionsleistung lag zwischen pH 6 und pH 8,2. Die Anwesenheit von konkurrierenden Anionen verringert die Sorptionskapazität für Phosphat. Hohe initiale Phosphat-Konzentrationen begünstigen die Sorption. Die Kinetik konnte durch ein „Pseudo-second-order Modell“, simuliert werden. Die multilineare Auswertung mittels eines „Intra-Partikel Modells“ zeigte, dass die Sorption zunächst auf Oberflächendiffusionsprozessen beruht, gefolgt von innerer Porendiffusion.

Die kontinuierlichen Untersuchungen wurden mit einer Festbettsäule, gefüllt mit körnigem LayneRT durchgeführt. Strömungsgeschwindigkeiten, pH-Wert und die Zusammensetzung des Schlammwassers sind die entscheidenden Faktoren für den kontinuierlichen Betrieb. Beim Betrieb mit Modell-Lösung, erreicht die Sättigungskapazität des Sorbens einen Wert von 30 mg PO_4^{3-}/g im Idealzustand. Mit Schlammwasser verringerte sich die Kapazität auf bis zu 7 mg PO_4^{3-}/g auf. Die Kapazität könnte durch Konditionierung des Schlammwassers, etwa durch pH Verringerung verbessert werden, so konnte z. B. eine Beladung von 10 mg PO_4^{3-}/g bei pH 6,47 erreicht werden. Höhere Phosphatkonzentration im Schlammwasser verkürzen die Betriebszyklen der P-Sorption und erhöhen die Effizienz des Ionenaustauschers.

Die Zusammensetzung des Schlammwassers wurde analysiert, um die vorherrschenden Stoffkonzentrationen, die die P-Sorption an LayneRT beeinflussen könnten, zu bestimmen. Neben konkurrierenden Anionen, spielen gelöste organische Stoffe (DOM) eine wichtige Rolle bei den Konkurrenzreaktionen. Die Ergebnisse der Größenausschluss-Chromatographie zeigten, dass die niedrigen Molekulargewichte (DOM <1300 da) die Hauptfraktion des Prozesswassers im Wettbewerb mit der Phosphat Sorption darstellen. Dieser Teil des DOM ist für die bis zu 35%-ige Reduzierung der Phosphat Sorptionskapazität verantwortlich. Um den negativen Effekt dieser Fraktion zu verringern und die Qualität des Endproduktes zu verbessern, könnten Aktivkohle oder spezifische Ionentauscher verwendet werden , um die niedermolekulare organische Fraktion des Schlammwassers vor der P-Sorption zu entfernen.

Die Regeneration des erschöpften Sorbens wurde unter Verwendung von verdünnter Natronlauge durchgeführt. Der Ionenaustauscher LayneRT weist ein enerseits hohes Wiederverwendungspotenzial auf und andererseits zeigt das regenerierte LayneRT Material eine erhöhte Phosphatsorptions-Kapazität von annähernd 25 mg PO_4^{3-}/g. Während des Regenerationsprozesses wurde das sorbierte Phosphat von dem Sorptionsmittel desorbiert, womit Natriumphosphat als Endprodukt entstand und über 95% des Phosphats zurückgewonnen werden konnten. Bei kontinuierlichen Tests wurde die Regeneration des erschöpften Sorbensbettes innerhalb von 5 Bettvolumen erreicht.

Abstract

Phosphorus (P) is not only an essential element for agriculture and industry, but generally a scarce resource in nature. Via modern municipal systems, phosphorus, after human consumption, arrives as wastewater at treatment plants and accumulates in sewage sludge. The phosphorus recovery from sewage sludge is not just an addition of P supply, but also at the same time a reduction in P pollution via back-contamination.

In this work, a two-phase technology, comprising sorption and electrodialysis for P-recovery, is examined. The selective sorption of phosphate ions from P-rich waters is a critical step for the overall system that determines the quality of the final product and the efficiency of the technology. In this work a hybrid anion sorption called LayneRT is used to eliminate phosphate ions from sludge liquor. Batch experiments were carried out to characterize the sorbent and to determine the optimal boundary conditions for the maximum sorption capacity. Isothermal tests showed a favorable balance in phosphate capacity of 20 mg PO_4^{3-}/g at one-component model solutions. The optimum pH for a high sorption was between pH 6 and pH 8.2. The presence of competing anions reduces the sorption capacity for phosphate. High initial phosphate concentrations favor the sorption. The kinetics could be simulated by a "pseudo-second-order model." The multi-linear analysis, using an "intra-particle model" showed that the sorption initially is based on boundary layer diffusion, followed by internal pore diffusion.

The continuous experiments were carried out with a fixed-bed column, filled with granular LayneRT. Flow rates, pH and the composition of the sludge liquor are the decisive factors for continuous operation. When operating with the model solution, the saturation capacity of the sorbent has reached a value of 30 mg PO_4^{3-}/g, in the ideal state. Using sludge liquor, the capacity decreased to up to 7 mg PO_4^{3-}/g. The capacity could be improved by conditioning the sludge liquor, for example by decreasing the pH, as a loading of 10 mg PO_4^{3-}/g at pH 6.47 was reached. Higher phosphate concentrations in the sludge liquor reduce the operating cycles of the P-sorption and increase the efficiency of the ion exchanger.

The composition of the sludge liquor was analyzed to determine the predominant substance concentrations which might influence the P-sorption on LayneRT. In addition to competing anions, dissolved organic matter (DOM) plays an important role in competitive reactions. The results of the size exclusion chromatography showed that the low molecular weights (DOM < 1300) constitute the major fraction of the process water in competition with the phosphate sorption. This part of the DOM is responsible for up to 35% reduction of the phosphate sorption capacity. To reduce the negative effect of this fraction and to improve the quality of the end product, activated carbon or specific ion exchanger could be used to remove the low molecular weight organic fraction of the sludge liquor before the P-sorption.

The regeneration of the used sorbent was carried out using dilute sodium hydroxide solution. The ion exchanger LayneRT has a high reuse potential on the one hand and on the other hand the regenerated LayneRT material shows an increased phosphate sorption capacity of approximately 25 mg PO_4^{3-}/g. During the regeneration process the sorbed phosphate was desorbed from the sorbent and sodium phosphate developed as an end product and about 95% of the phosphate could be recovered. In continuous test, the regeneration of the spent sorbent bed was reached within 5 bed volumes.

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There are a number of people without whom this thesis might not have been written and to whom I am greatly indebted.

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To my beloved family, especially my parents Jianhua Tang and Weiguo Ji, my grandmother and my fiancé Xuchang Fei, thank you for always supporting me and believing in me. Thank you for letting me be the person I am today. I would like you to know that you are my inspiration and motivation for everything, as I dedicate this thesis to all of you.

List of contents

List of Illustrations

List of Tables

Abbreviations and Symbols

Abbreviations

AAM		Anion exchange membrane
AbwV		Abwasserverordnung
ATV-DVWK		Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V.
BMBF		Bundesministerium für Bildung und Forschung
BMU		Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit
BOD	mg/L	Biological Oxygen Demand
BOD5	mg/L	Biological Oxygen Demand in 5 days
BV		Bed Volume
COD	mg/L	Chemical Oxygen Demand
Da		Dalton
DIN		Deutsches Institut für Normung e.V.
DM	mg/L	Dry matter
DOC	mg/L	Dissolved Organic Carbon
DOM	mg/L	Dissolved Organic Matter
DS		Digested sludge
DSM		Dry solid matter
DWA		Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V.
EBPR		Enhanced Biological Phosphorus Removal
EDI		Electrodeionization
EFMA		European Fertilizer Manufacturers Association
EN		European Norm
EPA		Environmental Protection Agency
ESEM		Environmental scanning electron microscopy
FAAS		Flame Atomic Absorption Spectrometry
FEG		field emission gun
FI		Flow rate controlling
FTIR		Fourier transform infrared spectrometer
HAIX		Hybrid anion exchange
HFO		Hydrated ferric oxide
KAM		Cation exchange membrane
KIT		Karlsruhe Institute of Technology
LDHs		Layered double hydroxides
LEM		Laboratory for Electron Microscopy
MAP		Magnesium Ammonium Phosphate
MTZ		Mass Transfer Zone
MW	Dalton	Molecular weight
oDM	%	Organic dry matter
PI		Pressure controlling
PS		Primary sludge
PSS		Sodium 4-styrenesulfonate

R_4N^+		Positively charged quaternary ammonium groups
R-P		Reclich-Peterson isotherm
SEC		Size-exclusion chromatography
SEM		Scanning electron microscope
SS		Secondary sludge
SS		Sludge stabilization
TBP		Tri-butyl-phosphate
TKN	mg/L	Total Kjeldahl Nitrogen
TOC		Total Organic Carbon
UBA		Umweltbundesamt
USDA		United States Departmeng of Agriculture
USGS		United States Geological Survey
WWTP		Wastewater treatment plant
Zr-FPS		Zirconium(IV) loaded bifunctional fibers

Symbols

α	mg/g·min	Initial sorption rate in Elovich model
a_R	dm^3/g	Reclich-Peterson constant
β		Exponent of Redlich-Peterson isotherm
β	g/mg	Extent of surface coverage in Elovich model
b_F		Freundlich constant
c	g/L or mg/L	Concentration
C	g/L or mg/L	Concentration of diffusing substance in Fick's first law
c_0	g/L or mg/L	Initial concentration
C_0	g/L or mg/L	Initial concentration of influent of a fixed bed column
C_B	g/L or mg/L	Breakthrough concentration of the target ion in a column
c_e	g/L or mg/L	Equilibrium concentration
C_e	g/L or mg/L	Concentration of effluent of a fixed bed column
C_i	g/L or mg/L	Concentration of the effluent at the time t_i
C_L	g/L or mg/L	Operating limit concentration of the column
D		Diffusion coefficient in Fick's first law
DS_{inS}	g/L or %	Dry solids in raw sludge
DS_{outS}	g/L or %	Dry solids in thickened sludge
F		Rate of transfer per unit area of section in Fick's first law
g N/(C·d)		Gram nitrogen per capita per day
g P/(C·d)		Gram phosphate/phosphorus per capita per day
g P/kg		Gram phosphate/phosphorus per kilogram solid
g/(C·d)		Gram per capita per day
k_1	L/min	Rate constant of pseudo first-order sorption
k_2	g/mg·min	Rate constant of pseudo second-order sorption

K_F		Freundlich constant
kg BOD_5/d		Kilogram biological oxygen demand per day
K_i	$mg/(g\cdot min^{0.5})$	Intra-particle diffusion constant
K_L		Langmuir constant
K_R	dm^3/g	Reclich-Peterson constant
L/(C·d)		Litre per capita per day
m		Metre
m	kg, g or mg	Mass
M	mol/L	Mole per litre
mg P/L		Milligram phosphate/phosphorus per litre
Mt		Megaton
^{o}C		Dgree Celsius
P		Phosphorus, phosphate
q	mg/g or g/g	Load of sorbate per unit mass of sorbent
Q	m^3/h or mL/min	Flow rate
q_0	mg/g or g/g	Initial load of sorbate per unit mass of sorbent
q_e	mg/g or g/g	Sorbate uptake per unit mass of sorbent at equilibrium
Q_{inS}	m^3/h or L/(C·d)	Flow volume of raw sludge before thickening
q_{max}	mg/g or g/g	Maximal load of sorbate per unit mass of sorbent
Q_{SL}	m^3/h or L/(C·d)	Flow volume of sludge liquor
q_t	mg/g or g/g	Load of sorbate per unit mass of sorbent at time t
R_i		Initial sorption factor of intra-particle diffusion model
R_L		Equilibrium parameter of Langmuir
t	s, min or h	Time
t P/a		Ton phosphate/phosphorus per year
V	L or mL	Volume
X		Space coordinate in Fick's first law
ρ	g/cm^3	Density

1 Introduction

1.1 Set-up of the problem

The element phosphorus (P) is a non-replaceable element for all organisms, yet an exhausting natural resource in the world. P is essential to all known life forms because it plays a key role in many physiological and biochemical processes. P occurs in complex DNA and RNA structures which hold and translate genetic information and so control all living processes in plants, animals and human. It is also an essential component of the energy transport system in cells (EFMA, 2000).

According to the report of European Fertilizer Manufacturers Association, in Western Europe some 79% is used to make fertilizer for use in agriculture for food production, around 11% is used to make feed grade additives for animal feeding stuffs, and approximately 7% is used to make detergents (EFMA, 2000). On basis of the population development and P consumption in agriculture and industry, some research suggested that the natural P reserves will be depleted in the coming 100-120 years (Cordell et al., 2009; USDA, 2012). As shown in Figure 1.1, apparent consumption of phosphate rock in the USA increases incessantly from 885,000 t/a in 1900 to 31,600,000 t/a in 2013 with the peak of 45,000,000 t/a in 1998. The fertilizer industry is the dominating consumer of phosphate rock and agriculture is the main end user of P. There are no alternative sources of P on the market that could replace the current global production of 20 megatons (Mt) of P from phosphate rock (Cordell et al., 2011).

The element P is not found free in nature, it is widely distributed in minerals, mainly in the form of phosphates. The natural phosphate reserves are limited. Inorganic phosphate rock, which is partially apatite, is today the chief commercial source of P. And the P-production is becoming difficult and expensive due to the decline in quality of phosphate rock. Besides, the worldwide phosphate reserves are geologically unevenly distributed. According to the report of US Geological Survey (USGS, 2014), over 85% deposits of phosphate rock are located in China, USA, Morocco, South Africa and Jordan. Western Europe has the only commercial deposit in Finland, which is short on supply and results in an entire dependency on P-import. As shown in Figure 1.1, the price of P was progressively increasing in the latest decade; the P-resource of Western Europe will be further strained by demands under this circumstances. Therefore, the interest in P recovery and reuse in European countries has increased over the last decade due to economic, environmental and political considerations (Sartorius et al., 2010).

On the other hand, P emission from agriculture and sewage is one of the key factors that responsible for eutrophication of receiving water bodies. Eutrophication generally promotes excessive plant growth and decay, favoring simple algae and plankton over other more complicated plants, causes the depletion of oxygen in aqua systems, and finally a severe reduction of water quality. Even the P-containing wastewater and runoff water are treated through wastewater treatment plants, the P-enriched sewage sludge would be a diffusive source of P-release to surface and groundwater (Stark, 2004). In addition, the release of hazardous materials, e.g. cadmium and uranium, during the P-exploitation contaminates the mining areas and inevitably destroys surrounding environment (UBA, 2001; Kratz, 2004). This means that even if there is no urgent need for P recovery in terms of supply-demand relationship, there are still sound reasons to extract P from alternative materials, e.g. sewage sludge, manure, compost. The recycling of P will not only preserve the limited natural resource for economic interests, but also protect the local environment by limiting contamination diffusion.

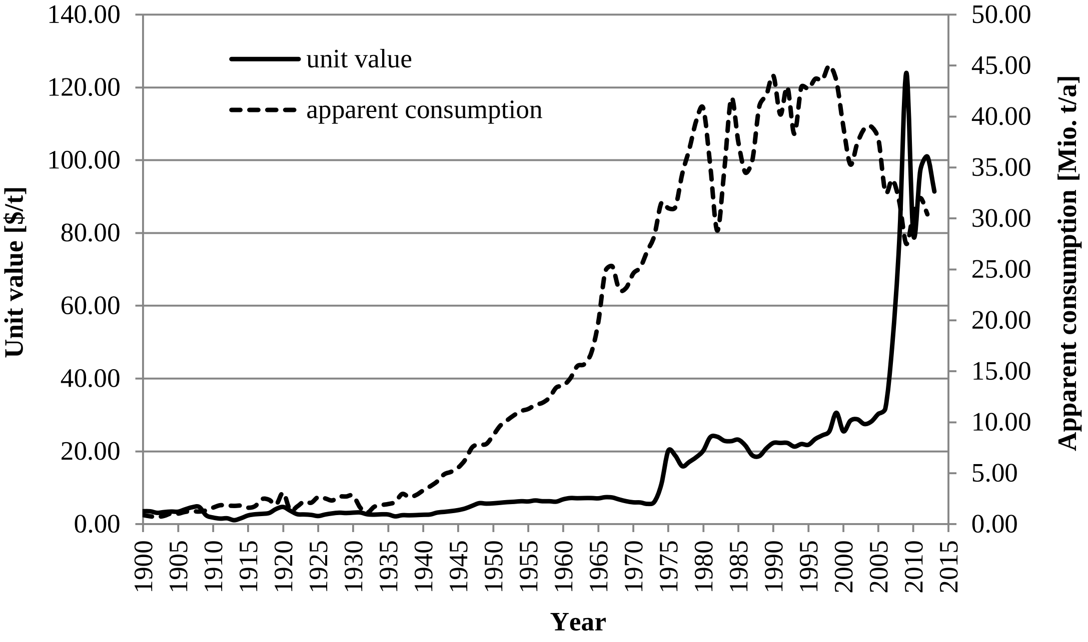


Figure 1.1: Price development and consumption of phosphate rock (P_2O_5) in the USA (USGS, 2014)

In modern municipal systems, nearly all of the P from human emission is collected as sewage at wastewater treatment plants (WWTPs) (Schröder et al., 2010). P-elimination with chemical or biological methods is an essential target of the plants. In Germany, approx. 75,000 t P/a (BMBF/BMU, 2011) are accumulated during the wastewater treatment process at 9,933 municipal WWTPs, where over 90% of the incoming P is incorporated into the sewage sludge after the P-elimination process. Compared with the annual average import volume of 100,000 t P/a in Germany, in theory, the recoverable P from WWTPs can substitute over 50% of the total P import (UBA, 2011). Anaerobic digestion of sludge releases substantial amount of soluble P as inorganic phosphate, which is normally recirculated to the inflow of the treatment process resulting in an extra P-loading to the system. A P-recovery during the sludge treatment process will therefore not only achieve the spare P resource, but also reduce the high P-loading to the wastewater treatment process and improve the water treatment efficiency.

1.2 Purpose of the study

The aim of the present study is to modify and ameliorate a combined system for P removal and recovery from process water of sludge treatment at wastewater treatment plants. The system was first invented by Morck (dissertation, 2011) at Karlsruhe Institute of Technology as a combination of ion exchange and electrodialysis units for nitrogen recovery from side streams of treatment plants. In this work, the former system is retrofitted to suit the removal and recovery of P. Varied parameters and boundary conditions are investigated to enhance the performance of the two-step system, particularly the first step of ion exchange.

The investigation comprises firstly the removal of phosphate anions from process water by means of anion exchange resins. The anion exchange material applied in the present work is expected to have good affinity and selectivity for phosphate anions due to its special properties. Besides good capacity for phosphate sorption, ion exchange resins must have outstanding physical and chemical stability for repetitious cycles of generation. Lab-scale batch experiments are conducted to define the properties of the ion exchange resins in terms of phosphate sorption capacity. A series of parameters, e.g. temperature, pH value, retention time, initial concentration, competition between ions, are considered during the experiments. In addition the potential of sustainable use of the material is also tested via repetitive isotherm plotting with model solutions.

As the liquid phase of the system, the process water, i.e. digested sludge liquor, is complex and rarely described in previous literatures. However, its components will significantly influence the quality of the product and the efficiency of the P-recovery system. Thus it is necessary to analyze it in detail in order to figure out the dominant components of sludge liquor, which is the most influent for the anion exchange process.

Fixed bed columns are set up to investigate the continuous performance of the P-sorption process. Compared with the batch experiments, the column experiments can realize larger-scale equilibrium within long-term operations. Both artificial and actual sludge liquors are used in the column experiment in order to find out the differences between the ideal and the real conditions. Through breakthrough curves, the capacity for phosphate sorption under different boundary conditions can be calculated and compared with the results from batch experiments.

To achieve these goals, the present study is divided into four parts:

- Characterization of P-sorption materials under batch experiments;
- Investigation of P-sorption mechanisms on the hybrid sorbent;
- Analysis and fractionation of digested sludge liquors;
- Evaluation of continuous performance of P-recovery with fixed-bed column.

1.3 Schedule of the present study

According to the objectives, the dissertation is divided into the following main sections. Chapter 1 gives a general introduction of the study. Then the current situation of P utilization and the state of the art for P-recovery are reviewed in Chapter 2. In this section, the author gives a review of the existing technologies for P recovery from wastewater treatment plants and describes the formation of digested sludge liquors. The background knowledge of adsorption is also reviewed in this chapter. In Chapter 3 the main materials and methods applied in the study are introduced. Chapter 4 presents the results from the lab-scale experiments in terms of batch and continuous experiments; and further interpretation for the results. Summary and discussions are presented in Chapter 5,. The dissertation is finalized with a conclusion of the study and perspectives for further studies in chapter 6. References are listed in the last section of the thesis. Supporting information is provided in Appendixes.

2 Basis and State of the Art

2.1 P recovery from WWTPs

2.1.1 P recovery potential at municipal WWTPs

According to the average P load of 2.0 g P/(C·d) in the raw wastewater (Pinnekamp, 2003) and the German wastewater mass flow of 200 L/(C·d), the influent concentration of P is approx. 10 mg P/L. In Germany, the discharge limit of P is 2 mg P/L for the treatment plants with a load of 600-6000kg BOD_5/d or; 1 mg P/L for the treatment plants with a load higher than 6000 kg BOD_5/d (AbwV, 2012). That means the elimination of P must be over 90-95 % of the P-inflow to meet the effluent standard. P exists in the municipal wastewater in forms of orthophosphates (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-},), polyphosphates and organically bound P (Maurer et al., 1999; Böhler et al., 2008). In the influent of wastewater treatment plants, around two third of the P appears as orthophosphates. Another third exists as organic P, which is 50% dissolved, and the other 50% in particulate form (Jardin, 2005). During the wastewater treatment process, the particulate P is hydrolyzed and dissolved in the water, so that the concentration of orthophosphates increases in the biological tank.

For a conventional wastewater treatment plant with primary sedimentation, activated sludge system and secondary sedimentation, the mass balance of P can be simplified into a flow chart that shown in Figure 2.1. In the primary settlement tank, most of the particulate-formed organic P in raw sewage is removed within the primary sludge (PS) (Jardin, 2002), which accounts for about 10% of the influent P load (ATV-DVWK, 2000a). In the aeration tank, the main part of P is taken up by bacteria as polyphosphate and then eliminated with the settlement of excess sludge, i.e. secondary sludge (SS). The P elimination in this tank is based on the physiological needs of the microorganism, which accounts for approx. 2%-3% of the dry mass of the bacteria cell (Jardin, 2005). With a dry matter content of 45 g/(C·d) (C = capita) or volatile solids content of 29 g/(C·d) (Loll and Glasenapp, 2003), the amount of P in the excess sludge accounts for approx. 0.7 g P/(C·d), which is about 35% of the influent P load. Compared with the discharge limit, at least 0.9 g P/(C·d) remaining in the main stream should be eliminated through specific P-elimination processes, i.e. by enhanced biological P removal (EBPR) or by chemical P precipitation.

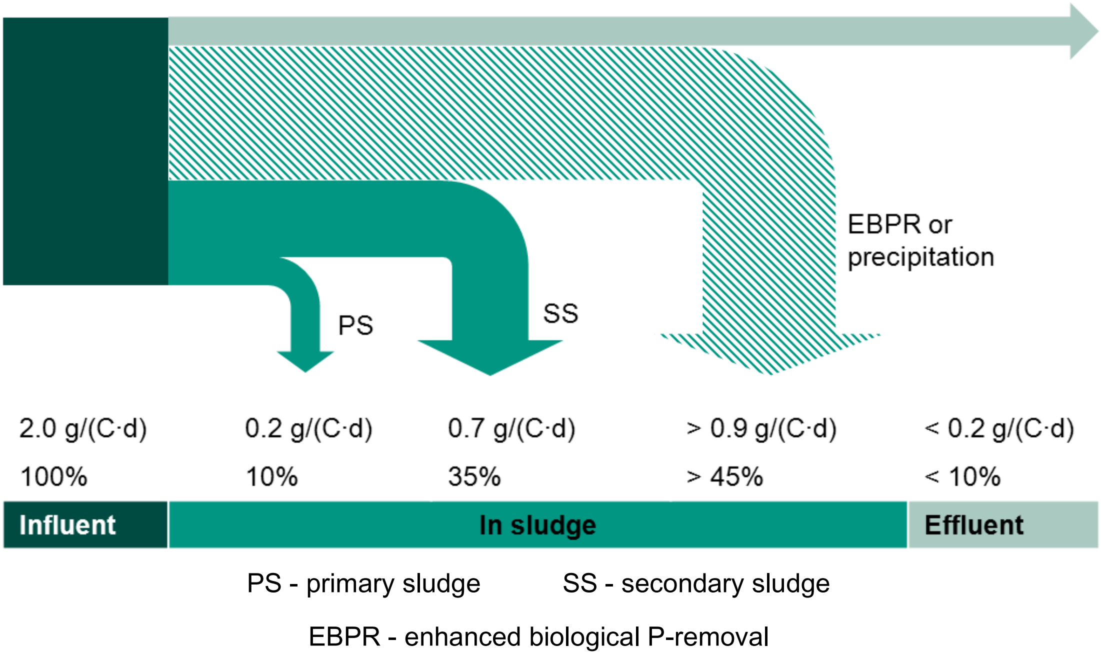


Figure 2.1: Phosphorus balance at a conventional wastewater treatment plant in Germany with biological P removal or precipitation (Cornel, 2009, modified)

No matter which P-elimination process is carried out at WWTPs, the P is always separated from the liquid phase and then accumulated in the solid phase. For instance, via bio-P removal, the P stored in the sludge accounts for 3-5% of dry solid matter (DSM). However, part of the accumulated P will be released back to the liquid phase during the subsequent sludge treatment process. According to the previous literature, 60% to 80% of the P in sludge would be released during anaerobic sludge digestion (e.g. Murakami et al, 1987; Ju et al., 2005). The degree of P-release depends on how the sludge is handled. In the case of primary sludge stabilization, up to 130 mg P/L can be released under anaerobic conditions. During the treatment of excess sludge, up to 20 mg P/L can be released into the gravity thickener overflow even before the anaerobic digestion (Pitman, 1991). Anaerobic digestion of excess sludge results in maximum solubilization of P (Jardin, 1996). The rate and extent of P-release is increased, when the excess sludge is mixed with the raw sludge, which contains relatively high amount of volatile fatty acids. Also, the release of P is firmly related to the retention time of anaerobic treatment and the components of sludge (Pitman, 1999). After the anaerobic digestion, the P-rich sludge liquor is normally separated from the digested sludge solids via dewatering devices.

The digested sludge (DS) after dewatering contains a concentration of P of 33 g P/kg DSM, according to around 10 g P/kg DS via chemical- or biological- bonding. For recovering P from the digested sludge, P is normally re-dissolved into the liquid phase by using extraction chemicals. The potential of P recovery from digested sludge reaches 90% of the incoming P to WWTPs (Montag, 2008).

2.1.2 Existent technologies for P recovery

The routes and technologies for P-recovery vary widely depending on local circumstances. The most direct route for P-recycling is to spread sewage sludge/bio-solids on agricultural land after appropriate sanitary treatment. This route fertilizes the land with P but also with nitrogen, potassium and other minerals. The application of sewage sludge on agricultural soils has been widespread in many countries around the world and has been shown to improve soil properties and increase plant productivity. However, this route must be sternly controlled due to contaminants, such as heavy metals and xenobiotic organic compounds in sewage sludge (Eriksson, 2008). These contaminants can be toxic to plants, soil organisms, as well as humans and animals along the food chain. Because of this potential threat, many countries have set quality criteria to minimize the hazardous constituents in bio-solids (BMU, 1992; EPA, 1993). In Europe the limit is more strict, for instance: Standards for heavy metals in fertilizers are up to 100 times lower than those allowed in the US standard (Renner, 2000), which means further separation or extraction process will be necessary to control the quality.

In order to enhance the security and feasibility of the P-rich bio-solids, the sewage sludge is preferred to be pre-treated via wet chemical or thermal technologies. They thus dissolve P from the bio-solids by using strong acids, bases, heat or pressure.

With an optimized thermal-treatment of sewage sludge, all organic substances and most of the volatile metal compounds are removed. **Thermal sewage inertisation processes** can be distinguished according to their thermal technologies or the chemicals uses. In the **Mephrec process** (Scheidig et al., 2009), the dried sludge or sludge ash is briquetted with coke and slag forming materials. The mixture is treated at 2000 ^oC to transfer P into mineral slags while heavy metals are transferred into the liquid phase (Fe, Cu, Cr, Ni) or into the off gas (Hg, Cd, Pb, Zn). The silico- phosphate containing slag is then separated from metal phases by being tapped at 1450 ^oC. The final product contains 4.6-12 % P_2O_5 with over 90% citric acid solubility.

In some other research (Mattenberger et al., 2008; Adam et al., 2009), a two-step thermal treatment is proposed, including mono-incineration of sewage sludge and subsequent thermochemical treatment of the ashes. In the first step, organic pollutants are completely destroyed by the mono-incineration, while P and hazardous substances remain in the ashes. Therefore, the second thermochemical step, which is also known as **ASH DEC process**, aims to transfer P into mineral phases available for plants, and to evaporate heavy metals at around 1000 ^oC as gaseous chlorine metals (Hermann, 2011).

The **wet chemical processes** for sewage sludge treatment differ in the application of extraction chemicals, operating pressure, temperature and the input feedstock as well.

These processes commonly require intensive use of chemicals to dissolve the phosphate in the liquid phase. **Seaborne technology** started a pilot plant in Owschlag, Germany in the year of 2000 and the first large-scale plant was established in 2005 at the WWTP Gifhorn in Germany (Günther et al., 2008). In this process, the digested sludge is treated with acid, whereby a part of heavy metals, P and organic substances go into solution. The organic solids are separated through centrifugation and filtration and then are combusted in a furnace. The ash can be fed back with the sludge inflow. Apart from this, the heavy metals are precipitated via supply of digested gas containing H_2S. Thereby the digested gas is desulphurised simultaneously. Finally, in the heavy-metal-free liquid phase containing NH_4^+ and PO_4^{3-} as struvite is precipitated by adding magnesium hydroxyl under alkaline condition (Müller et al., 2007).

In the wet chemical processes, different approaches are technically feasible to remove cations from the acidic leachate of sludge ashes. The **PASH process** applies 8% HCl to dissolve 90% P from the incinerate sludge ashes. A liquid-liquid-extraction step using a two-stage mixer-settler with alamine 336 and tri-butyl-phosphate (TBP) is followed to separate Fe (> 99%) and heavy metals (> 95%) from the ash leachate. Afterwards, the P is precipitated by adding lime or limestone to form the calcium phosphate at pH 3.5- 4.0, which can be applied as a slow-release fertilizer in agriculture (Pinnekamp et al., 2010). In the technology developed by **Takahashi**, the incinerated sludge is treated by adding H_2SO_4 to elute P into the leachate. Later by adding alkali to raise the pH value of the leachate, P will be recovered as aluminum phosphate via filtration; by adding alkali till pH10, the heavy metals are subsequently precipitated (Takahashi et al., 2001). The **SESAL-Phos** is a two-step elution process, in which heavy metals are eliminated by sequential precipitation first before the precipitation of phosphate (Petzet et al., 2012). In Sweden (Svensson, 2000), in Switzerland (Franz, 2008) and in UK (Donatello et al., 2010) similar routes to get purified P products from acid leachate of sludge ashes by applying ion exchange resins were proposed. Also cation exchange membranes can be used to remove metal ions after the acid leaching step (Güney et al., 2008). Some economic by-products, e.g. orange waste gel (Biswas et al., 2012) and aluminum mining waste (Cheng et al., 2009) are modified and utilized as adsorbents to remove phosphate from the acid leachate of sludge ashes.

Krepro process (Recktenwald, 2002) involves preliminary leaching of sludge with sulfuric or hydrochloric acid (pH 1.5-2), ferrous phosphate dissolution, biomass filtration and after the addition of MgO (pH 2-2.8), $Fe_3(PO_4)_2 \cdot 2H_2O$ precipitation. After centrifugation, precipitate containing 65% of water and up to 15% P in dry mass is obtained. The process **Cambi/Krepro** (Sievers et al.,2005) involves hydrolysis of dewatered sludge with the use of steam, combustion of post-hydrolysis residues of sludge and biological oxidation of organic compounds present in hydrolysate. The process developed by **Bayer Technology Services** combines a low pressure wet oxidation for sewage sludge decomposition as well as P dissolution and a membrane system to separate P from heavy metals and to obtain a clean diluted phosphoric acid (Blöcher et al., 2012). Zimmermann and Dott used bioleaching bacteria and poly-P accumulating bacteria to dissolve and to collect phosphate from the sludge (Zimmermann et al., 2009).

As a brief summary, both wet-chemical processes and thermal-metallurgical treatments are complex. The wet-chemical process requires an intensive use of chemicals whereas the thermal-metallurgical treatment process requires an abundant supply of energy which leads to high operation costs for both kinds of processes. As a result of Fraunhofer Institute's survey, more than half of the experts (53%), who are working on P-recovery techniques, fully or predominantly agreed that the liquid phase of sewage treatment, especially the internal streams, are the most important alternative source for P-recycling at WWTPs (Sartorius et al., 2012).

The P-rich side-streams at WWTPs present opportunities for P-recovery directly from the liquid phase with concentrations higher than 50 mg/L, which provide sufficient phosphate to reach thermodynamic super-saturation for chemical precipitation or crystallization. Multivalent metal ions, e.g. Magnesium and calcium, are usually dosed to promote the precipitation spontaneously. Hydroxyl apatite ($Ca_{10}(PO_4)_6(OH)_2$), heptahydrate ($CaNH_4PO_4 \cdot H_2O$) and struvite ($NH_4MgPO_4 \cdot 6H_2O$) are the most common products being used in industry and agriculture (de-Bashan et al., 2004; Le Corre et al., 2009).

The development of **crystallization technology** started in the 1970s, in response to more stringent P removal requirements and the desire to produce more marketable end-products. The leader in this area is the **DHV Crystalactor® process** developed in Netherlands, which is based on the crystallization of calcium phosphate on seeding grains, typically sand, in a fluidized bed (van Dijk et al., 1984). After a compacted installation of the system, highly purified phosphate pellets with extreme low water content are produced, which can be used as industrial raw materials (Giesen, 1999). Other technologies for P crystallization were also developed; all of them are based on crystal nucleation and growth chemistry, e.g. **Crystalactor®**, but with some variation (Morse et al., 1998).

In the **Phosnix® Process of Unitika Ltd. Japan**, Magnesium Ammonium Phosphate (MAP) is produced by adding magnesium into the side-streams from sludge treatment process under weak alkaline conditions (Shimizu et al., 1994; Münch et al., 2001). **Ostara's Pearl® Process** is a similar technology producing a commercial fertilizer called Crystal Green in North America (Ostara, 2013).

Since precipitation from the liquid phase is simpler than the other routes, the Berliner Wasserbetriebe developed the **AirPrex process**. The chemical coagulation and precipitation agent $MgCl_2$ is added into the anaerobic sludge before centrifugation. The extraction of CO_2 from the digested anaerobic sludge, by air injection through a fine-bubble surface aeration system at the tank bottom, raises the pH value to approx. pH 8. This induces a deliberate and controlled precipitation of larger quantities of MAP and smaller quantities of calcium phosphate, which are then pumped together with the digested sludge into the centrifugal thickeners. Afterwards, the precipitated MAP is separated from the digested sludge by hydro-cyclones (Heinzmann et al., 2003).

The **Prisa process** developed at RWTH Aachen is proposed to be integrated into the sludge treatment process at WWTPs. The process water from sludge treatment process is mixed in an equalizing tank and solids are removed by a fiber filter. By dosing MgO and adjusting the pH value with NaOH, phosphate and ammonium precipitate as struvite in the crystallization reactor (Montag et al., 2007).

In order to catch phosphate ions from liquid phases through **adsorption technologies**, various adsorbents have been developed including industrial materials and byproducts, e.g. iron oxide tailings (Zeng et al., 2004), fly ash (Oguz, 2005), blast furnace slag (Kostura et al., 2005), steel slag (Xiong et al., 2008), crab shells (Jeon et al., 2009) and red muds (Huang et al., 2008; Yue et al., 2010); natural or synthetic minerals, e.g. goethite (Wei et al., 2014), dolomite (Mangwandi et al., 2014), alunite (Özacar, 2003); metal oxide/hydroxide, e.g. aluminum oxide hydroxide (Tanada et al., 2003; Guan et al., 2005; Kawasaki et al., 2010), iron oxide/hydroxide (Daou et al., 2007; Yoon et al., 2014), zirconium oxide (Chitrakar et al., 2006; Su et al., 2013) hydrous niobium oxide (Rodrigues et al., 2009) and mixed binary oxide Fe-Mn (Zhang et al., 2009), Fe-Cu (Li et al., 2014); and other artificial materials, e.g. layered double hydroxides (LDHs), ion exchange fiber and hybrid anion exchange (HAIX) resin. Literature about P-removal and P-recovery via adsorption technologies are listed in Appendix 1.

Layered double hydroxides (LDHs) are layered materials with hydroxide sheets, where a net positive charge is developed on the layer due to partial substitution of trivalent for divalent cations, balanced by exchangeable charge compensating anions and water molecules, which are present in the interlayer space (Goh et al., 2008). The ability of LDHs removing harmful oxyanions such as arsenate, chromate, phosphate, etc. from contaminated water has been investigated in many studies. Uncalcined Mg-Al LDHs (Kuzawa et al., 2006), calcined Mg-Al LDHs (Lazaridis, 2003; Bakhti and Ouali, 2006; Das et al., 2006), calcined Zn-Al LDHs (Cheng et al., 2009); calcined Mg-Mn LDHs (Tezuka et al., 2004a; Chitrakar et al., 2005), uncalcined Ca-Fe LDHs (Seida and Nakano, 2002) and uncalcined chloride-Mg-Al LDHs (Shin et al., 1996) are utilized as sorbents in the previous literature for P-adsorption. Adsorption capacities of these LDHs for phosphate range from 7.3 to 81.6 P mg/g LDHs. The operational pH values for P-adsorption range between pH 5 and pH 8.6. The P-adsorption on calcined Mg-Al LDHs was reported to reach a maximum at pH 5 by Das et al. (2006), while on calcined Mg-Mn LDHs between pH 7-9 by Chitrakar et al. (2005). The P-adsorption capacity by calcined LDHs was found to be higher than the capacity by uncalcined LDHs. For instance, the maximum P-adsorption by calcined Mg-Al LDHs reaches 81.6 P mg/g (Lazaridis, 2003), while the maximum P-adsorption by uncalcined Mg-Al LDHs is 47.3 P mg/g (Kuzawa et al., 2006).

Desorption of phosphate from the exhausted LDHs could be achieved using a mixed solution of NaCl and NaOH (Chitrakar et al., 2005; Kuzawa et al., 2006), and a good P-sorption has been exhibited even after seven cycles of the adsorption/desorption (Chitrakar et al., 2005). Kuzawa et al. (2006) reported that P-loaded LDHs were effectively regenerated with $MgCl_2$ solution and the adsorption capacity after 10 regenerations was 60% of the initial materials. Kuzawa et al. (2006) also proposed a scheme whereby the desorbed phosphate in the desorption solution could be recovered as calcium phosphate precipitate by addition of $CaCl_2$, and the remaining spent desorption solution could also be reused after supplementing additional NaOH (Figure 2.2).

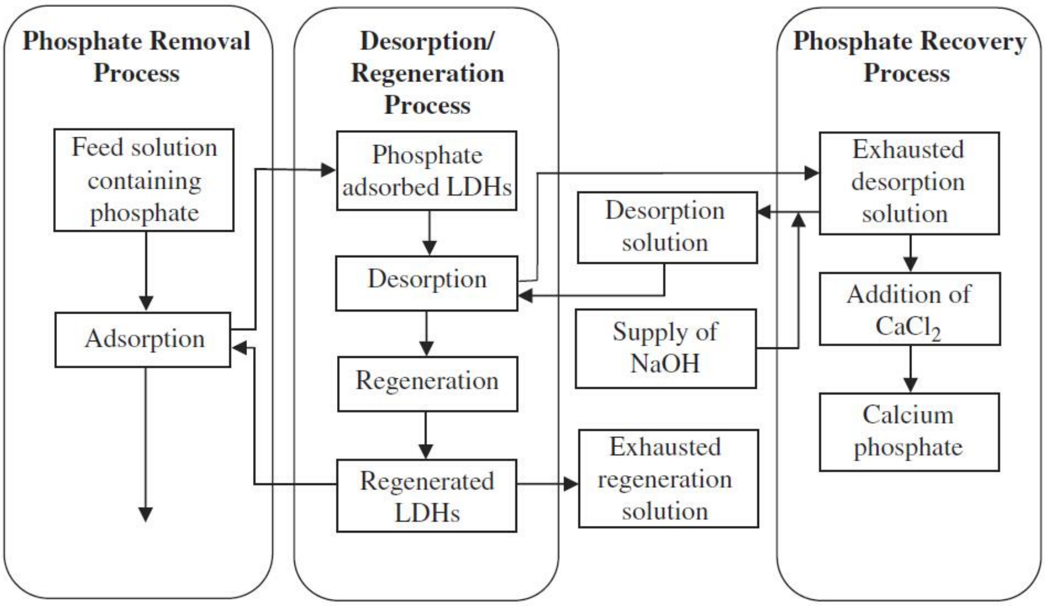


Figure 2.2: Schematic diagram of the P-removal/recovery system using LDHs (proposed by Kuzawa et al., 2006)

For an adsorption medium in a practical system, one of the important considerations is the sorbent stability. To date, few studies have ensured the physical and chemical stability of the low-cost adsorbents during the adsorption and regeneration processes. There is a risk that the precursor metals in the materials might be released into the solutions, particularly under aggressive environments, e.g. at lower pH values (Ferreira et al., 2006), which would result in a contamination to the final products and to the environment. Particle sizes of the adsorbents were commonly not characterized in most of the published research works investigating phosphate adsorption. The particular characteristic is indeed an important parameter that can affect the rate and capacity of adsorption processes (Goh et al., 2008). Particle size is also a key consideration for the application of adsorbents in flow-through columns, where pressure drops and particle carryover should be concerned.

Most of the reviewed low-cost adsorbents are effective in the removal of phosphate from liquid phases in the form of powders due to the large surface areas. However, it is a challenge to recover the adsorbed phosphate from the powdered spent adsorbents. For instance, approx. 60% of adsorbed phosphate is desorbed when Aluminum oxide hydroxide is used for P-recovery (Tanada et al., 2003). The adsorbents in the form of fine powders are difficult to be separated in a solid-liquid system, which will limit its application in large-scale. Also the fine powders may clog columns and lead to pressure drops in continuous operation. On the other hand, most of the low-cost adsorbents for P are multi-component comprising of mixtures of metal oxides and clay. The dissolution of harmful elements such as heavy metals must be concerned carefully during the regeneration of these adsorbents under aggressive environments, i.e. by using acids or alkalis during adsorption and regeneration steps.

Compared to adsorption, **ion exchange** provides better selectivity for target ions and it is generally a reversible process, in which the target ions can be recovered and the exhausted media can be reused through appropriate regeneration steps. Therefore, novel ion exchange materials e.g. metals loaded ligand exchange fibers and resins, are developed to enhance the capacity and selectivity for phosphate uptake.

Zirconium(IV) loaded bifunctional fibers (Zr-FPS) (Awual et al., 2011) are reported exhibiting high performances for P-sorption in continuous column experiments. The pH increased in feeds solution brought the decreasing in breakthrough points and breakthrough capacities as well as total adsorption of phosphate. The maximum uptake of phosphate reached 0.057 mmol/g after 625 bed volumes operation with the initial pH 2.01. P-adsorption by Zr-FPS was not adversely affected in presence of chloride and sulfate but slightly increased, indicating no interference of these competing anions despite enhancement of total adsorption. Phosphate adsorbed on Zr–FPS was quantitatively eluted with 0.1 M aqueous NaOH. Almost 95% adsorbed phosphate was eluted within 15 BV of the eluent. After the column regeneration with 0.5 M H_2SO_4 solution at a flow rate of $4h^{-1}$, the Zr-FPS could retain its adsorption capability after multiple regenerations cycles without loss of original efficiency. However, the preparation of Zr-FPS required sophisticated instrument which is quite expensive, relatively high cost of long-term operation will be a barrier in practical application in industry.

Recent research has focused on polymeric ligand exchange resin and **hybrid anion exchange (HAIX) resin** for selective removal of phosphate from water and wastewater. HAIX resin consists of strong-base anion exchange resin and metal oxide nanoparticles. For example, in Zhao's research (Zhao et al., 1998) a specialty chelating resin Dow 3N was converted into copper(II)-loaded form by passing 500 mg/l Cu(II) solution at pH 4.5 through the resin in a column until saturation. The new resin Dow 3N-Cu exhibited a sorption capacity around 2 mg P/g at pH 7. For the column experiment, the phosphate breakthrough of Dow 3N-Cu took place after 1000 bed volumes although competing anions, i.e. chloride, sulfate, nitrate and bicarbonate were present at concentrations 10-20 times greater than phosphate influent concentration (4 mg/L). The column was regenerated by 6% NaCl solution and about 91% phosphate recovery was obtained in less than 8 bed volumes.

Hydrated ferric oxide (HFO) is a popular adsorption medium because it is an environmentally benign, chemically stable, and cost-effective substance. HFO particles, however, are physically weak that hardly to be used in long-term operation. Polymeric anion exchange resin is durable and can be reused but lack the specificity to target certain anions. Combining HFO particles and anion exchange resin creates a durable and reuseable material that is efficient in phosphate removal because of strong binding between HFO and phosphate (Blaney et al., 2007; Pan et al., 2009; Sengupta and Pandit, 2011).

HAIX resin containing HFO has been tested for phosphate removal from lake and and stream water (Boyer et al., 2011), domestic secondary wastewater effluent (Blaney et al., 2007; Sengupta and Pandit, 2011), industrial wastewater (Pan et al., 2009), reverse osmosis (RO) concentrates from wastewater treatment (Kumar et al., 2007) and human urine (Sendrowski and Boyer, 2013). According to the results of previous studies, HAIX resin is selective for phosphate in the presence of sulfate, chloride, bicarbonate and nitrate. The exhausted HAIX resin can be effectively regenerated with alkalic brine solution. And solid phase products (struvite or calcium phosphate) can be obtained by precipitation from the regeneration solution.

For example, two types of phosphate-selective HAIX resins were tested in Kumar's study: laboratory prepared Dow 3N-Cu-loaded and commercial iron nano-particle impregnated phosphate selective resin PhosX^{np} obtained from Solmetex, USA (Kumar et al., 2007). Both resins were applied in bench-scale columns to catch phosphate ions from RO concentrates. The complete phosphate breakthrough with resin PhosX^{np} occurring at 900 bed volumes exhibited better affinity for phosphate than Dow 3N-Cu. The elution of adsorbed phosphate was accomplished within 10 bed volumes with 6% NaCl solution. The eluted phosphate is then recovered by struvite precipitation. The optimum molar ratio of P:Mg^{2+}:NH_4^+ was 1:1.5:1. About 99% of the eluted phosphate could be recovered as struvite at pH 9.0.

Despite the advantages of the HAIX resin, several gaps in knowledge are preventing the implementation of this strategy. Foremost, there is no previous research on the removal/recovery of phosphate from sludge liquor using HAIX resin. Sludge liquor has a complex composition than secondary wastewater effluent, which is the most commonly studied source for P-recovery by using HAIX resin. The HAIX resin has never been applied in electrodeionization systems for P-recovery. Other gaps in knowledge include rate of P-sorption by HAIX resin and kinetic sorption modelling, equilibrium capacity and isotherms, effect of competing ions and dissolved organic matters.

Accordingly, the specific objectives of this study are to evaluate the performance of phosphate removal using HAIX resin in the artificial solution and the actual sludge liquor in terms of kinetics, isotherms, pH values, temperature, competing ions etc. Regeneration experiments are conducted to assess the reuse potential of the resin. Fixed-bed columns are set to evaluate the continuous performance of the P-sorption and P-elution from actual sludge liquor in different conditions. The composition of digested sludge liquor is analyzed and fractionated to identify the most interfering component that affects the P-sorption on HAIX resin. The P-sorption process by HAIX resin can be followed by an electrodialysis process on purpose to recover phosphate from the spent resin and to regenerate the resin simultaneously. The combination of ion exchange and electrodiaylsis units for P-recovery is named **PHOSIEDI** in this study.

2.1.3 The PHOSIEDI process

PHOSIEDI is a novel system for P-recovery from liquid phase. This system consists of two phases, the first phase is an ion exchange unit catching the ions from liquids, the second phase is an electrodialysis units regenerating ion exchanger and eluting ions from the solid phase simultaneously. When the ion exchanger is implemented in the compartments of the electrodialysis unit, the process is also known as the electrodeionzation (EDI).

The EDI gained increasing attention for removal/recovery of ions from water. A typical EDI device contains alternating permselective anion exchange and cation exchange membranes. The spaces between the membranes are configured to create liquid flow compartments with ion exchange resins. A transverse DC electrical field is applied by an external power source using electrodes at the ends of the membranes and compartments, as shown in Figure 2.3(Arar et al., 2014). Because of the permselective properties of the ion exchange membranes and the direction of the electrical potential gradient, ions in the solution become depleted in the dilute compartment and become concentrated in adjacent (concentrate) compartment (Tanaka, 2007). With unique “electro-regeneration”, the EDI unit can be considered as a mixed-bed ion-exchange column with continuous regeneration, and therefore is capable of deep deionization. Comparing with the electrodialysis and ion exchange, respectively, the EDI has had superior results in water desalination (Wang et al., 2000).

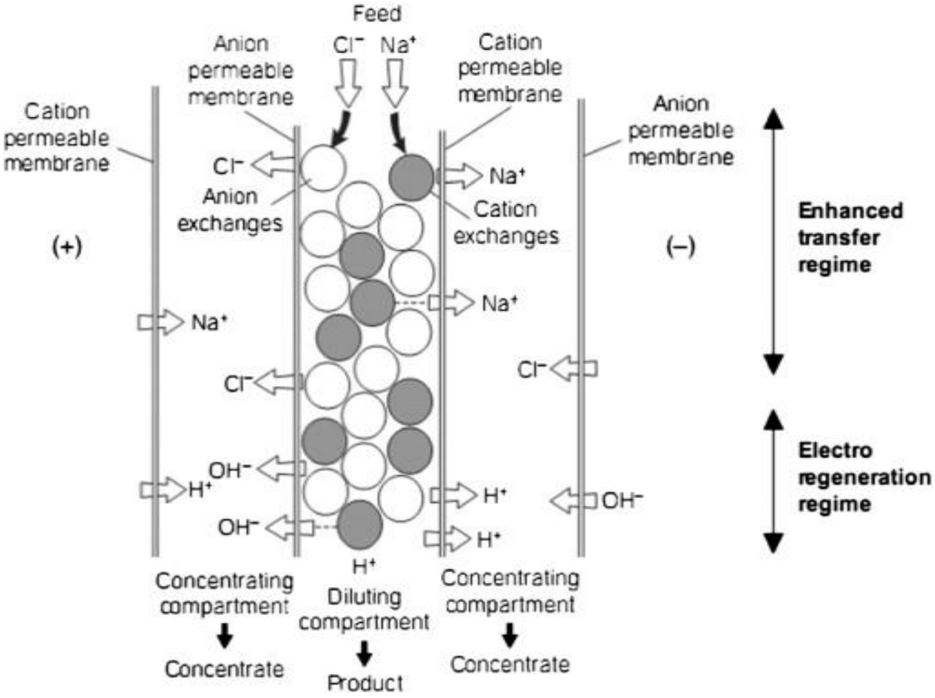
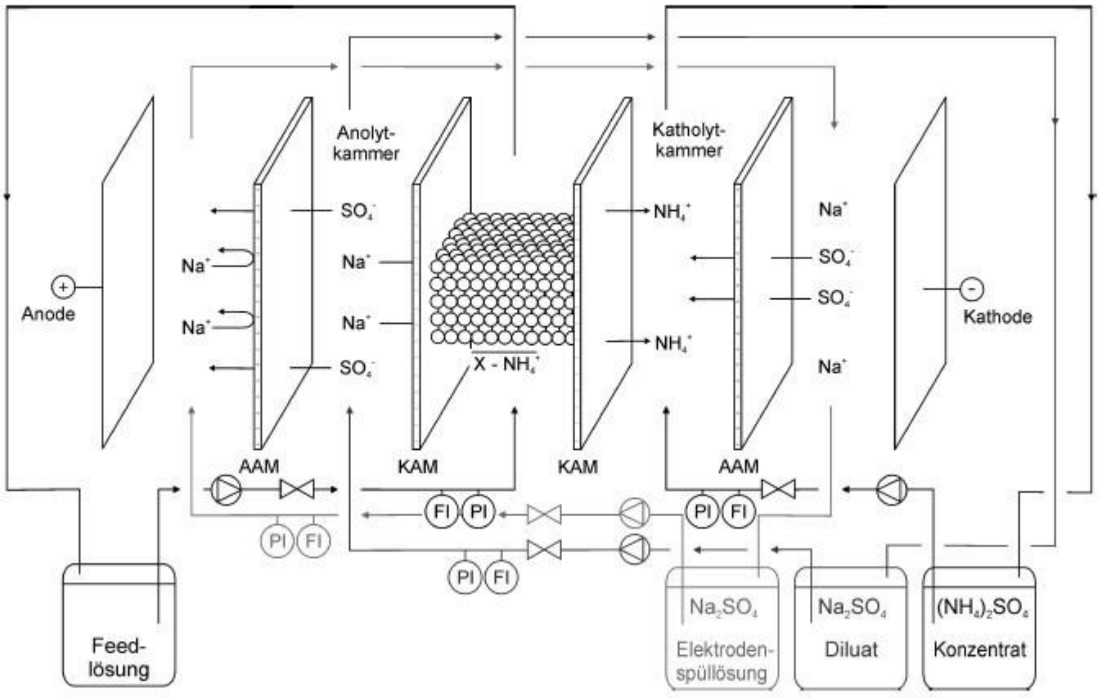


Figure 2.3: Schematic of EDI process and ion transfer in EDI (Arar et al., 2014).

The EDI systems are widely applied in the production of pure water from different kinds of RO permeates (Liang et al., 1992; Auerswald, 1994; Wang et al., 2000; Song et al., 2005). The EDI are also used for the removal of metal ions such as Cu^{2+} (Mahmoud and Hoadley, 2012), Ni^{2+} (Dzyazko, 2006), Co^{2+} (Yeon and Moon, 2003), Cr (VI) (Alvarado et al., 2009), Zn^{2+} (Grebenyuk et al., 1998), Cd^{2+} (Feng et al., 2007), Pb^{2+} (Basta et al., 1998) etc. The presented examples of applicaitions have shown that EDI process is very efficient in production of ultrapure water, removal of hazardous ions and for the recovery of some valuable species.

An EDI system is earlier applied by Morck (Morck, 2011) to recover ammonium from wastewater. In the case of ammonium recovery, the modified zeolite is applied as cation exchanger to catch the ammonium ions from the liquid phase. As shown in the Figure 2.4, the dilute chamber of electrodialysis is formed between two cation-exchange membranes and fed with the ammonium-loaded zeolites. The ion exchanger acts to retain the ions, allowing them to be transported across the ion exchange membranes by means of the direct current field. The anolyte and catholyte compartment are separated by inserting anion exchange membranes between the electrodes and the cation membranes. When the system is started, the ammonium ions pass through the cation membrane into the catholyte compartment and form the product $(NH_4)_2SO_4$ with the sulfate ions from the cathode. In the meanwhile, Na^+ cations from the anolyte compartment are migrating in to the dilute chamber and regenerating the exhausted zeolites continuously.



AAM - anion exchange membrane KAM - cation exchange membrane
FI - flow rate controlling PI - pressure controlling

Figure 2.4: Scheme of the electrodeionisation system for ammonium recovery (Morck, 2011)

Different to the case of ammonium removel, the phosphate recovery process is realized by implementing the hybrid anion exchange resins in the dilute chamber. And the dilute chamber is formed between the anion-exchange membranes (AR204, GE Water & Process Technology, USA). The "base" and "acid" chambers are separated by bipolar membranes (fumasep® FBM, Fumatech, Germany) from the electrode rinsing chambers. The bipolar membrane consists of a cation-exchange layer and an anion-exchange layer that can split solvents (distilled water) into OH^- and H_3O^+ at the interface under reverse potential bias (Pourcelly et al., 2000). Under the force of the electric field, the phosphate ions pass through the anion exchange membrane into the anolyte compartment and form phosphoric acid with H_3O^+ from the bipolar membrane. On the other side, the hydroxyl ions migrate from the catholyte compartment to the center chamber filled with ion exchanger, substitute the phosphate ions on the resins and thus regenerate the exhausted resins in situ. The electrodes are rinsed with a separate circuit of 0.1M Na_2SO_4. The

PHOSIEDI process can be performed continuously without chemical regeneration and thus save a great amount of acids and bases needed for conventional ion exchange process.

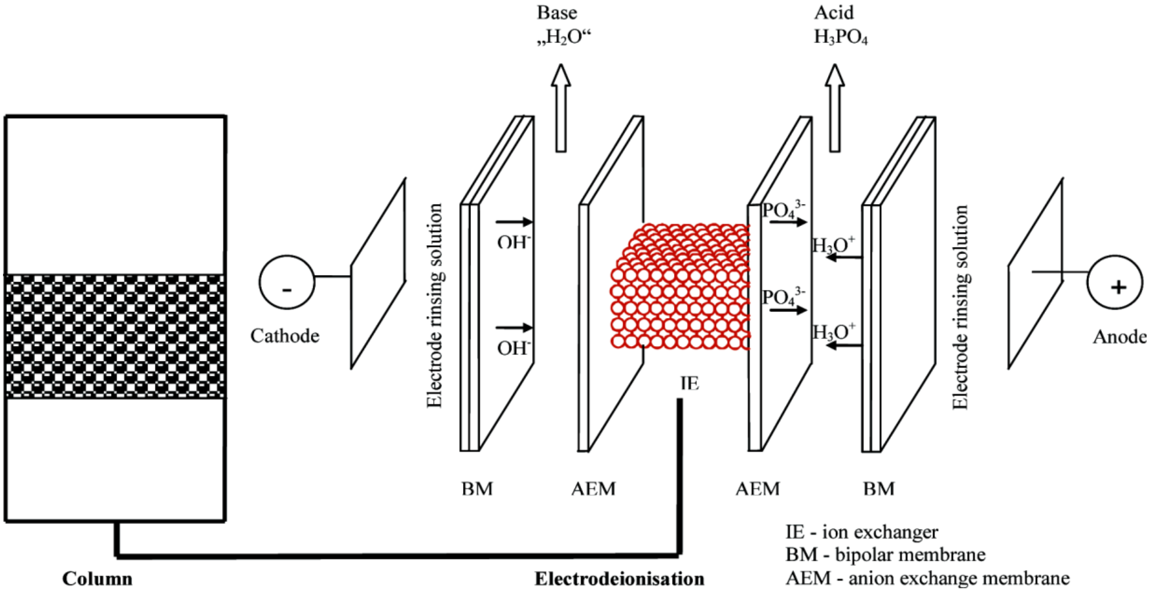


Figure 2.5: Scheme of PHOSIEDI process for phosphate recovery (Hoffmann and Homa, 2011)

Compared with the other P-recovery technologies, the **PHOSIEDI process** can generate highly pure phosphoric acids as its final product, while other processes remove/recover P by the precipitation/crystallization of calcium phosphate or magnesium ammonium phosphate (MAP). By using the bipolar membranes in the electrodialysis unit, no extra regenerating reagent or solvent is needed and no by-product is generated during the P-recovery process. Compared with the **PHOSIEDI process**, other P-recovery routes, e.g. via the precipitation/crystallization of calcium phosphate, in most cases, do not occur spontaneously unless seed crystals, such as sand (Giesen et al., 2005) or calcium silicate hydrate (Berg, 2005), is added to initiate the reaction. And the recovery products, such as struvite and calcium phosphate, their utilization in industry is limited (Cornel et al., 2009). The liquid product of **PHOSIEDI process**, i.e. 85% phosphoric acid (H_3PO_4), can be widely used as raw material in industry.

2.2 Return-stream from the sludge treatment

Sludge treatment process is an indispensable part of wastewater treatment plants (WWTPs), which represents up to 50% of the current operation costs of a WWTP (Appels et al., 2008). The target of sludge treatment is to minimize the water content of the raw sludge, to transform the perishable high molecular organic matter into a relatively stable or inert organic/inorganic residue, and to reduce the associated health problems (European Commission 1986). After the treatment, the solid-residue will be disposed or lead to the material recycling (Dewil et al., 2007), while the liquid-fraction, which is called sludge liquor, will be recirculated to the chemical/ biological wastewater treatment process.

2.2.1 Formation of sludge liquor

According to the DIN-EN-1085 (2007), sludge liquor is defined as “the separated liquids from sludge”, i.e. the supernatant from a thickener, the filtrate from a filter or the concentrate from a centrifuge. In modern wastewater treatment plants, the solids-liquids separation can be carried out before, after or during anaerobic sludge stabilization. Typical producing positions of sludge liquor in terms of different solids-liquids separation routes are listed in the Table2.1.

The sludge liquor emerging in the thickening process before sludge stabilization (SS) is generated from the raw sludge, which has higher biological activity due to the material conversion process of waste activated sludge (Peters et al., 1975; Cizinska et al., 1992). The volume of the sludge liquor from pre-thickeners depends substantially on the mass flow of inlet thin-sludge and its degree of concentrating. For the case that the solids content in the inlet-thin-sludge is much less than that in outlet-thick-sludge, the volume of sludge liquor can be calculated by the following equation:

$$Q_{SL} = Q_{inS} \cdot \left(1 - \frac{DS_{inS}}{DS_{outS}}\right) \; [m^3/h \; or \; L/(C \cdot d)] \qquad (2.1)$$

where Q_{SL} $[m^3/h \; or \; L/(C \cdot d)]$ is the volume of sludge liquor, Q_{inS} $[m^3/h \; or \; L/(C \cdot d)]$ the flow volume of raw sludge before thickening, DS_{inS} $[g/L \; or \; \%]$ the dry solids in raw sludge, DS_{outS} $[g/L \; or \; \%]$ the dry solids in thickened sludge.

Table 2.1: Typical producing positions of sludge liquor before, after and during sludge stabilization (SS) process (DWA- Arbeitsgruppe AK-1.3, 2000)

Sites	**process**	**Unit of solid- liquid separation**	**Description of sludge liquor**
Before SS	thickening	gravity drainage system	supernatant liquid
		centrifugate	centrifugal effluent
		screening drum	filtrate
After SS	dewatering	gravity drainage system	supernatant liquid
		centrifugate	centrifugal effluent
		belt filter press	filtrate
		chamber filter press	filtrate
During SS		pre- acidification	hydrolyzate
		digestion	digestive supernatant

The biological stabilization, i.e. anaerobic digestion, decomposes the raw sludge and produces considerable mass of liquids for the subsequent dewatering process (Kim et al., 2003). The degree of material-release can be simplified through the expected degradation of organic matter, and estimated by the results of different substance conversion processes (Gujer et al., 1983). The amount of sludge liquor from the dewatering facility can be assessed with the help of equation 2.1. The average volume of sludge liquor from municipal WWTPs ranges from 1 to 10 $L/(C \cdot d)$ (Pinnekamp, 2002).

2.2.2 Properties of sludge liquor

The properties of sludge liquor depend on the incoming sludge sources and the various operational strategies of sludge treatment lines. The property of liquids from sludge thickeners differs by whether primary and excess sludge are concentrated separately or together. With the sole thickening of primary or excess sludge, the nutrients release needs a retention time in the thickener much longer than 1 day (Jardin, 2008). Pre-acidification of primary sludge is frequently applied before the thickening process to enhance the efficiency of denitrification and biological P elimination. This pre-acidification step releases approximate 1-2% of nitrogen in the back flow to the activated sludge unit (DWA- Arbeitsgruppe AK-1.3, 2000). The separated excess sludge is usually thickened with the facilities of centrifuge, drum sieving or flotation before stabilization. In this short thickening period, the degree of mass conversion of excess sludge is limited, and as a result the volume of liquids is relatively low.

If primary and excess sludge are thickened together, excess sludge from secondary settlement tank is usually initiated into the primary settlement tank firstly, and then pumped into the pre-thickener. The efficiency and yields of the thickening process depend on the retention time of sludge in the primary settlement tank, temperature and degree of mass conversion, especially on the biological P-transfer process, which may release the bio-bonded P back to the liquid phase (Jardin, 1995).

During the anaerobic stabilization of sludge, about 60% of organic materials are metabolized by the microorganisms. The breakdown of proteins during the sludge digestion dissolves ammonium ions (NH_4^+), with bicarbonate (HCO_3^-) as counter-ions. Therefore, the molar ratio between bicarbonate and ammonium is generally observed to be around 1. Co-digestion with external substrates often increases the nitrogen load, but substrates rich in carbohydrates or fats can reduce the ammonium content by increased biomass production in the digesters (Gustavsson et al., 2010). The COD concentration of sludge liquor relates to the solid content, the boundary condition of digestion and the degree of stabilization (Lützner, 1998). The liquid product from the stabilization reactor, which returns to the inlet of the biological wastewater treatment process, increases the COD load of the water-line and affects the effluent quality of WWTPs. This return-flow can amount to 0.5-2.0 % of the average incoming flow (Imhoff et al., 2007) and can contribute BOD concentrations of 200-5000 mg/L to the process stream (EPA, 1997). As an example, the balance of relevant COD flow at the Buchenhofen treatment plant of the Wupperverband shows that, the anaerobic stabilization brings about 4-5 mg/L COD into the effluent of the plant, which is equivalent to 10% of the COD outlet concentration (DWA- Arbeitsgruppe AK-1.3, 2000). The return load of nitrogen from sludge treatment is about 1.5g N/ (C· d), which contributes 15- 25 % to the total nitrogen load of the WWTP inlet (Jardin et al., 2006).

For the return load of P from sludge treatment, it should be noticed that, the P is not only incorporated as a result of biomass growth in digestion reactors, but also results of the preceding chemical-physical P-elimination or additional biological P- elimination. Normally, the release of P after chemical-physical P-elimination is negligible, because the form of $FePO_4$ or $AlPO_4$ at alkalescent pH is relatively stable compared to the bio-bonded P.

2.2.3 Conditioning of sludge liquor

The return flow of sludge liquor brings suspended solids, nutrients and organic compounds to the inlet of wastewater treatment units. The substantial release of P and nitrogen during the anaerobic digestion leads to struvite precipitation (Maqueda et al., 1994) and that may cause blockage of the pipes. Besides, high concentrations of heavy metals can accumulate in sludge liquors which may be toxic to biological treatment units. The prudent management of return liquors is necessary to ensure that they do not harm the biological treatment process and will not damage the treatment facilities.

As a chemical method, lime has been used extensively in the treatment process primarily because of its low cost (Hwang et al., 1998). The results of previous studies on the application of lime for the removal of phosphate, nitrogen, color, suspended solids and BOD_5 have been reported in the literature (EPA, 1980). For the sludge liquor treatment, liquid lime or hydrated lime suspensions are commonly applied, which can successfully reduce the content of BOD/COD in liquor and, improve the biodegradability of the liquor for further biological treatment (Britishlime, 2013). Ammonia stripping is another physical-chemical method adopted to eliminate ammonium from sludge liquors. The ammonium in aquatic system is first converted to slightly volatile gaseous ammonia by adjusting the pH value to 10 and the temperature to 70 ^{o}C. The gas is then physically stripped out from the liquid phase (Pfennig, 1996).

There are three biological approaches for elimination nitrogen from sludge liquor in side-streams (Figure 2.6): First, the classical method of nitrification/denitrification, second nitritation/denitritation and third deammonification (Jardin et al., 2006).

Nitrification/dinitrification techniques require the use of supplementary carbon sources on account of the mostly unfavorable C/N ratio prevailing in sludge liquors. Besides, the operational costs for the oxygen supply for the nitrification step and the carbon demand of the denitrification step is higher than the other options. To save these costs, it is possible to restrict ammonium oxidation which occurs during the nitritation step. The formed nitrite can then be reduced to molecular nitrogen in the denitritation step. Via this route about 25% of the oxygen demand and over 40% of the carbon demand can be saved (Abeling et al., 1992). By the two-step deammonification process, the ammonium is directly and almost completely converted to molecular nitrogen. In its first step, a fixed portion of ammonium in the aqueous phase will be fully oxidized to nitrite; in the second step, the ammonium elimination takes place under anoxic conditions with simultaneous reduction of nitrite and gaseous nitrogen as the end product (van de Graaf et al., 1995).

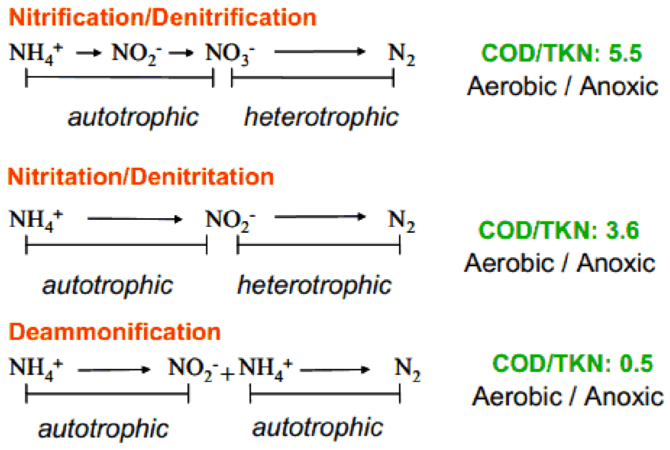


Figure 2.6: Classification of process steps of biological N-removal (Jardin et al., 2006).

According to the overview of literature, most of the methods focused on the elimination of ammonium in sludge liquors, while the high concentration of phosphate was ignored, although phosphate is the key factor of eutrophication as well. An additional step for P-removal and recovery before recirculation is recommended to get the best benefit for both receiving water body and resource preservation.

2.3 Description of sorption process

Well-designed sorption processes have high performance in resulting good quality effluent after the treatment. In order to improve the efficiency of the process with low-cost, thermodynamic and kinetic aspects are commonly involved to learn more details about the reaction pathways and the mechanisms of the sorption (Ho et al., 1999).

2.3.1 Sorption equilibrium

Sorption equilibrium provides fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation. Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature and pH (Ho et al., 2001). An accurate mathematical description of the equilibrium isotherm is based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage, and possibility of interaction between the sorbate species (Rodrigues et al., 2009).

In 1918 **Langmuir** developed a theoretical equilibrium isotherm relating the amount of gas adsorbed on a surface to the pressure of the gas (Langmuir, 1918). The Langmuir sorption model is based on the assumption that sorption takes place at mono-layer homogeneous sites, and the maximum sorption corresponds to a saturated mono-layer of solute molecules on the sorbent surface, with no lateral interaction between the adsorbed molecules. It has achieved good agreement with a wide variety of experimental data and can be represented by equation (2.2):

$$q_e = q_{max}\frac{K_L C_e}{1+K_L C_e} \tag{2.2}$$

The Langmuir constants, K_L can be calculated through linearization of equation (2.3):

$$\frac{1}{q_e} = \frac{1}{q_{max}K_L C_e} + \frac{1}{q_{max}} \tag{2.3}$$

By plotting $1/q_e$ against $1/C_e$ the value of q_{max} (mg/g) can be obtained from the intercept, which is ($1/q_{max}$), and the value of K_L (L/mg) from the slope, which is ($1/q_{max}K_L$). The Langmuir constants q_{max} and K_L are related to the adsorption capacity and energy of adsorption, respectively. The essential characteristics of the Langmuir isotherm may be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (Weber et al., 1974), R_L, which is defined as equation (2.4),

$$R_L = \frac{1}{1+K_L C_0} \tag{2.4}$$

R_L value lying between 0 and 1 indicates favorable adsorption (McKay et al., 1982).

The **Freundlich** adsorption isotherm is an empirical expression, which can be applied for non-ideal sorption on heterogeneous surfaces and multi-layer sorption (Freundlich, 1906). This widely used isotherm is an exponential equation (2.5):

$$q_e = K_F C_e^{b_F} \tag{2.5}$$

In this equation K_F and b_F are the Freundlich constants, being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. This expression is characterized by the heterogeneity factor b_F, and the Freundlich isotherm is employed to describe heterogeneous systems (Al Duri et al., 1988). Theoretically, by this expression, an infinite adsorption can occur. Compared with the Langmuir equation, the Freundlich equation does not reduce to the linear isotherm at low surface coverage. To determine the constants K_F and b_F, the linear form of the equation can be used to plot ln(q_e) against ln(C_e):

$$\ln q_e = \ln K_F + b_F \ln C_e \tag{2.6}$$

On basis of the linear form of the equation, slope ranges between 0 and 1 is a measure of sorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero, whereas a value below unity implies chemisorption processes where the slope above one is a sign of cooperative adsorption (Haghseresht and Lu, 1998). Freundlich isotherm is criticized for its limitation of lacking a fundamental thermodynamic basis, not approaching the Henry’s law at vanishing concentrations (Ho et al., 2002).

Redlich-Peterson isotherm (Redlich and Peterson, 1959) is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporate three parameters into an empirical equation (Prasad and Srivastava, 2009). The model has a linear dependence on concentration in the numerator and an exponential function in the denominator (Ng et al., 2002) to represent adsorption equilibria over a wide concentration range, that can be applied either in homogeneous or heterogeneous systems due to its versatility (Gimbert et al., 2008).

$$q_e = \frac{K_R C_e}{1+a_R C_e^{\beta}} \tag{2.7}$$

Where K_R is R-P constant (dm^3/g), $a_R$is R-P constant (dm^3/mg) and β is the exponent which lies between 1 and 0. When the exponent β equals 1,

$$q_e = \frac{K_R C_e}{1+a_R C_e} \tag{2.8}$$

i.e. the Langmuir equation. And when β equals 0,

$$q_e = \frac{K_R C_e}{1+a_R} \tag{2.9}$$

i.e. the Henry’s Law equation.

In the limit, it approaches Freundlich isotherm model at high concentration (as the exponent tends to zero) and is in accordance with the low concentration limit of the ideal Langmuir condition (as the values are all close to one) (Jossens et al., 1978). For the calculation of isotherm constants, it is impossible to solve the three-variable equation by simple linearization, thus a trial and error procedure, which is applicable to the Solver add-in function of the Microsoft spreadsheet Excel, by minimizing the respective error function across the concentration ranges (Wong et al., 2004). Such an approach was developed to determine the isotherm parameters by optimization routine and consequently to maximize the correlation coefficient between the experimental data points and theoretical model predictions.

2.3.2 Sorption kinetics

The study of sorption kinetics will not only determinate the reaction rate of sorbate uptake at the solid-solution interface, but also help to understand the reaction pathways and mechanism of sorption reactions. Besides, sorption kinetics is the base to determine the performance of fixed-bed or any other flow-through systems, one can know the scale of a sorption apparatus based on the kinetic information (Qiu et al., 2009).

The transfer of solute molecules from the bulk liquid phase onto a sorbent particle surface may be described as occurring in three consecutive steps (Koumanova et al., 2003):

1. external mass transfer of sorbate molecules from the bulk solution to the sorbent external surface through the boundary layer diffusion;
2. intra-particle diffusion of the sorbate from the external surface into the pores of the sorbent;
3. sorption and desorption at interior sites, the sorbate molecules transport from the larger pores to micro pores of sorbents.

The last step is considered to be an equilibrium phase and is usually assumed to be rapid in comparison to the first two steps; therefore, it is negligible during the speculation of rate-controlling step. The overall rate of sorption will be controlled by the slowest step, which would be either boundary layer diffusion or intraparticle diffusion (Ofomaja, 2008).

The mathematical theory of diffusion is based on the hypothesis that the rate of transfer of diffusing substance, through unit area of a section, is proportional to the concentration gradient measured normally to the section, i.e., Fick’s first law (Fick, 1855):

$$F = -D\frac{dC}{dX} \tag{2.10}$$

Where F is the rate of transfer per unit area of the section, C is the concentration of diffusing substance, X is the space coordinate, and D is the diffusion coefficient.

Fick's second law of diffusion, modified for application to spherical particles, describes the diffusive mass transfer process presumed to take place. The fundamental differential equation of diffusion in a medium where a concentration gradient along the X axis is given by Fick's second law:

$$\frac{dC}{dt} = D\frac{d^2C}{dX^2} \tag{2.11}$$

Many molecular adsorption processes involve diffusive mass transport and the rigorous interpretation of overall behavior in terms of "true" diffusivity and intrinsic equilibrium sorption properties is difficult. A meaningful diffusion coefficient often cannot be derived: the standard procedure of fitting the overall rate behavior to the classical solution of Fick's equation results in the derivation of apparent diffusion coefficients that often vary with concentration (Alexander et al., 1978). In order to investigate the controlling mechanism of the sorption process such as chemical reaction, mass transfer and diffusion control, several kinetic models have been proposed to validate experimental data.

In case of sorption preceded by diffusion through a boundary, the kinetics most likely follows **the pseudo-first-order equation** (Lagergren, 1898, Ho, 2004), which is generally expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.12}$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g), k_1 is the rate constant of pseudo first-order sorption (L/min).

After integration and applying boundary conditions for $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the integrated form of equation (2.13) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}\, t \tag{2.13}$$

The values of $\log(q_e - q_t)$ were linearly correlated with t. The plot of $\log(q_e - q_t)$ against t will give a linear relationship from which k_1 and q_e can be determined from the slope and the intercept, respectively.

If the rate of sorption follows a second-order mechanism, **the pseudo-second-order** chemisorption kinetic rate equation is expressed as (Ho et al., 1999):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2.14}$$

Where k_2 is the rate constant of pseudo second-order sorption (g/mg·min).

Integrating this equation for the same boundary conditions becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{2.15}$$

And this equation can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2.16}$$

and

$$h = k_2 q_e^2 \tag{2.17}$$

where h is the initial sorption rate (mg/g·min).

The Elovich model, originally presented in 1939, is satisfied in chemical adsorption processes and is suitable for systems with heterogeneous adsorbing surfaces (Aharoni et al., 1970). It is given as follows (Chien et al., 1980; Sparks, 1986):

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \tag{2.18}$$

Where α is the initial sorption rate (mg/g·min), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

The integration of the rate equation with the same boundary conditions as the pseudo first- and second-order equations was expressed by the linearized Elovich equation:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{2.19}$$

The nature of the diffusion process responsible for the sorption performance can be determined by specifying the rate controlling step between film diffusion and intra-particle diffusion. Weber's (Weber et al., 1963) models are most widely used for studying the mechanism of sorption processes.

Weber intra-particle model can be expressed as equations. (2.20-2.24):

$$q_t = K_i t^{0.5} + C \tag{2.20}$$

$$q_{ref} = K_i t_{ref}^{0.5} + C \tag{2.21}$$

$$\left(\frac{q_{ref}}{q_t}\right) = 1 - R_i\left[1 - \left(\frac{t}{t_{ref}}\right)^{0.5}\right] \tag{2.22}$$

$$R_i = \left(\frac{K_i t_{ref}^{0.5}}{q_{ref}}\right) \tag{2.23}$$

$$R_i = \frac{q_{ref} - C}{q_{ref}} = 1 - \left(\frac{C}{q_{ref}}\right) \tag{2.24}$$

where K_i is the intra-particle diffusion constant (mg/(g·min$^{0.5}$)), C is the intercept, R_i is defined as the initial sorption factor of intra-particle diffusion model. q_t is then plotted against $t^{0.5}$ to investigate the rate-controlling step for the phosphate sorption process. The intercept *C* often referred to the thickness of the boundary layer (Mall et al., 2005), and a large *C* value is indicative of external mass transfer as being significant in the sorption process, thereby acting as the rate-controlling step. If the data fit a linear form, intra-particle diffusion is involved in the sorption process and if the fit passes through the origin ($C = 0$), intra-particle diffusion is considered to be the rate-limiting step (Cheng et al., 2010; Lin et al., 2011).

2.3.3 Breakthrough of fixed bed column

For a comprehensive description of the sorption process not only the static sorption capacity but also the dynamic sorption performance is particularly important. Despite of the sorption in batch systems to understand the interface interaction between sorbent and sorbate and to select the best operational condition, the investigation in columns are the preferential mode for the application in the technical scale up, once the process can be performed continuously (Viera et al., 2008). The dynamic sorption performance can be determined by infiltrating the solution with target ions through a fixed bed column, which is filled with the sorbents. The solution travels through the pore spaces from inlet to outlet of the column. The effluent is collected at certain time intervals and analyzed to get the concentration of target ions for plotting the breakthrough curve. The dynamic sorption performance depends on the composition of the solution, the design and operating parameters of the column system as well as the properties of the sorbents.

The sorption performance of a fixed bed column depends both on space and time. Ideally, the sorption was always an equilibrium process so that the full capacity of the sorbent would be used and a linear type breakthrough would occur. In reality, the sorption can hardly always keep equilibrium over the operation time thus the front of the sorption is more or less vague (Krech, 2014). As the solution enters the bed, the sorbate contact with the sorbent and fill up some of the available sorption sites. The section of the column becomes saturated gradually, and the sorption front appears as a “wave”. As the wave front moves through the bed, most of the mass transfer is occurring in a limited active region, which is defined as the mass transfer zone (MTZ). The saturation of the bed within the MTZ varies from zero to the full saturation. This zone of partial saturation moves through the column in the direction of the flow at a certain velocity which is predominantly determined by the sorbate loading, sorbent capacity, and the column feed rate (Naja and Volesky, 2006). The column is operational until the MTZ reaches the end of the column.

At the end of the bed, breakthrough point occurs when the concentration of the effluent reaches a pre-set limit (breakthrough concentration). The bed then becomes ineffective. Usually, the breakthrough concentration is set to be the maximum amount of the solute that can be acceptably leaked, typically between 1 and 5 percent of the inflow concentration.

The breakthrough curve is a concentration profile of the effluent from the fixed-bed column, which presented the front shape of mass transfer zone of the column. Favorable isotherms such as Langmuir and Freundlich lead to the formation of sharp zones in sorption columns. Conversely, unfavorable equilibrium isotherms give rise to broad and expanding zones in the column (Volesky, 2003).

The movement of the MTZ through a fixed bed column and the breakthrough curve of the column are presented in Figure 2.7. Where C_0 is the initial concentration of the target ion in the influent; C_e is the concentration of the target ion in the effluent; C_B is the breakthrough concentration of the target ion and; C_L is the operating limit concentration.

During the continuous operation of the column, the ion concentration of the effluent C_i at the time t_i varies with the time (t) from 0 to C_0 theoretically. Furthermore, the ion concentration of the effluent can be described with the function of t as $C_i = f\,(t_i)$. The mass of the target ion adsorbed by the sorbent during the column operation can be calculated via the equation 2.25, where q_t is the ion loading of the sorbents at the time t; Q is the flow rate of the column feeding; ρ is the density of the sorbents; V is the total volume of the sorbents.

$$\begin{aligned} q_t &= \frac{Q}{\rho \cdot V}\int_0^{\infty} (\mathrm{C}_0 - \mathrm{C}_i)dt \\ &= \frac{Q}{\rho \cdot V}\int_0^{\infty} (\mathrm{C}_0 - f(\mathrm{t_i}))dt \qquad (2.25) \end{aligned}$$

The loading of the sorbents reaches the maximal capacity when the effluent concentration is reaching the initial concentration of influent, which also means the sorption process completed at the moment.

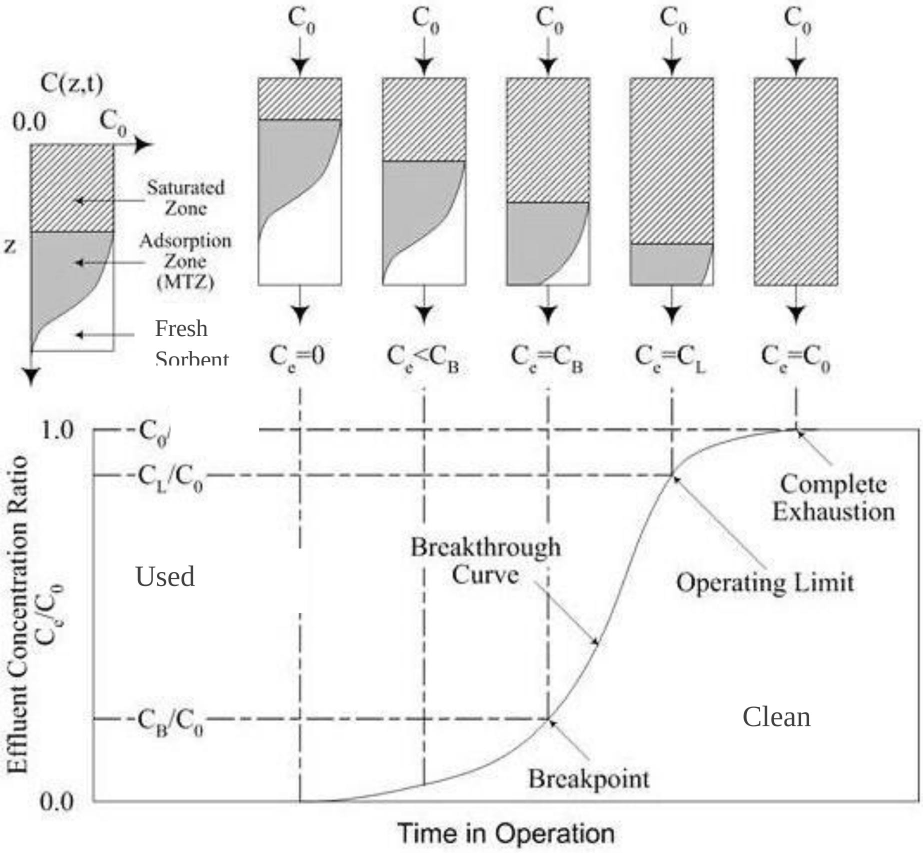


Figure 2.7: Mass transfer zone and breakthrough curve of a fixed bed column with sobent (modified from Gutierrez-Miravete, 2013)

Fixed-bed columns for sorption processes are ideal candidates for reduction of dissolved phosphate to near-zero level provided the sorbent is phosphate selective, cost effective and amenable to efficient regeneration and reuse. Extensive research studies were undertaken to explore the effectiveness of fixed-bed processes for phosphate removal due to their operational simplicity and adaptability to changing wastewater flow rates and compositions. Granular activated alumina, zirconium oxide and iron oxide particles are a few well-studied inorganic adsorbents in this regard (Das et al., 2007; Blaney et al., 2007; Pan et al., 2009). However, the inorganic metal oxide particles lack the mechanical strength and attrition resistance properties for prolonged operation in fixed-bed units. Furthermore, they tend to form fines leading to increased head loss in the column. Hence, they are mostly recommended for single-use applications. On the contrary, polymeric materials offer better durability, desired mechanical strength and specific selectivity for phosphate in the presence of competing sulfate ions, inevitably present in wastewater or process water streams.

3 Materials and Methods

3.1 Characterization of sludge liquor

3.1.1 Chemical analysis of sludge liquor

The sludge liquor used in this study was collected from the filtrate of dewatering centrifuges at the wastewater treatment plant Rastatt. The treatment plant Rastatt serves about 70000 residents living in the region of Rastatt with an annually average wastewater influent of 20000 m^3/d. The wastewater is treated through the Anaerobic-Anoxic-Oxic process to remove the contaminants. The P in wastewater is eliminated via both biological and chemical processes in the aerobic tank; hereafter the P is accumulated in the sludge and settled in the secondary sedimentation tank. The excess sludge is pumped into the pre-thickener to reduce the water content from 98-99% to circa 92%. Then the pre-thickened sludge is digested in the anaerobic tank at a retention time of 20 days. Afterwards, the digested sludge is dewatered again with the centrifuge. The water content of sludge is reduced to 75%. The thickened sludge is trucked regularly to an incineration plant. The digested sludge liquor, which is rich in P, collected from the dewatering facility is used in the study as the P-resource.

The sludge liquor taken from the treatment plant was filtrated through the 0.45 µm-pore-diameter membrane before analysis and storage. The pH-value of samples was measured following the standard DIN-38404-5 with the pH meter WTW 330i connected with an electrode WTW SenTix 41. The conductivity was measured following DIN-EN-27888 with the conductivity meter WTW LF320 connecting the electrode WTW Tetracon 325.

Orthophosphate was determined via the spectrophotometric method DIN-EN-ISO-15681-1 with the QuikChem 8500 flow injection analysis system by LACHAT. The other anions, e.g. chloride, sulfate and nitrate were determined following the standard DIN-EN-ISO-10304-1 with a DIONEX DX-120 ion chromatography.

The ammonium nitrogen in samples was determined according to DIN-38406-5 with HACH quick-test method. The cations, e.g. calcium, magnesium, potassium and sodium, were determined following the standard methods DIN-EN-ISO-7980, DIN-38406-13 and DIN-38406-14 with flame atomic absorption spectrometry (FAAS) PERKIN ELMER 1100b. The metals zinc and iron were determined following standard methods DIN-38406-8 and DIN-38406-32 with the FAAS PERKIN ELMER 1100b as well. The test solution was sprayed into the air-acetylene/air-ethyne flame of the atomic absorption spectrophotometer and, the absorbance at the appropriate wavelength was measured for distinguished metals.

The chemical oxygen demand (COD) of the homogenized and filtrated samples was measured following DIN-38409-41or with a quick-test method by HACH LANGE. The filterable dry matter and the organic dry matter were determined via DIN-38409-2. The suspended solids in sludge liquor were separated by filtration from a measured volume of the sample and dried in an oven at 105±2 °C. Subsequently, the dried sample was burned in a muffle furnace at 550-600 °C for calculating the content of organic dry matter.

The digested sludge liquor was sampled at the wastewater treatment plant Rastatt monthly from June, 2009 to Novermber, 2010 and aperiodically afterwards. The outcome of chemical analysis for the sludge liquor from Rastatt was listed in Table 3.1. The synthetic solutions used in batch and column experiments were prepared on basis of this table of composition.

Table 3.1: Characterization of sludge liquor from Rastatt

Parameter	Unit	Range	Parameter	Unit	Range
pH		7.9– 8.5[b]	DM	mg/L	164 – 538[a]
Conductivity	mS/cm	2.3 – 2.7[b]	oDM	%	69.6– 91.7[a]
PO_4^{3-}	mg/L	125– 563[b]	NH_4^+-N	mg/L	1030 – 1780[b]
Cl^-	mg/L	224– 338[b]	Ca^{2+}	mg/L	40.7 – 59.6[b]
SO_4^{2-}	mg/L	16.2– 19.6[b]	Mg^{2+}	mg/L	1.55 – 3.40[b]
NO_3^-	mg/L	0 – 1.9[b]	$Fe^{2+/3+}$	mg/L	5.5 – 13.4[b]
COD	mg/L	905– 1312[a]	Zn^{2+}	mg/L	0.28 – 0.63[b]
	mg/L	690– 983[b]	Na^+	mg/L	22 – 58[b]
Alkalinity	mg/L	1886 – 2829[b]	K^+	mg/L	186 – 356[b]

[a] measured with the homogenized sample, [b] measured in the filtrated sample.

3.1.2 Size-exclusion chromatography for sludge liquor

The analysis parameter dissolved organic carbon (DOC) is a broad classification for organic molecules of varied origin or composition within aquatic systems. It generally represents a whole group of soluble organic matters with rather complex nature and a broad range of chemical and physical properties. As the dissolved organic matter (DOM) in sludge liquor may give a significant interference in the phosphate adsorption process, it is necessary to gain more detailed information on organic molecules via appropriate fractionation methods.

The size-exclusion chromatography (SEC) is a standard technique for the purification, or fractionation of protein and peptide samples. It has been used extensively to study the molecular size distribution of natural organic matter samples (Mueller et al., 2000). The fractionation of DOM with SEC would figure out which portion of DOM in the sludge liquor mainly affects the phosphate adsorption in terms of molecular size.

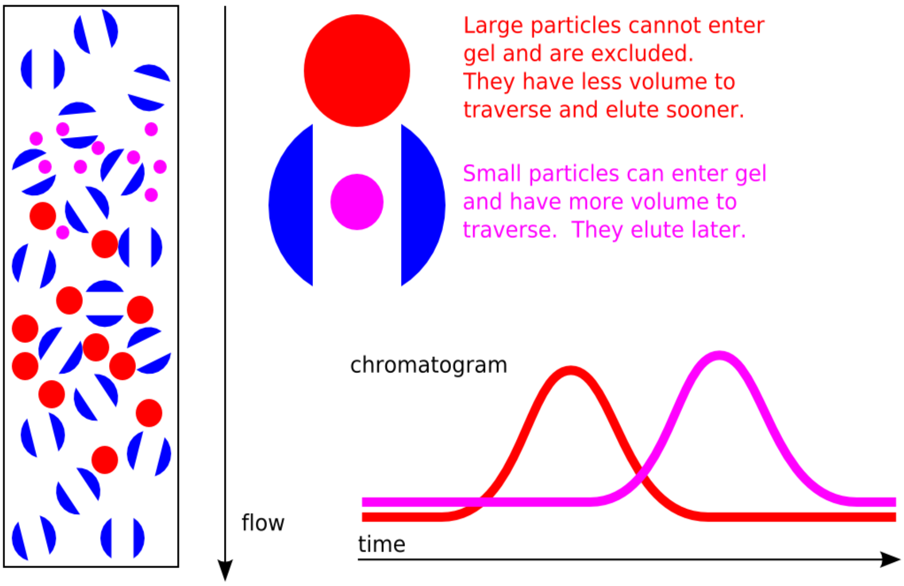


Figure 3.1: A sketch illustrating the theory behind size exclusion chromatography (from Wikipedia SEC, 2014)

The SEC experiment is commonly established in a column, which is filled with substrates that separate compounds on the basis of the molecular exclusion principle. One popular substrate is Sephadex, a modified dextran obtained by crosslinking linear macromolecules. Sephadex is neutral and contains few ionic sites. Its pores are determined by the degree of crosslinkage of the polymer (Flodin, 1963). Separation on Sephadex columns is achieved by a type of molecular sieving. A small volume of the concentrate (less than 3% of the column volume) to be separated is placed on the top of the column. Small molecules move with the eluent both within and outside the porous Sephadex particles. Molecules larger than the pore size of the gel particles cannot penetrate the particles and, therefore, move rapidly down the column with the eluent. The smaller molecules penetrate the gel particles to a varying extent, depending on their shape and size. Some compounds, such as protein, aromatics and heterocyclic, are adsorbed by or interact with the gel particles. Therefore, separation achieved by Sephadex columns is dependent on size, shape and, to some extent, the functional groups present in the molecule.

Each SEC column has a range of molecular weights that can be separated. In this study, Sephadex G-50 was applied as the chromatography gel, which offered a fractionation range between 500 and 10000 Dalton (Da). The chromatography column was set up with a glass tube of 60 cm long and of 1cm internal diameter. The upper end of the column was screwed with a cap with two openings, one for the sample injection and the other for the continuous supply of eluent. The column was mounted vertically. The bottom end of the column was narrowed and, constricted by a plug of glass wool in order to prevent the leakage of the gel. The column was filled to one-third of its volume with 0.15 M NaCl solution. Sephadex G-50, the fine dry powder (3.53 g) was allowed to swell in the 0.15 M salt solution and to form the gel. The packed gel column had a bed height ca. 52 cm and a gel bed volume of approximately 41 mL. The flow rate of eluent was 1 mL/min. The injection volume of samples was 0.5 mL for standards (1.2 % of the column volume) and 1.0 mL for testing samples (2.4% of the column volume), respectively. The fraction volumes were 1.5-2.5 mL. Forty fractions were collected with an automatic sample collector. DOC of each fraction sample was then analyzed by the Dimatec TOC-Analyzer DIMA TOC 100. The exclusion volume V_0 was determined using poly (sodium 4-styrenesulfonate) (PSS) with an average MW of 70000. The permeation volume V_p was determined by injection of glucose with the MW of 180.

3.2 Characterization of the sorbent for phosphate sorption

Oxides of polyvalent metals, namely, Fe(III), Ti(IV) and Zr(IV) exhibit very favorable ligand sorption properties through formation of inner sphere complexes (Dzombak and Morel, 1990; Stumm and Morgan, 1995; Suzuki et al., 2000; Dutta et al., 2004). Among them, the hydrated ferric oxide (HFO) is environmental benign, chemically stable over a wide pH range, and cost effective. In previous studies, the HFO were proven practical to remove anionic pollutants, e.g. arsenite/arsenate (Jang and Dempsey, 2008), selenate (Peak and Sparks, 2002), or phosphate (Khare et al., 2005; Majzlan, 2011) from contaminated waters. Extremely high surface area to volume ratio of these tiny particles ($\approx$30000 m^2/m^3) offers very favorable kinetics for selective sorption and oxidation-reduction reactions. However, these fine particles, whose sizes vary between 10 and 100 nm (Kney and SenGupta, 2001), cannot be directly used in fixed-bed columns, in underground reactive barriers or in any plug-flow type configuration due to excessive pressure drops and poor durability (Cumbal et al., 2003). To overcome this technical bottleneck, several researchers focused on dispersing nano-sized HFO particles within various support materials, e.g. alginate, zeolite, cation exchange resin and activated carbon (Zouboulis and Katsoyiannis, 2002; Onyango et al., 2003; Demarco et al., 2003; Jang et al., 2008).

3.2.1 The hybrid sorbent LayneRT

SenGupta and his group found that the ligand sorption capacity can be greatly increased by dispersing HFO nanoparticles within polymeric anion exchangers (Cumbal and SenGupta, 2005). And this enhancement in sorption capacity results from the Donnan membrane effect exerted by the fixed positive charges of an anion exchanger. Dispersing HFO nanoparticles within an anion exchanger is scientifically challenging because both ferrous (Fe^{2+}) and ferric ion ($Fe^{3+)}$ are repelled by the positively charged quaternary ammonium groups (R_4N^+) in anion exchange resins. Anyway, a patent route (SenGupta et al., 2005) was discovered to overcome this difficulty by a series of steps. Firstly, permanganate anion (MnO_4^-) is loaded onto an anion exchange resin through the following reaction:

$$\overline{R(\mathrm{CH_3})_3\,\mathrm{N^+Cl^-}} + M_nO_4^- \longleftrightarrow \overline{R(\mathrm{CH_3})_3\,\mathrm{N^+}\,MnO_4^-} + Cl^- \tag{3.1}$$

The reactant and product below the lines represent the species that adhered at the surface of the sorbent. $\overline{R(\mathrm{CH_3})_3\,\mathrm{N^+Cl^-}}$ is an anion exchange resin with a quaternary ammonium functional group in chloride form.

The second step is concurrent permanganate desorption, Fe(II) oxidation and HFO formation within the anion exchange resin. During this step, the permanganate loaded anion exchange resin is brought into contact with 5% ferrous sulfate solution. Desorption of MnO_4^- by sulfate, reduction of MnO_4^- to MnO_2(s) and oxidation of Fe^{2+} to Fe^{3+} and finally, precipitation of $Fe(OH)_3$(s) within the anion exchanger matrix, took place in accordance with the following:

$$2\overline{R(\mathrm{CH_3})_3\,\mathrm{N^+}\,MnO_4^-} + SO_4^{2-} \longleftrightarrow \left[R(\mathrm{CH_3})_3N^+\right]_2 SO_4^{2-} + 2MnO_4^- \tag{3.2}$$

$$MnO_4^- + 4H^+ + 3e^- \xrightarrow{reduction} \overline{MnO_2}(\mathrm{s}) + 2\,\mathrm{H_2O} \tag{3.3}$$

$$3Fe^{2+} \xrightarrow{oxidation} 3Fe^{3+} + 3e^- \tag{3.4}$$

$$3Fe^{3+} + 9OH^- \xrightarrow{precipitation} \overline{3Fe(\mathrm{OH})_3}(\mathrm{s}) \tag{3.5}$$

As the third step, anion exchange resins from the second step are washed with acetone and dried in a furnance at 35 °C for 12 hours.

The structure of the final product is described as hybrid anion exchange resin by the sketch in Figure 3.2. The quaternary ammonium groups (R_4N^+) are introduced after the crosslinking has been completed and they are distributed both inside the particle as well as on its surface. The hydrous ferric oxide nanoparticles are presented by the small red dots that are deposited on the macroporous (pore size > 50 nm) resin granule.

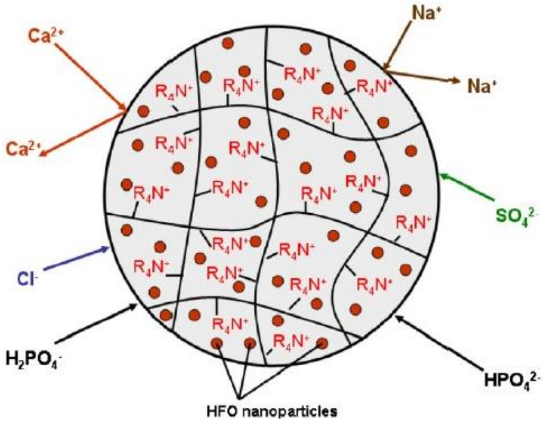


Figure 3.2: Sketch of of an hybrid anion exchange resin (Blaney et al., 2007)

The hybrid anion exchanger (LayneRT) has been commercialized and is available in large quantities from the American company SolmeteX Co. in Massachusetts. LayneRT has been initially developed for arsenic removal. Table 3.2 presents main product information that is provided by the inventor and the manufacturer.

Table 3.2: Product information of LayneRT (SenGupta et al., 2005; Layne Co., 2014)

Properties	LayneRT from Solmete X Co.
Form	chloride/sulfate
Apparent density	790 – 820 g/L
Moisture content	35- 65%
Particle size	300-1200 mm, mostly 450- 600 mm
Thermal resistence	1- 80 °C
pH tolerance	6- 8
Slight affinity	HCO_3^- , SO_4^{2-}, Cl^-
Iron content	250- 300 mg Fe/g LayneRT

3.2.2 Morphological analysis of LayneRT

The surface morphology including roughness, cracks and pore distribution of the sorbent were analyzed by environmental scanning electron microscopy (ESEM). It is well known that scanning electron microscope (SEM) is a powerful system for morphological research of novel objects. But since it requires drastic drying condition imposed by high vacuum, the wet materials samples must undergo a complex preparation, which may potentially damage the samples, that limits the application of SEM on this kind of specimen and often causes the introduction of artifacts (Muscariello et al., 2005). The introduction of environmental scanning electron microscope, working in low vacuum or gaseous atmosphere, represented a new perspective in aqueous environmental research. The ESEM is a SEM that allows for the option of collecting electron micrographs of specimens that are “wet”, uncoated, or both by allowing for a gaseous environment in the specimen chamber. The key advantage of ESEM over conventional SEM is that hydrated samples can be looked at in their natural state with essentially no prior specimen preparation. This can achieved because water vapor can be maintained in the specimen chamber (Donald, 1998).

In an ESEM system, the microscope column is divided into differential pressure zones that allow the electron gun to remain under high vacuum while the sample chamber contains a few torr of gas (Danilatos, 1993). Collisions between electrons and gas molecules produce positive ions that can balance the accumulation of negative charges on the surface of specimens. This consequently eliminates the need of a conductive surface coating on sample surface. Moreover, the signal detected by the positively biased environmental detector is amplified by the electrons that are produced via “cascade effect”. Eventually, when the microscope is equipped with a Peltier stage, the adjustable chamber pressure and temperature ranges enable the observation of wet samples in their natural state. But, the ESEM also is not omnipotent, for samples that are not only wet, but totally submerged in a liquid phase, only the top layer of the sample surface can be imaged, which results in poor contrast, and possible drifting of objects (Bogner et al., 2005).

The observations of sorbent in this study have been performed with a FEI Quanta 650 FEG ESEM at Laboratory for Electron Microscopy (LEM) at Karlsruhe Institute of Technology (KIT). This scanning electron microscope allows studies at pressures up to 4000 Pa for wet samples. The field emission gun (FEG) systems contain an S/TEM detector for bright-field and dark-field sample imaging. The analysis conditions for getting better images can be found in the data bar of the images:

- acceleration voltage (HV) : 30 kV;
- the pressure in the sample chamber : about 740 to 800 Pa;
- the temperature of the sample: 3°C;
- and the humidity: about 100%.

The sorbent samples to be tested were prepared as: (a) the original sorbent LayneRT from the fabricant; (b) the sorbent after the sorption of phosphate and; (c) the regenerated sorbent. The original sorbent sample (a) was only washed with distilled water. The sorbent sample (b) was prepared by reacting with phosphate solution of 300 mg/L for 1 hour. Afterwards, a portion of used sorbent was regenerated with 1M NaOH and rinsed with distilled water.

3.3 Batch experiments

Batch experiments were conducted to evaluate the sorption performance of the hybrid sorbent LayneRT under different boundary conditions (e.g. initial concentration of bulk solution, retention time, pH-value, ambient temperature, competing ions). For batch experiments, different synthetic model solutions containing certain amount of specific constituents were prepared for different objectives. All chemicals used were of analytical grade, unless otherwise mentioned. The P-sorbent was mixed with a specific volume of bulk solution in glass vessels and then agitated by a shaker. After an adequate retention time, the solid-liquid mixture was settled and separated for further measurement. The supernatant was collected in polythene tubes for chemical analysis. The solid phase retained and would be regenerated for the next cycle of reaction.

The two-phase mixture was agitated on a shaking table (Gerhardt RO 500) with horizontal circular movement at 100r/min at room temperature. A water-bath shaker (Gyrotory Model G76) was also used for variation of the ambient temperature. The concentration of initial and remaining phosphate ion in bulk solution were determined by QuikChem 8500 from LACHAT.

3.3.1 Sorption isotherms

The purpose of determining the sorption isotherms is to reveal the specific relation between the equilibrium concentration of sorbate in the bulk and the adsorbed amount at the surface. For a single-component sorption system, the equilibrium isotherms can be achieved via a series of batch experiments. The relationship between the amount of sorbate uptake on the solide-phase (q_e) and the concentration of dissolved sorbate in the liquid-phase (c_e) at equilibrium can be expressed by the following mass balance equation (3.6):

$$m \cdot q_0 + V \cdot c_0 = m \cdot q_e + V \cdot c_e \tag{3.6}$$

Since there was no initial load of sorbate per unit mass of sorbent ($q_0 = 0$), the sorbate uptake per unit mass of the sorbent at equilibrium (q_e) can be calculated via the following equation:

$$q_e = \frac{V}{m}(c_0 - c_e) \tag{3.7}$$

The Equation (3.7) represented the finishing point of the sorbent's working curve, which describes the variation of solution concentration and the loading progress of sorbents. The slope V/m leads from the initial condition (c_0, $q_0 = 0$) to the sorption equilibrium (c_e, q_e). An equilibrium is established when the amount of solute being adsorbed is equal to the amount being desorbed. Plotting solid-phase concentration against liquid-phase concentration graphically depicts the equilibrium sorption isotherm (Allen et al., 2004). Several empirical and theoretical models were developed to describe the data obtained from the experiment.

For plotting the isotherms, a series of experiments were conducted in a series of glass centrifuge tubes, which were filled with 50 mL of bulk solutions having an identical initial concentration. Different masses of sorbents were weighted and dosed into each of the glass centrifuge tubes. The mixture of sorbent and bulk solution then reacted in the tubes for 2 h to get equilibrium. Two phosphate model solutions (250 mg PO_4^{3-}/L and 200 mg PO_4^{3-}/L) used in the isotherm tests were prepared with the analytical grade potassium hydrogen phosphate (K_2HPO_4) from Merck Co., Germany in distilled water. The isotherm tests were conducted at room temperature around 25 ^oC.

3.3.2 pH value

The effect of the initial pH of bulk solutions was studied at pH 4.1, pH 5.2, pH 6.0, pH 6.8, pH 7.1, pH 8.2, pH 9.4 and pH10.3 to determine the optimal pH range for the highest phosphate sorption capacity. Eight phosphate model solutions at different pH values were prepared with the analytical grade potassium dihydrogen phosphate (KH_2PO_4) and potassium hydrogen phosphate (K_2HPO_4) in distilled water. The pH-value was adjusted with hydrochloric acid (HCl) and sodium hydroxide (NaOH). The pH tests were conducted at room temperature around 25 ^oC.

3.3.3 Sorption kinetics

To determine the appropriate reaction time for the sorption process to get equilibrium, batch experiments for kinetics were performed in a series of vessels. Model solutions with phosphate concentrations of 25 mg/L, 50 mg/L, 100 mg/L and 300 mg/L were prepared with K_2HPO_4 in distilled water. In each vessel, 0.5 g sorbent LayneRT was mixed with 50 mL phosphate model solution. The kinetic tests were conducted at room temperature around 25 ^oC. Samples of supernatant were collected from each vessel at particular time intervals and were analyzed afterwards. By setting different initial concentrations of phosphate from 25 mg/L to 300 mg/L, the effect of the initial concentration on sorption kinetics could be revealed subsequently.

3.3.4 Temperature

The effect of ambient temperature was investigated via batch experiments in the water-bath shaker Gyrotory Model G76. Isotherm tests for phosphate sorption were conducted with two different model solutions at the temperature of 20 ^oC, 30 ^oC and 40 ^oC. For the first group of isotherms, the pure phosphate model solution without competing anions was prepared with K_2HPO_4 in distilled water. For the second group of isotherms, the effect of temperature variation on phosphate sorption was studied in the presence of interfering ions, i.e. 100 mg/L sulfate, 200 mg/L chloride and 10 mg/L nitrate. The seconde model solution was prepared by mixing K_2HPO_4, Na_2SO_4, KCl and KNO_3 in distilled water.

3.3.5 Selectivity

The interference of competing anions, i.e. sulfate, chloride and nitrate, was investigated via batch experiments. Isotherms for phosphate sorption were plotted in the presence of competing anions. For each group of isotherms, the initial concentration of phosphate was identical for 100 mg/L; the initial concentration of target competing ions was increased. For instant, the initial concentrations of interfering sulfate were 50 mg/L, 100 mg/L and 200 mg/L; for chloride the initial concentrations were 100 mg/L, 200 mg/L and 400 mg/L and for nitrate the initial concentrations were 10 mg/L, 25 mg/L and 50 mg/L. The competing tests were conducted at the room temperature around 25 ^{o}C.

3.3.6 Regeneration

The potential of regeneration of the sorbent LayneRT was investigated through a series of repeated experiments. The exhausted LayneRT after sorption in batches was regenerated by filling 50 mL 1M NaOH in the vessels for 2 h. Isotherms for phosphate sorption with the recycled sorbent were plotted repetitively to observe the variations of maximal loading capacity. Phosphate model solutions (385 mg PO_4^{3-}/L and 190 mg PO_4^{3-}/L) used for the isotherm tests were prepared with K_2HPO_4 and distilled water. The regeneration and repetitive isotherm tests for regenerated sorbents were performed at room temperature around 25 ^{o}C.

3.4 Fixed-bed column experiments

The continuous performance of LayneRT for phosphate sorption was investigated via the fixed-bed column experiments under varying boundary conditions. A certain amount of the sorbent LayneRT was packed uniformly in the lab-scale filter column with an inner diameter of 1.5 cm and a total length of 55 cm. After a saturated uniform packing, a bed length of 42 cm can be obtained. During the experiment, the inflow solution/ liquor was pumped from the reservoir into the column with a peristaltic pump (Minipuls 2, GILSON). The liquid flowed from the bottom up in vertical direction. The effluent was monitored and collected continuously to determine the flow volume at time t. Afterwards, these samples of effluent would be analyzed to observe the variation of chemical constituents in solution/liquor. All column tests were performed at room temperature around 25 ^{o}C. The scheme of the system set-up is shown in Figure 3.3.

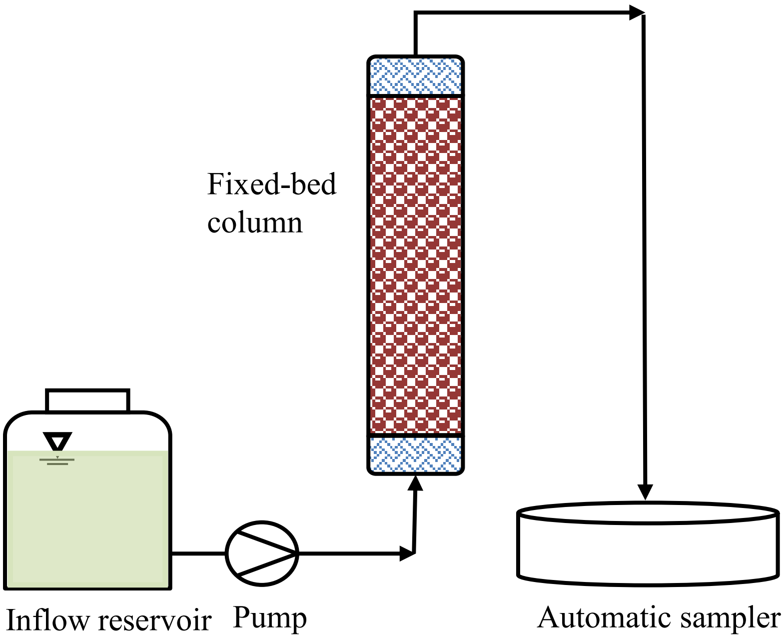


Figure 3.3: Scheme of the fixed-bed column system for continuous experiments

3.4.1 Flow rate

The first step to start the continuous experiment was to determine the dynamic parameters of the column with synthetic solutions. For investigating the impact of input-flow-rate on the performance of the column, the phosphate model solution with a concentration of 350 mg PO_4^{3-}/L was pumped into the column at the rate of 4 mL/min, 8 mL/min and 12 mL/min respectively. The outflow was collected at regular intervals for further chemical analysis in order to draw the breakthrough curves under each flow rate.

3.4.2 Performance with model solution

Before the application of the column for real sludge liquor treatment, a phosphate model solution (338 mg PO_4^{3-}/L) was used to determine the breakthrough and exhaustion points in ideal condition. The model solution was prepared with K_2HPO_4 and distilled water and was continuously pumped into the column at the flow rate of 8 mL/min. The outflow was collected at certain time intervals and analyzed to determine the breakthrough time and the exhaustion time. The breakthrough capacity and saturation capacity can also be calculated through the breakthrough curve.

3.4.3 Performance with real sludge liquor

When the basic operating conditions were determined, the cases with real sludge liquor were then investigated in the column experiments. Sludge liquors under different pH conditions were pumped through the ion exchange column to see the continuous phosphate sorption performance of the column. The composition and concentration of sludge liquor varied in each operation. HCl and NaOH were used for the pH value adjustment of sludge liquor. The operating flow rate was controlled constant at 8 mL/min. The outflow of the column was collected at certain time intervals and analyzed to see the behavior of different compositions of sludge liquor through the column.

3.4.4 Regeneration of the sorbent column

After each round of sorption, the exhausted sorbent LayneRT was rinsed with distilled water at a relatively high velocity (~ 20 BV/h) to sweep the unloaded ions away before regeneration. The regeneration was accomplished via the similar operation as applied in the sorption process but at a lower input flow rate (~ 6 BV/h). The lower input flow rate resulted in a longer effective retention time of regenerating reagent (1M NaOH) in the column, which led to a better effect of regeneration. After the regeneration, the column was rinsed again with distilled water to wash the excess regenerating reagent away until the pH value of outflow was stable (> 7.0).

4 Results and Interpretation

4.1 Morphological characterization of sorbent

To observe the morphological difference of the LayneRT before and after applications, environmental scanning electron microscopy (ESEM) was used in this study. The analysis conditions of ESEM for each sample were adjusted as consistent as possible, cf. Chapter 3.2.2. The ESEM images were taken at 682×, 811× and 20000 × magnifications for comparison.

Figure 4.1 illustrated the ESEM observations of (a), (b), (c) raw LayneRT, (d) OH-form LayneRT, (e) LayneRT after P-sorption in phosphate model solution and (f) LayneRT after P-sorption in sludge liquor. Figure 4.1a and 4.1b presented the enlarged view of granular LayneRT particles in moist condition. On the surface of raw LayneRT (Figure 4.1c), small humps and ditches appeared occasionally, which were the dispersed functional materials adhered unevenly on raw granules. Through the pretreatment or regeneration with 1.0M NaOH, a coarsened exterior was optimized; the granule surface was smooth and flat. The porous matrix of the granule could be seen as dark dots in Figure 4.1d, and the macropores (> 50 nm) spread relatively evenly on the LayneRT. The sorbent granule also exhibited its good tolerance to the strong alkaline conditions.

After the reaction in phosphate model solution, no visual evidence of erosion and collapse was found on the surface of LayneRT (Figure 4.1e), reflecting a good resistance to mechanical damage via physical agitation. Compared with the unused LayneRT granule, the macropores on the used sorbent surface were covered by irregular crystals. The surface condition of the LayneRT reacted with phosphate in the actual sludge liquor was presented in the Figure 4.1f. In this case, larger crystals appeared on the surface of the sorbent, and the roughness of the surface seemed reduced comparing with the Figure 4.1e. The difference between the two images might be attributed to the complicated compositions of the actual sludge liquor, such as dissolved organic matters, which also occupy the sorption sites on the sorbent and tend forming a “film” on the sorbent surface that make the surface look less rough and the crystals look larger.

The ESEM technique has advantages such as fast scanning speed, and it is possible to observe samples in their native state using the environmental mode. Nevertheless, one disadvantage of this type of microscopy is that the morphological analysis obtained is only qualitative in character. Consequently, quantification of the sorption capacity of the sorbent and the sorption mechanism were conducted through batch and continuous experiments.

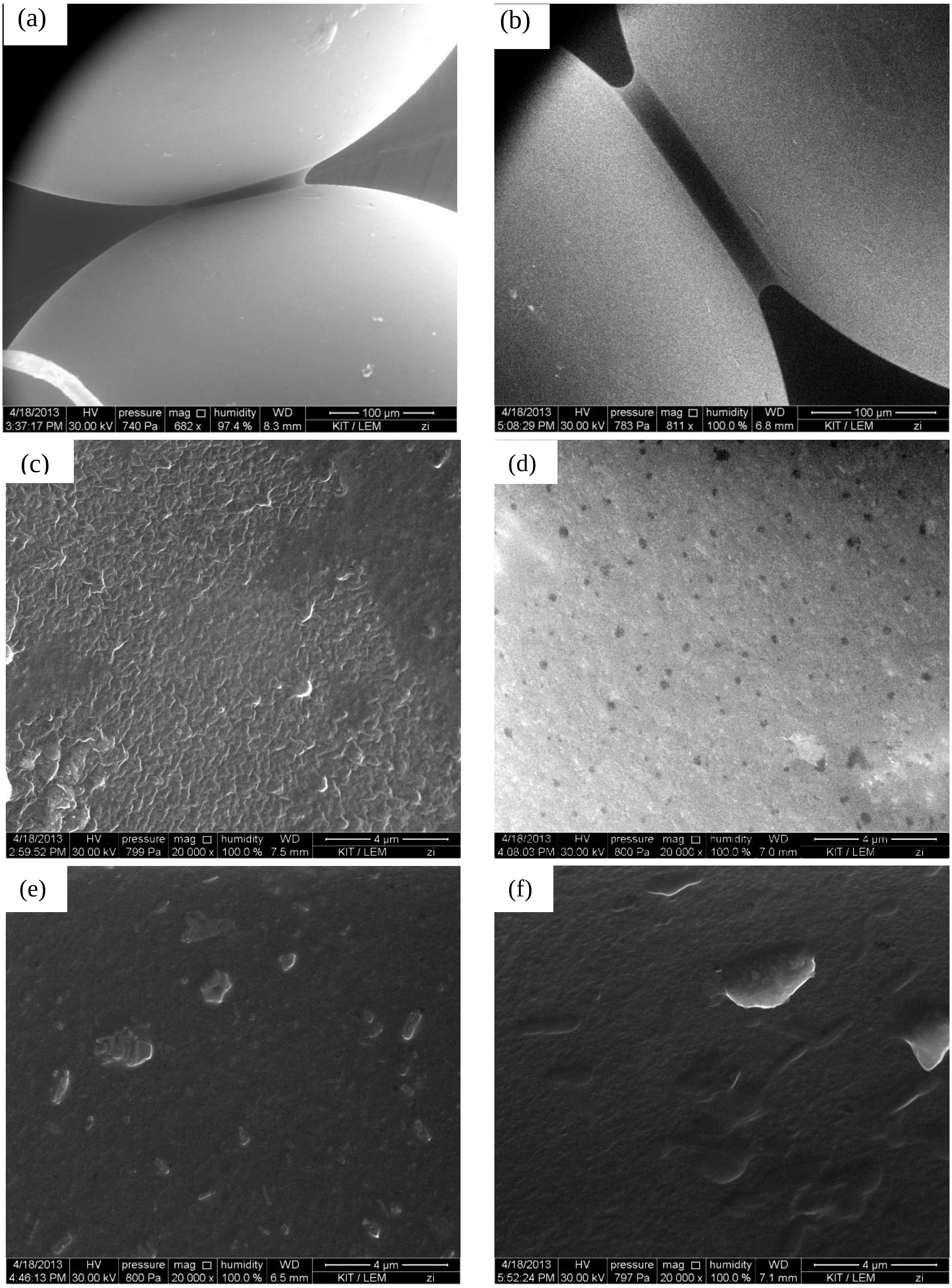


Figure 4.1: The ESEM photography of selected samples: (a) (b) raw LayneRT particles in moist condition at 682× and 811×magnifications; (c) raw LayneRT at 20000 × magnification; (d) OH-form LayneRT (regenerated) at 20000 × magnification; (e) LayneRT after model P-sorption at 20000 × magnification and (f) LayneRT after P-sorption in sludge liquor at 20000 × magnification.

4.2 Batch experiments of P sorption with LayneRT

4.2.1 Influence of the pH-value

The adsorption of most anions and anionic polyelectrolytes from water onto hydroxides occurs by electrostatic bonding to positive surface sites. The surface site density, which relates to the anion exchange capacity, is strongly governed by the pH value of the bulk solution and the acid-base character of solids (Morrison Jr., 1984). To determine how the pH value influences phosphate sorption onto the sorbent LayneRT, batch experiments were carried out by using phosphate model solutions with an initial concentration of 100 mg/L but at various pH values from 4.06 to 10.33. 0.1g of the sorbent LayneRT was dosed into each 50 mL phosphate solution.

Figure 4.2 (a) presented the variation of P-sorption capacities of the sorbent under different pH conditions. It is noted that the optimal pH values for phosphate sorption by LayneRT range from 6.0 to 8.2. The pH value of solution determines the protonation of phosphate groups and that is coupled with changes in the predominant phosphate ion species, as shown in Figure 4.2 (b). The relative amounts of phosphate species H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} can be determined by the phosphoric acid equilibria:

$$H_3PO_4^0 \rightleftharpoons H_2PO_4^- + H^+, pK_{a1} = 2.23 \tag{4.1}$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+, pK_{a2} = 7.21 \tag{4.2}$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+, pK_{a3} = 12.32 \tag{4.3}$$

The point pH= pK_a is where the two species reaches the equilibrium, which means the fractional composition of both species is fifty-fifty.

As depicted in Figure 4.2(b), dihydrogen phoshpate $H_2PO_4^-$ and hydrogen phosphate HPO_4^{2-} are the major phosphate species in the aqueous solution in the pH range between 6.0 and 8.2. Decreasing pH values lower than 5.0 inevitably result in the increase of none charged phosphoric acid and less charged hydrogen phosphate, which is unfavorable for the phosphate sorption. It is generally known that the negatively charged phosphate is selectively trapped by hydrated ferric oxide (HFO) through formation of the inner-sphere complexes, and HPO_4^{2-} tends to form stronger bi-dentate complexes than $H_2PO_4^-$ (Zeng et al., 2008). However, increasing the pH blindly is also inadvisable, because multivalent metal hydroxides exhibit amphoteric behavior. Under high alkaline conditions, HFO is tending to be deprotonated and negatively charged, so are the phosphate species. Consequently, Donnan co-ion exclusion or electrostatic repulsive forces are operative, which is favorable for the desorption of the loaded phosphate (Cumbal and Sengupta, 2005).

This may explain why LayneRT presented the best affinity for phosphate in the pH range between 6.0 and 8.2. This also intimated that the nanoparticles of hydrous ferric oxides (see Figure 3.2), which were deposited on the resin matrix, played a key role in the uptake of phosphate from bulk solution. From the viewpoint of application, the pH value of the digested sludge liquor is usually around 8.0, thus no extra addition of pH adjustment chemicals will be necessary. This diminishes the risk of adding total dissolved salts into the aqueous system and minimizes the amount of contaminant that can be taken up by the sorbents.

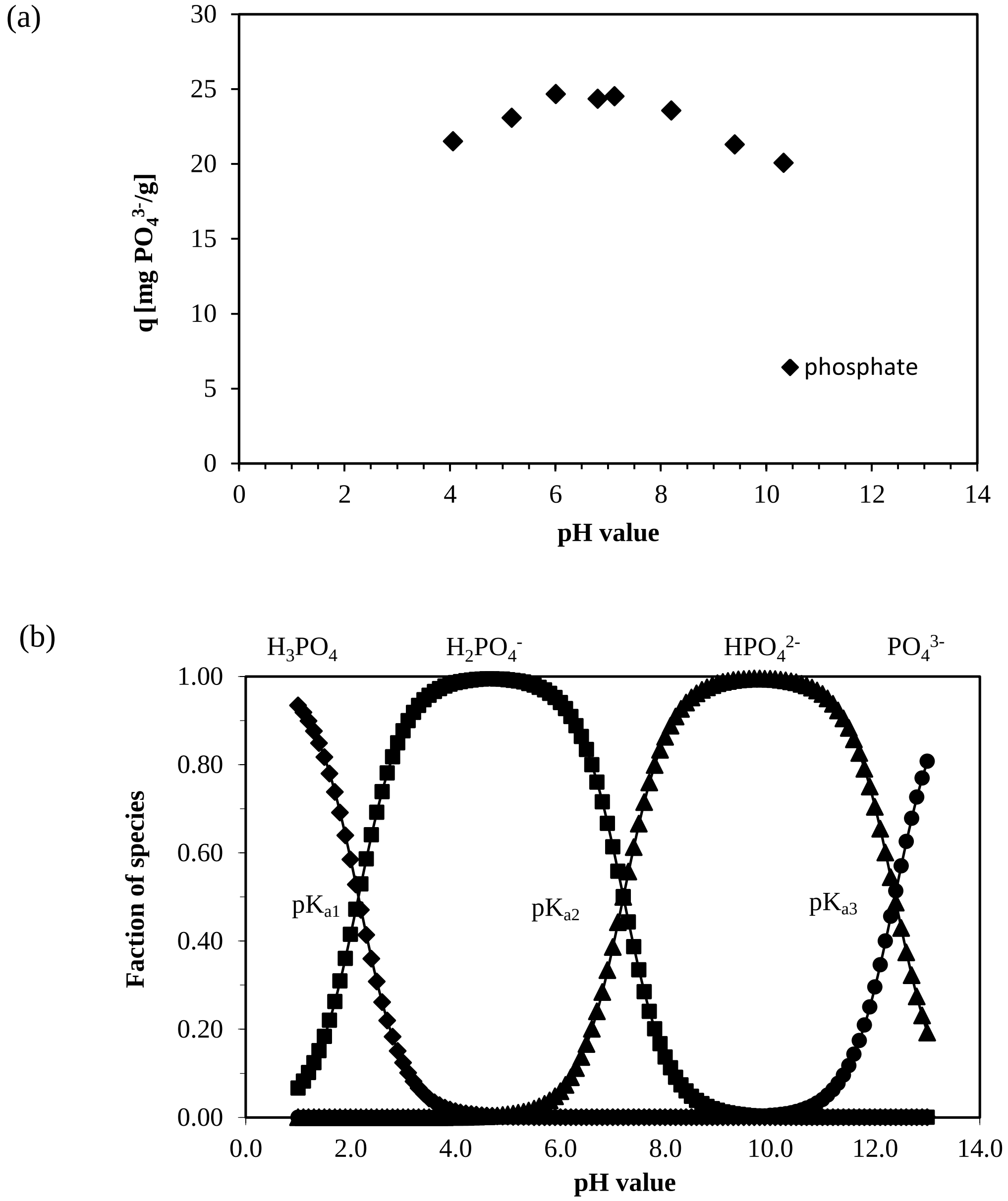


Figure 4.2: Effect of solution pH on (a) the phosphate sorption by LayneRT, LayneRT dosage = 2.0 g/L, initial phosphate = 100 mg/L, at 25 ^oC; and (b) the distribution of phosphate species (Bialkowski, 2004).

4.2.2 Sorption isotherms

The isotherm results of phosphate on LayneRT at a constant temperature of 25 °C were analyzed using three important isotherms including the Langmuir, Freundlich and Redlich-Peterson isotherm models. The first two are two-parameter equations and the Redlich-Peterson is a three-parameter equation. A simple way to determine isotherm constants for two-parameter isotherm models is to transform the isotherm variables, by this the equations are converted to a linear form for linear regression and least squares estimation. For a three-parameter isotherm like Redlich-Peterson, linear analysis is not possible. The model equation is reformed as the following equation:

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \beta \ln C_e + \ln a_R \tag{4.4}$$

which involves varying the isotherm parameters, K_R, a_R and β to obtain the maximum value of the correlation coefficient between the theoretical data for q_e predicted from equation and the experimental data. The isotherm constants were evaluated by using trial and error procedures, which are applicable in the Solver add-in with Microsoft spreadsheet Excel. Two forms of sorbents were involved in the isotherm study. The Cl-form was pretreated with 1.0 M NaCl and the OH-form was pretreated with 1.0 M NaOH. Table 4.1 shows the parameter values along with the coefficient of determination, R^2 and constants for each isotherm models for both Cl-form and OH-form sorbent LayneRT. Figure 4.3 and Figure 4.4 show the comparison of different models for the sorption of phosphate with the experimental results. The best fit model could be selected on the basis of the value of correlation coefficient. More detailed experimental data can be found in Appendix 2 and 3.

Table 4.1: Equlibrium isotherm constants of phosphate sorption on Cl-form and OH-form LayneRT at 25°C.

Isotherm	Linear form	Parameters	Cl-form LayneRT	OH-form LayneRT
Langmuir	$\frac{1}{q_e} = \frac{1}{q_{max} K_L C_e} + \frac{1}{q_{max}}$	q_{max}	8.425	14.86
		K_L	0.4186	0.1809
		R^2	0.87	0.7706
Freundlich	$\ln q_e = \ln K_F + b_F \ln C_e$	K_F	2.4789	3.2281
		b_F	0.2919	0.3596
		R^2	0.9694	0.9608
Redlich-Peterson	$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \beta \ln C_e + \ln a_R$	K_R	5452	3.6556
		a_R	3170	0.7203
		β	0.6248	0.7268
		R^2	0.9947	0.9721

As is evident from the data of Table 4.1 and Figure 4.3 and 4.4, Langmuir isotherm could not represent the data reasonably well with correlation coefficients of 0.87 and 0.77 for the Cl-form and the OH-form LayneRT, respectively. The calculated maximum sorption capacities for phosphate are 8.34 mg PO_4^{3-}/g and 14.38 mg PO_4^{3-}/g, which are both much lower than the experimental capacities. From this unsuccessful modeling with the Langmuir equation, one may speculate the phosphate sorption reaction is far more than a simple mono-layer homogeneous process. Further, the values of R_L for this study were 0.0095 and 0.0287, which indicated that the sorption was spontaneous, as the R_L values laying between 0 and 1 were favorable (Webi et al., 1974).

Freundlich isotherm had a better match to the experimental results, and the values of R^2 were found to be above 0.96 for both the Cl-form and the OH-form LayneRT. From the plotting of the Freundlich equation, one can get the information that the sorption sites on the Cl-form LayneRT were more heterogeneous than the sites on the OH-form sorbent as its value of the slope (b_F) was closer to zero. A value of slope below unity implied a chemisorption process whereas the slope above one was a sign of cooperative adsorption (Haghseresht and Lu, 1998). The calculated sorption capacity for phosphate via the Freundlich equation in this study were 12.26 mg PO_4^{3-}/g and 20.33 mg PO_4^{3-}/g for the two forms of sorption, which were closer than the Langmuir calculation. However, the Freundlich isotherm was theoretically an expression for an infinite sorption process and was criticized for its limitation of lacking a fundamental thermodynamics basis, not approaching the Henry's law at vanishing concentrations (Ho et al., 2002).

For the three-parameter isotherm, i.e. Redlich-Peterson, since the method used to derive the isotherm parameters maximized the linear correlation coefficient, it is unsurprising that in both cases the Redlich-Peterson isotherms exhibit high R^2 values, i.e. 0.99 and 0.97, which produced a considerably better fit compared to the preceding two-parameter isotherms. The values of the exponent β in the study are both below unity, i.e. 0.6248 and 0.7268, which indicates the degree of heterogeneity. The maximum sorption amount of phosphate on LayneRT calculated from Redlich-Peterson isotherm equation defines the total capacity of the sorbent LayneRT for phosphate. The calculated capacity of Cl-form LayneRT and OH-form LayneRT are 13.42 mg PO_4^{3-}/g and 19.87 mg PO_4^{3-}/g, compared with the experimental capacity of 14.58 mg PO_4^{3-}/g and 18.97 mg PO_4^{3-}/g, respectively.

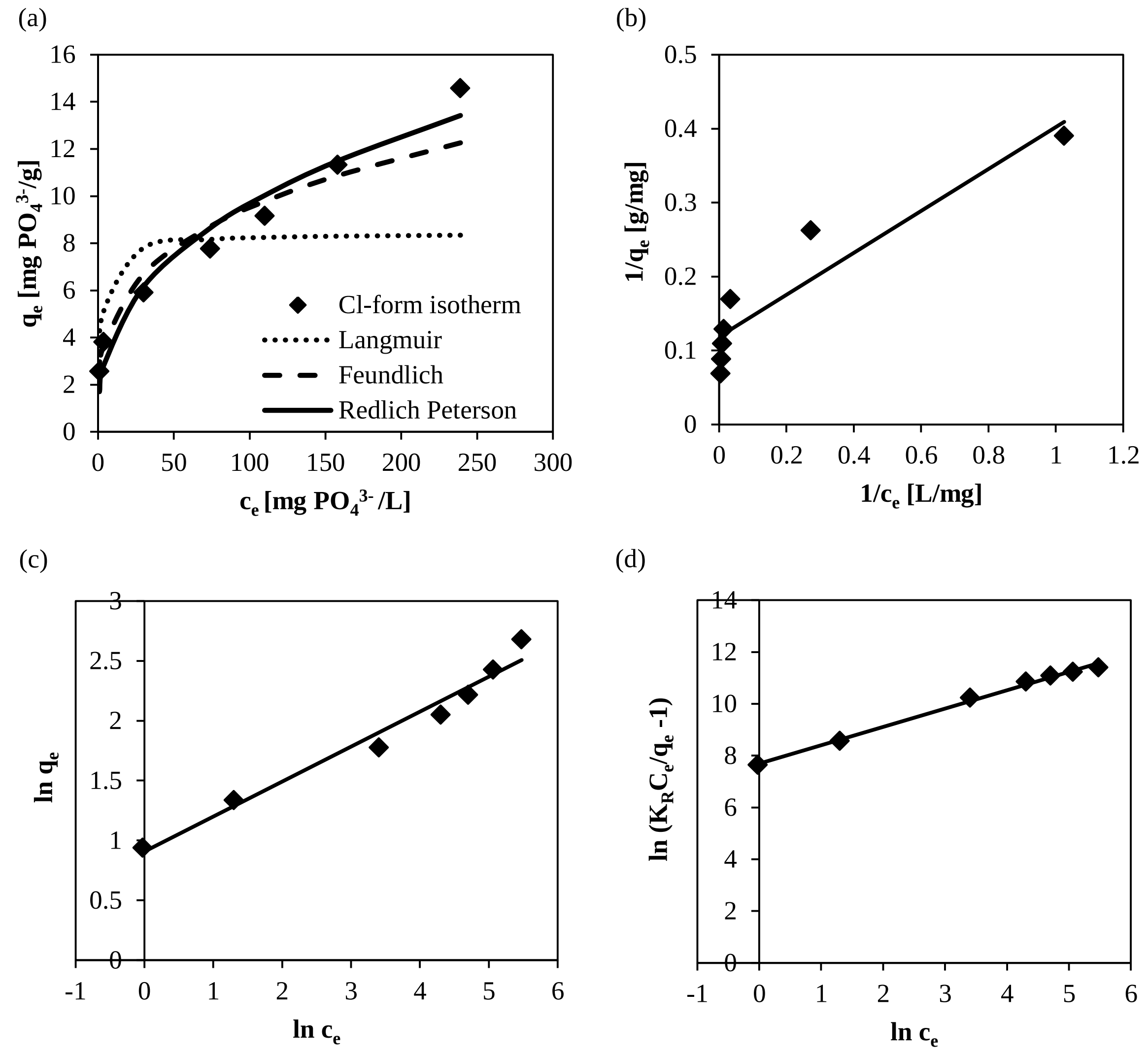


Figure 4.3: Different isotherm models for phosphate sorption on the Cl-form LayneRT: (a) comparison of modeling isotherms with experimental results; (b) linearization of the Langmuir model; (c) linearization of the Freundlich model and (d) linearization of the Redlich- Peterson model.

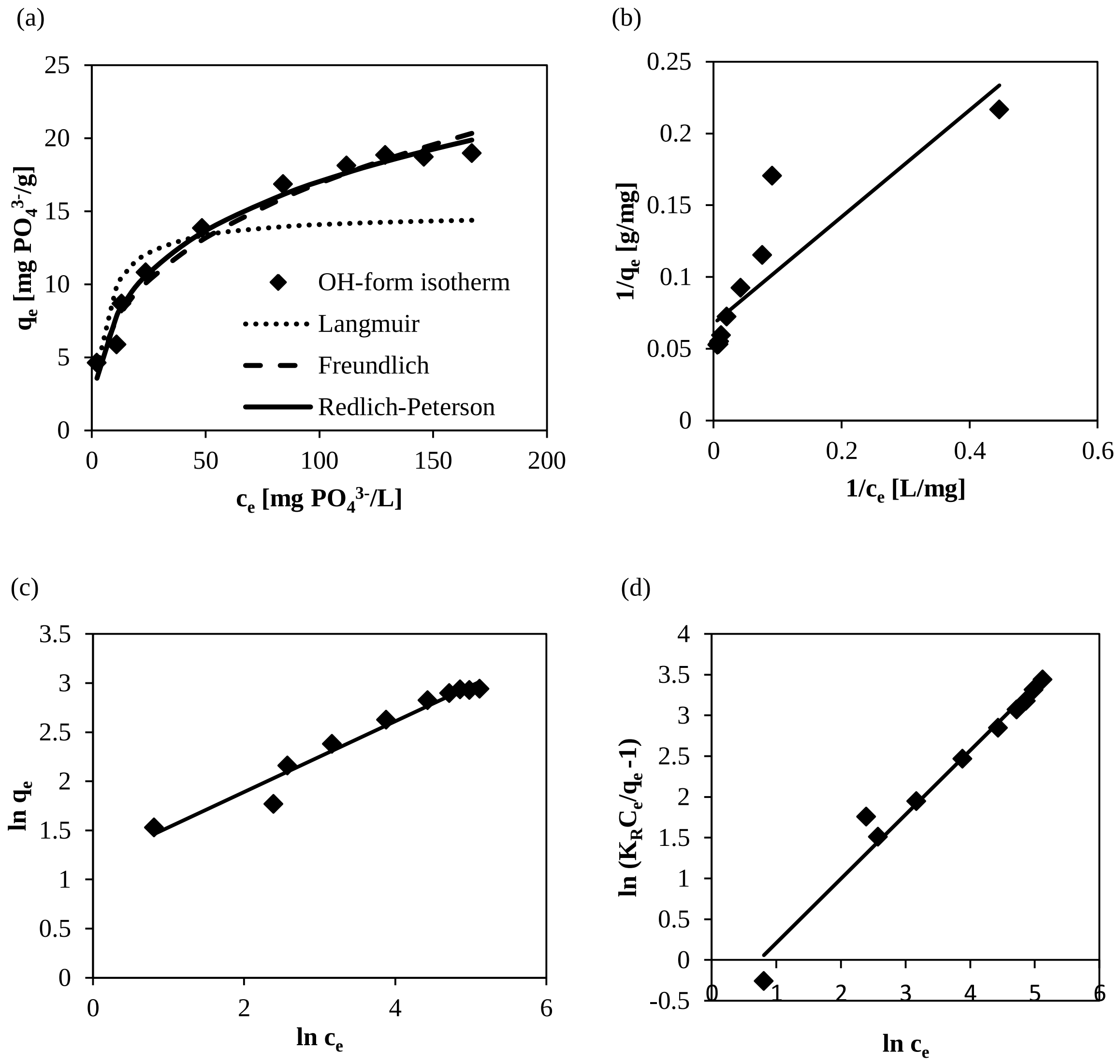


Figure 4.4: Different isotherm models for phosphate sorption on the OH-form LayneRT: (a) comparison of modeling isotherms with experimental results; (b) linearization of the Langmuir model; (c) linearization of the Freundlich model and (d) linearization of the Redlich- Peterson model.

Comparing the three isotherm models, taking logarithms, e.g. the linear transformation of the Freundlich equation, may lead to a better match at the extremes of concentrations since linear regression implicitly minimizes the sum of the squares of the errors to determine the equation parameters. In this study the Redlich-Peterson isotherm presented the best constitutive relationships in the modelling of P-sorption with the sorbent LayneRT and offered the most accurate prediction for the P-sorption capacity of the sorbent. In the case of gas adsorption, many isotherms have been developed based on thermodynamic theories but in the liquid phase sorption, the relationship is more or less empirical, nothing more than a curve fitting procedure (Tien, 1994).

4.2.3 Influence of initial concentration

The effect of the initial phosphate concentration on the uptake rate of phosphate onto the OH-form LayneRT was investigated. As described in chapter 3.3.3, a series of time-depending batch experiments were carried out to observe the phosphate sorption procedure from model solutions with different initial concentrations, i.e. 25 mg/L, 50 mg/L, 100 mg/L and 300 mg/L. The phosphate uptake per unit mass of the sorbent LayneRT (q_t) at the reaction time (t) was determined by equation 4.5:

$$q_t = \frac{V}{m}(c_0 - c_t) \tag{4.5}$$

Where c_o and c_t respectively refer to the initial concentration of phosphate and the residual concentration of phosphate in solution at the reaction time t and V refers to the volume of the reaction solution and m is the dosage of LayneRT in each vessel.

The phosphate sorption with respect to reaction time was plotted in Figure 4.5. The variation of real-time mass loading q_t (mg/g) illustrated the rapid progress of the phosphate sorption from bulk solutions by LayneRT. The phosphate sorption equilibria were all achieved after about 30 min under all conditions with different initial phosphate concentration. The mass loading of phosphate occurred rapidly in the initial stages and then gradually increased at a slower pace until the equilibrium was achieved. The equilibrium sorption capacities of phosphate were 2.37, 4.92, 9.32 and 17.50 mg/g, respectively, for the initial phosphate concentrations of 25, 50, 100 and 300 mg/L. The result exhibited that the higher initial concentration of phosphate the greater the loading on the sorbents. Bulk solutions with high initial phosphate concentrations provided more phosphate anions to meet the highly dynamic conditions, which meant an important drive to overcome mass transfer resistances of the phosphate between the aqueous and solid phases before equilibrium (Zheng et al., 2009).

On the contrary, the removal efficiency of phosphate decreased from 99.8% in the 25 mg/L initial solution to 61.9% in the 300 mg/L initial solution (Figure 4.6). This phenomenon was due to the ratio between phosphate ions and the available binding sites on sorbents (Wang et al., 2006; Özer et al., 2005). Under the conditions of lower initial concentrations, the sorbent LayneRT was unsaturated, having abundant available binding sites for phosphate sorption. For the solution with high phosphate concentrations, the sorbent LayneRT was saturated, which could not offer plenty of binding sites for the massive amount of phosphate ions. The surplus phosphate remained in the bulk solution, causing an increased residual solution concentration, which also set up a diffusion gradient between solution and surface, which would further encourage the sorption to occur until the point of equilibrium.

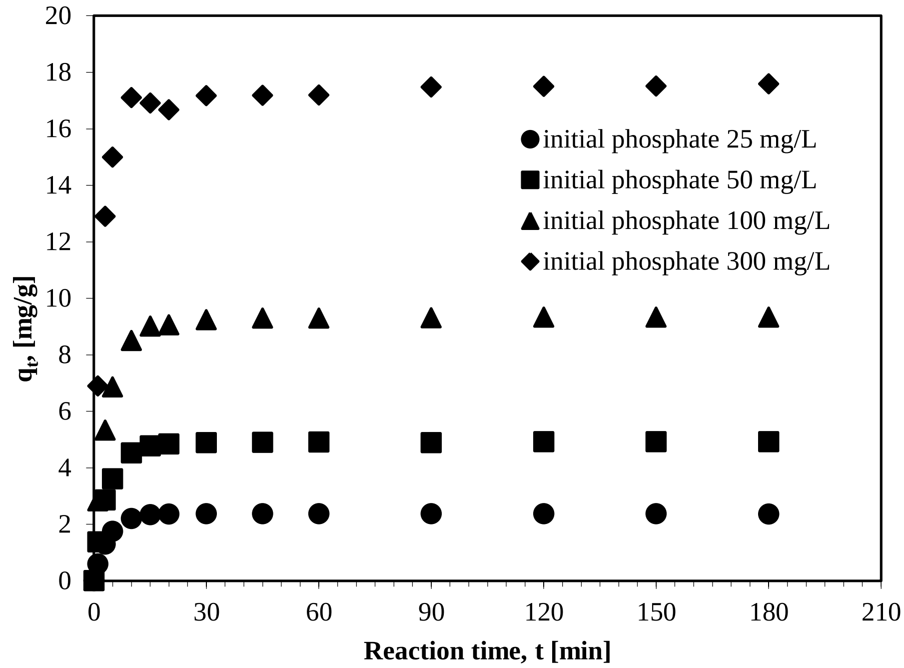


Figure 4.5: Sorption kinetics with different initial phosphate concentrations. LayneRT dosage = 10 g/L, at 25 ^{o}C.

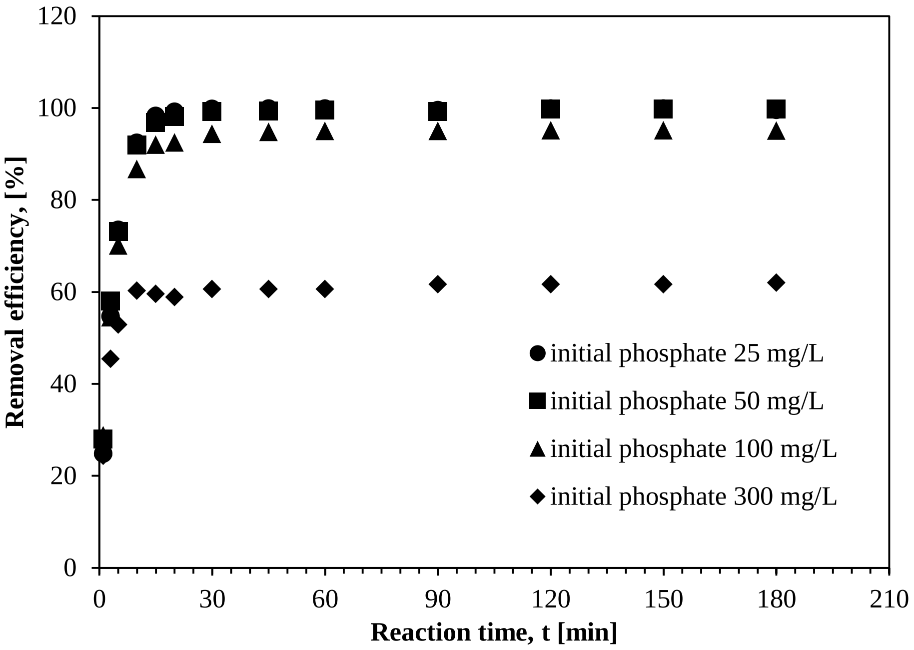


Figure 4.6: Removal efficiency of phosphate from solutions with different initial concentrations.

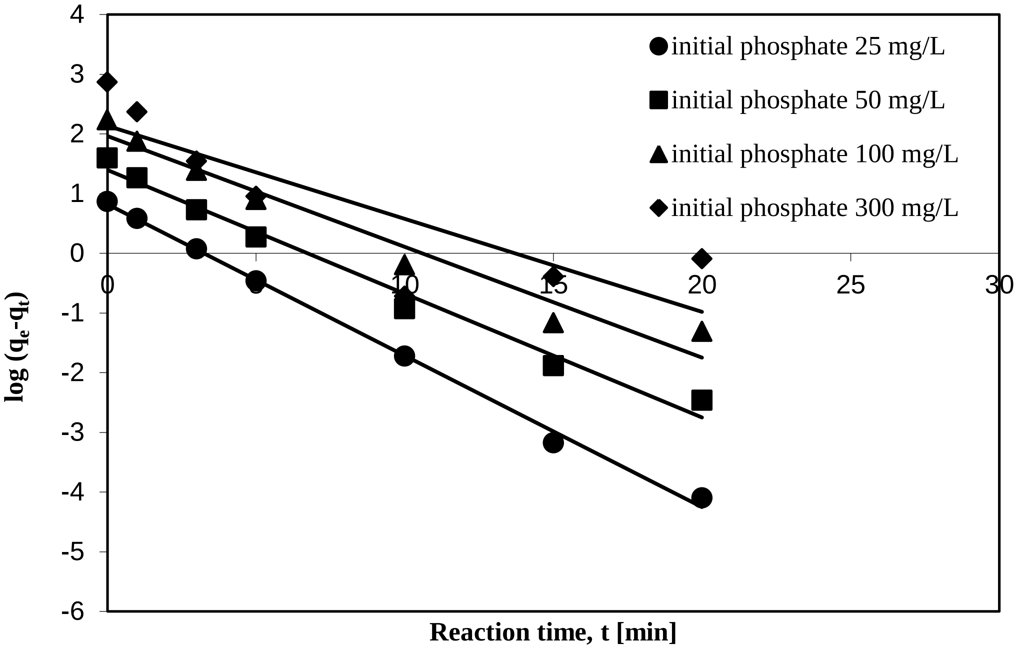
4.2.4 Sorption kinetics

The sorption equilibrium represents a stable state which is established after a sufficiently long contact time between the sorbate in aqueous phase and the sorbent as solid phase, while the sorption kinetics describes the sorption procedure from the temporal perspective. Several kinetic models were proposed to clarify the mechanism of the phosphate sorption from bulk solutions onto the sorbent LayneRT.

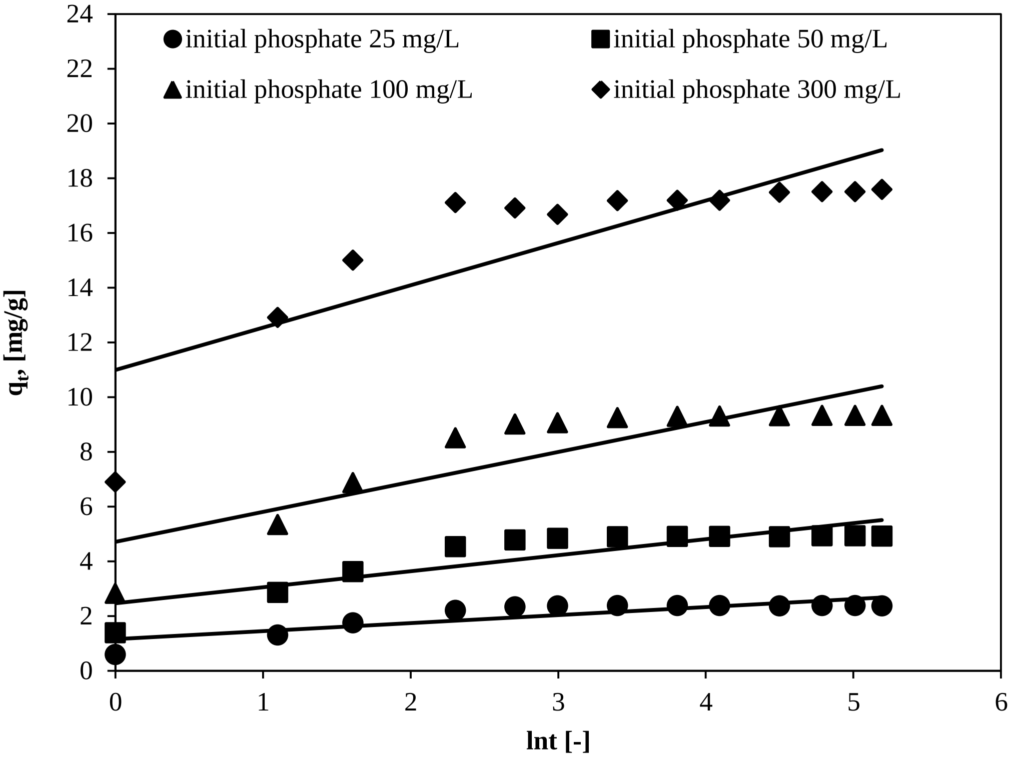
The linearized plots of pseudo-first-order, Elovich and pseudo-second-order models for solutions with different initial phosphate concentrations are presented in Figure 4.7. The calculated kinetic parameters in different model solutions with regression coefficient (R^2) are presented in Table 4.2. According to the value of R^2, it was found that the pseudo-second-order model in Figure 4.7c provided the best match to the experimental data ($R^2 >$ 0.999) all over the sorption process. The good agreement with pseudo-second order model implied that the rate limiting step could be the chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate (Ho and McKay, 2000). The calculated initial phosphate sorption rates ($h = k_2 q_e^2$) were 2.30, 4.59, 8.54, 19.8 mg/g·min in the solutions with initial concentrations of 25, 50, 100 and 300 mg/L, respectively, which increased with the increasing of initial concentrations and implicated that the initial phosphate sorption rate depended on the concentration gradient between the bulk solution and the sorbent surface.

The R^2 of the pseudo-first-order kinetic model was lower compared with those of pseudo-second order models, and it could only describe the very initial phase of phosphate sorption, but not the entire process in all solutions (Figure 4.7a). The pseudo-first-order model was proposed for the second-order reactions in which one of the reactants is present in such great excess concentration that its effect is not seen. In this study, the dose of sorbent and the initial concentration of bulk solutions were proportioned rationally to achieve the kinetics under normal conditions rather than under extreme conditions. Thus, the pseudo-first-order can only match the first phases of the sorption process, because in these early phases the concentrations of sorbate in bulk solution are relatively excessive to the sorbent. And this excess of sorbate gradually disappears as the reactions proceed, so that the pseudo-first-order does not work anymore.

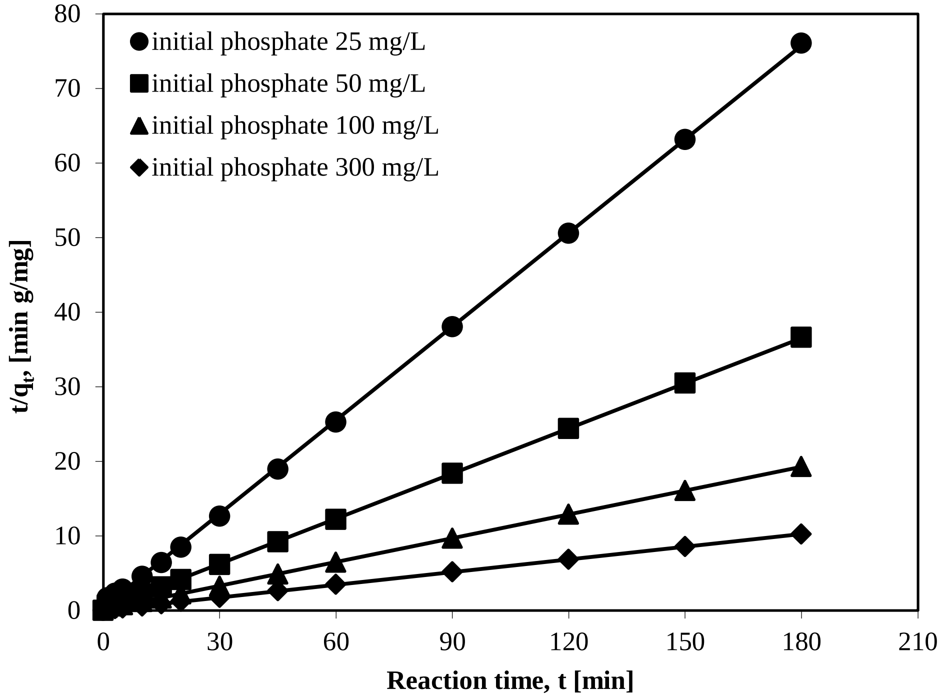
According to the Elovich kinetic model, the rate of sorption decreases exponentially with the loading increase of sorbate on the surface of the sorbent. The general explaination for this kinetic model involves a variation of the energetics of chemisorption with the active sites. These are heterogeneous and therefore, exhibit different activation energies for chemisorption (Teng and Hsieh, 1999). As shown in Figure 4.7b in this study, the Elovich model cannot provide a good match to the experimental results along the entire course of reaction.



(a) Pseudo-first-order kinetic model



(b) Elovich kinetic model



(c) Pseudo-second-order kinetic model

Figure 4.7: Different kinetic models for the sorption of phosphate onto the sorbent LayneRT: (a) pseudo-first-order kinetic model; (b) Elovich kinetic model and; (c) pseudo-second-order kinetic model.

Table 4.2: Kinetic parameters for the effect of initial solution concentration on phosphate sorption onto LayneRT

Experimental data	initial conc.	mg/L	25	50	100	300
	$q_{e,\,exp.}$	mg/g	2.37	4.92	9.32	17.5
Pseudo-first-order *	$q_{1,\,cal.}$	mg/g	2.28	4.03	7.13	8.46
	k_1	L/min	0.607	0.477	0.428	0.359
	R_1^2	-	0.997	0.985	0.959	0.712
Elovich	a	-	14.5	39.8	80.9	1883
	b	-	3.4	1.71	0.913	0.646
	R_E^2	-	0.724	0.742	0.758	0.677
Pseudo-second-order	$q_{2,\,cal.}$	mg/g	2.39	4.96	9.41	17.6
	k_2	g/mg·min	0.402	0.187	0.0965	0.0637
	R_2^2	-	0.999	0.999	0.999	0.999
	h	mg/g·min	2.3	4.59	8.54	19.8

* The modelling via pseudo-first-order equation covered only the first 20 min of the sorption procedure, while the modelling results of other equations covered the entire procedure for 180 min.

The phenomena that fast initial uptake of phosphate followed by slower further adsorption process until equilibrium indicated that the sorption of phosphate onto LayneRT could be more complicated than a single, one-step binding process. However, the pseudo-second-order kinetic model includes the whole removal procedure, such as, precipitation, co-precipitation, external film diffusion, surface adsorption and intra-particle diffusion. Therefore, an intra-particle diffusion model, i.e. the Weber's model, was applied to provide more comprehensive view of sorption as a series of distinct steps. According to Weber's intra-particle model, during the transfer of phosphate from the aqueous phase to the sorbent, the sorbate molecules diffuse from the bulk solution to the porous sorbent and this transfer can be explained step by step. The plotting of Weber's intra-particle model presented a multi-linear relationship between the mass loadings q_t and the square root of time $t^{0.5}$.

Figure 4.8 shows the intra-particle modeling results of phosphate sorption on LayneRT. The curve presented the dependence of the sorption process on the initial concentration of phosphate. As is evident from Figure 4.8, the plots of q_t vs. $t^{0.5}$ at different initial phosphate concentrations are multi-linear, which indicated that more than one process affected the sorption. Based on the plots, the sorption processes of phosphate are comprised of two phases, implying that the intraparticle diffusion is not the rate-limiting step for the whole reaction (Ho and Ofomaja, 2005). The first section of the plot, i.e. the first 15 min reaction, indicated an external mass transfer (boundary layer diffusion) whereas the second linear section after 15 min until the equilibrium was due to intraparticle diffusion (Aguilar-Carrillo et al., 2006). The uptake rate was initially very fast and then slowed down. It is likely that the phosphate molecules are initially transported to macropores and later slowly diffused into micropores (Kumar et al., 2007).

The values of the rate parameters $K_{i,1}$ and $K_{i,2}$ evaluated through regression analysis from the linear slope suggested that the rate parameters for macropore diffusion were higher than those for micropore transports. The decrease in the pore sizes leads to the decrease in the free path of the molecules in the sorbent pores and hence to a decrease in the values of the measured intra-particle rate parameter. As more phosphate is adsorbed on the surface of LayneRT, the pores are covered by the sorbate so that the pore dimensions decrease, the free path becomes smaller, with possible pore blockage occurring and hence the dramatic reduction in diffusion parameters (Koumanova et al., 2003). The value of intercept C refers to the thickness of the boundary layer, and a large C value is indicative of boundary layer diffusion as being significant in the sorption process. Comparing the plotting results, it is apparent that extreme high initial concentration of the bulk solution, i.e. 300 mg/L that were beyond the capacity of the sorbent, led to a thicker boundary layer on the interface of the sorbent due to the relative redundancy of phosphate molecules. Thus in this case of high initial concentration, intra-particle diffusion is not the unique rate-controlling step in the initial phase but also the external mass transfer. But in the cases of reasonable dose ratio, intra-particle diffusion obviously increases with the increase in the concentration gradient between bulk solution and adsorbent surface. The adsorption kinetics for the resin in this study favors its use in a continuous column application.

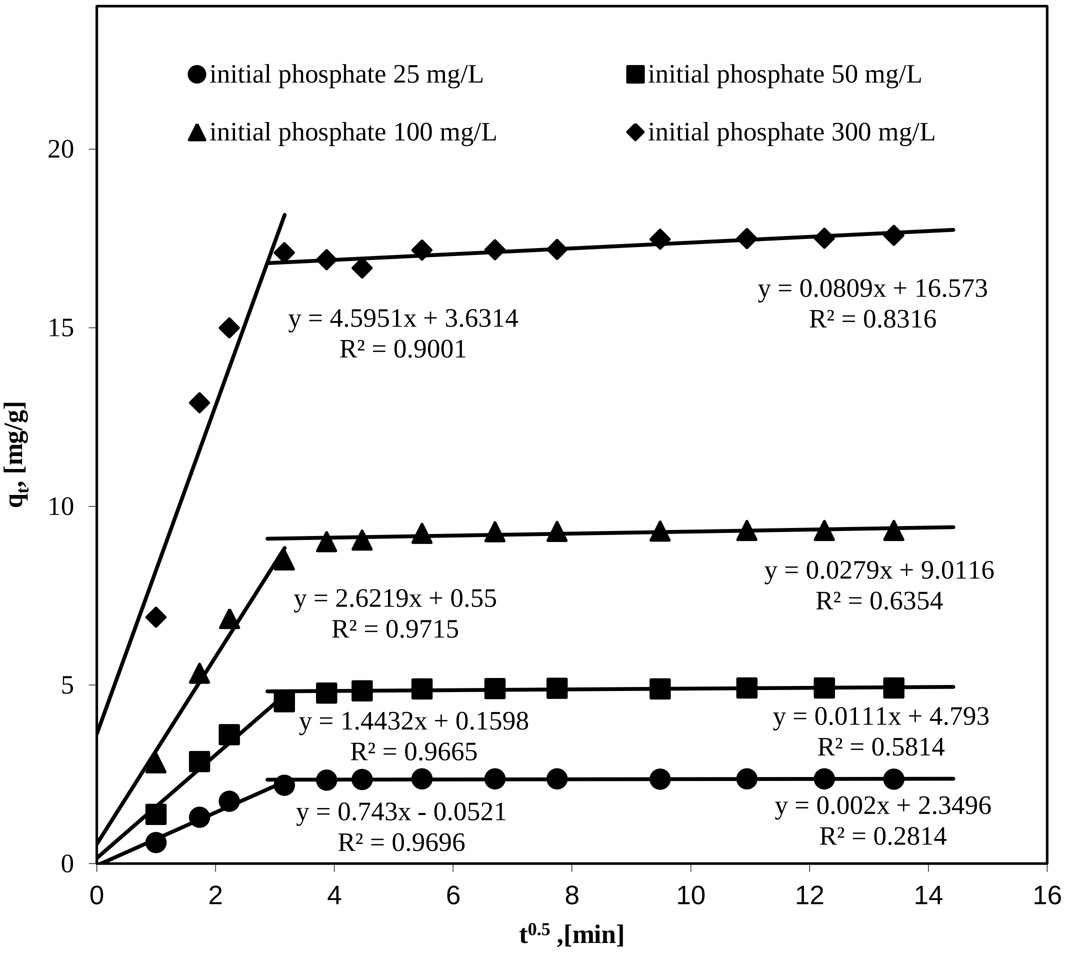


Figure 4.8: Multi-linear plotting with the intra-particle diffusion model according to kinetics data.

Table 4.3: Intra-particle diffusion constants for phosphate sorption onto OH-form LayneRT

Initial conc. of PO_4^{3-} mg/L	$K_{i,1}$	C_1	R^2	$K_{i,2}$	C_2	R^2
25	0.7430	0.0521	0.9696	0.0020	2.3496	0.2814
50	1.4432	0.1598	0.9665	0.0111	4.7930	0.5814
100	2.6219	0.5500	0.9715	0.0279	9.0116	0.6354
300	4.5951	3.6314	0.9001	0.0809	16.573	0.8316

In general, the rate of uptakes in systems with poor mixing, having residual sorbate molecules at low concentration in bulk solutions, high affinity towards sorbent and small particles is governed by external transport. In contrast, transport in systems with different characteristics than those mentioned above is limited by an intra-particle diffusion step (Kumar et al., 2007). The calculation of mass loading via a pseudo-second-order equation and an intra-particle diffusion model were shown in Figure 4.9. Both model calculation results agreed well with the experimental results of the three low ranges of initial concentrations over the entire sorption process. For the high initial concentration of 300 mg/L, intra-particle diffusion was not the unique rate-controlling factor in the first 15min, thus the calculated result in this section was not that coincident with the experimental data.

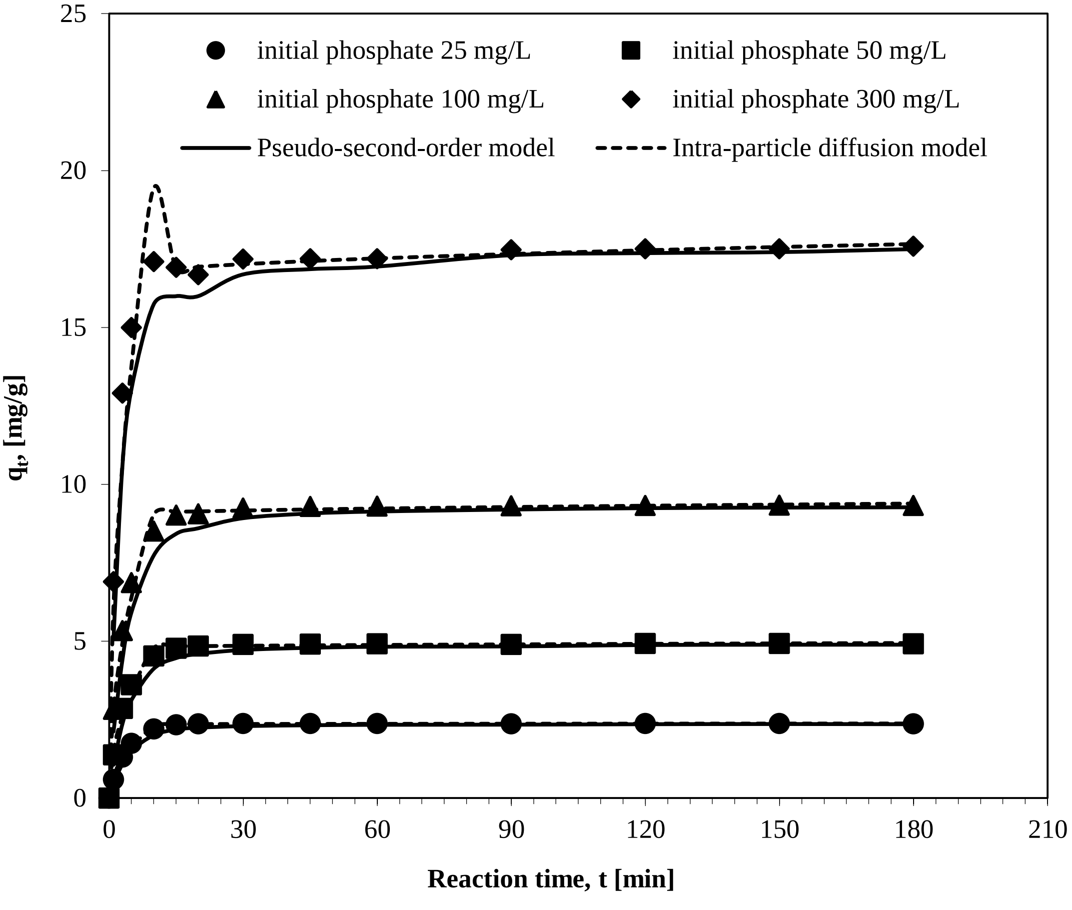


Figure 4.9: Comparison of the experimental outcome and the kinetic modeling calculations (via pseudo-second-order and intra-particle diffusion models) for phosphate sorption.

4.2.5 Influence of competing anions

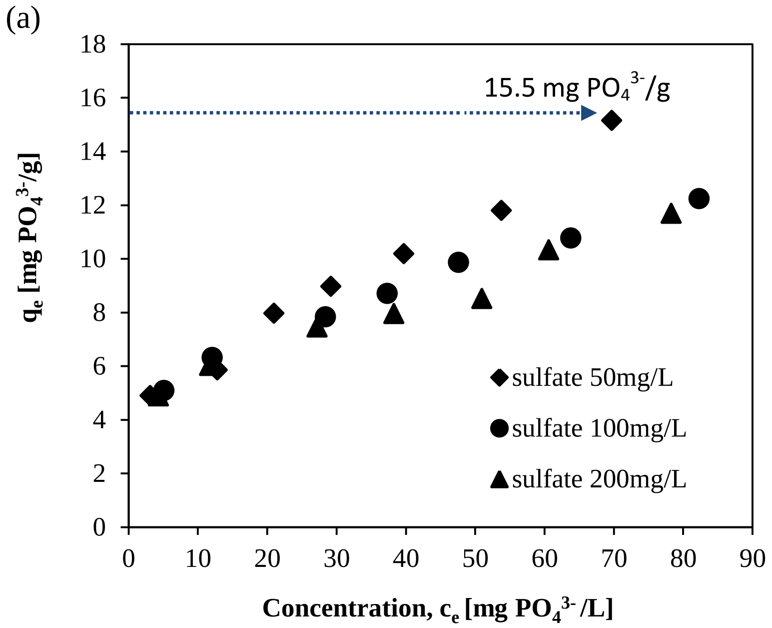
To quantify the effects of potential competing anions such as sulfate, chloride and nitrate on phosphate sorption by LayneRT, isotherm tests were carried out within different synthetic solutions. A group of orthogonal experiment was designed to manage the nine different synthetic solutions containing various ratios of anions. The detail of solution compositions was listed in Table 4.4. All solutions were prepared with a constant initial concentration of phosphate, while the interfering ion had a concentration gradient in each set of experiment. The purpose of this design is to ensure the single variable in each set of experiment so that provides an independent contrast. For example, in the investigation of interference of sulfate, the model solution of Nr. 1, Nr. 2 and Nr. 3 were involved. The initial concentrations of phosphate, chloride and nitrate in the three solutions were identical, i.e. approximate 100 mg/L, 200 mg/L and 10 mg/L, respectively. On the other hand, the initial concentrations of sulfate in the three solutions were gradients as variable 50 mg/L, 100 mg/L and 200 mg/L.

Table 4.4: Experiment design for the investigation of interfering effects of sulfate, chloride and nitrate on phosphate sorption on LayneRT

Nr.		Phosphate mg/L	Interfering ions Sulfate mg/L	Chloride mg/L	Nitrate mg/L	pH value	Conductivity µS/cm
1	Sulfate	101	51.50	207.9	10.4	7.49	276
2		107	94.10	207.5	10.3	7.49	303
3		102	207.9	208.6	9.08	7.38	350
4	Chloride	101	97.70	104.7	9.33	7.24	189
5		102	103.3	220.0	7.94	7.16	273
6		101	95.90	408.4	9.09	7.09	430
7	Nitrate	103	97.70	207.9	10.4	7.34	295
8		105	103.3	207.5	25.5	7.28	317
9		101	102.9	208.6	50.9	7.02	432

The quantified results of interfering effects of competing anions are depicted in Figure 4.10. Detailed information of this test can be found in Appendix 4. As shown in Figure 4.10a, the addition of sulfate in the phosphate-containing solution results in an obvious drop of phosphate sorption capacity from 20 mg/g (Figure 4.4a) to 15.15 mg/g. However, the increase of the sulfate concentration from 50 to 200 mg/L does not aggravate the negative effect on phosphate retention. It can be reasonably interpreted by its specific structure of LayneRT. As introduced in Chapter 3.2.1, the hybrid sorbent Layne RT consists of two basic sections, the anion exchange resin matrix and the dispersed HFO nanoparticles. Generally speaking, any anions including phosphate and sulfate can be effectively ion exchanged onto LayneRT through electrostatic interaction or formation of outer-sphere complexes. Obviously, the added sulfate greatly competes with phosphate for the adsorption sites of LayneRT that result in the reduction of capacity for phosphate sorption. However, HFO interacts with phosphate mainly through the formation of the inner-sphere complexes within the coordination sphere of $FeOH_2^+$ (Khare et al., 2005), but sulfate anions are usually bound by HFO through outer-sphere complex particularly at pH > 6.0 (Lefevre, 2004; Wijnja and Schulthess, 2000). This is why further increase in sulfate concentration made no more negative effect on phosphate sorption by LayneRT.

Similar results of effects of chloride and nitrate on phosphate sorption were presented in Figure 4.10b and 4.10c. The P-sorption capacities in both cases were decreased compared with the maximum capacity of 20 mg/g under ideal conditions (the result of isotherm test in Figure 4.4a). It is widely accepted that multivalent and bivalent anions are preferable to the anion exchanger in bulk solutions, which can be ascribed to their size and charge effects. Besides the particular inner-sphere complex with HFO on the sorbent surface, the multivalent phosphate has better affinity than the monovalent anions such as chloride and nitrate. This priority over sulfate on ion exchange is not that obvious, but still acceptable in the application of P-recovery from sludge liquor, because the content of sulfate in the sludge liquor is much lower than the content of phosphate, cf. Table 3.1 in Chapter 3.1.1 .



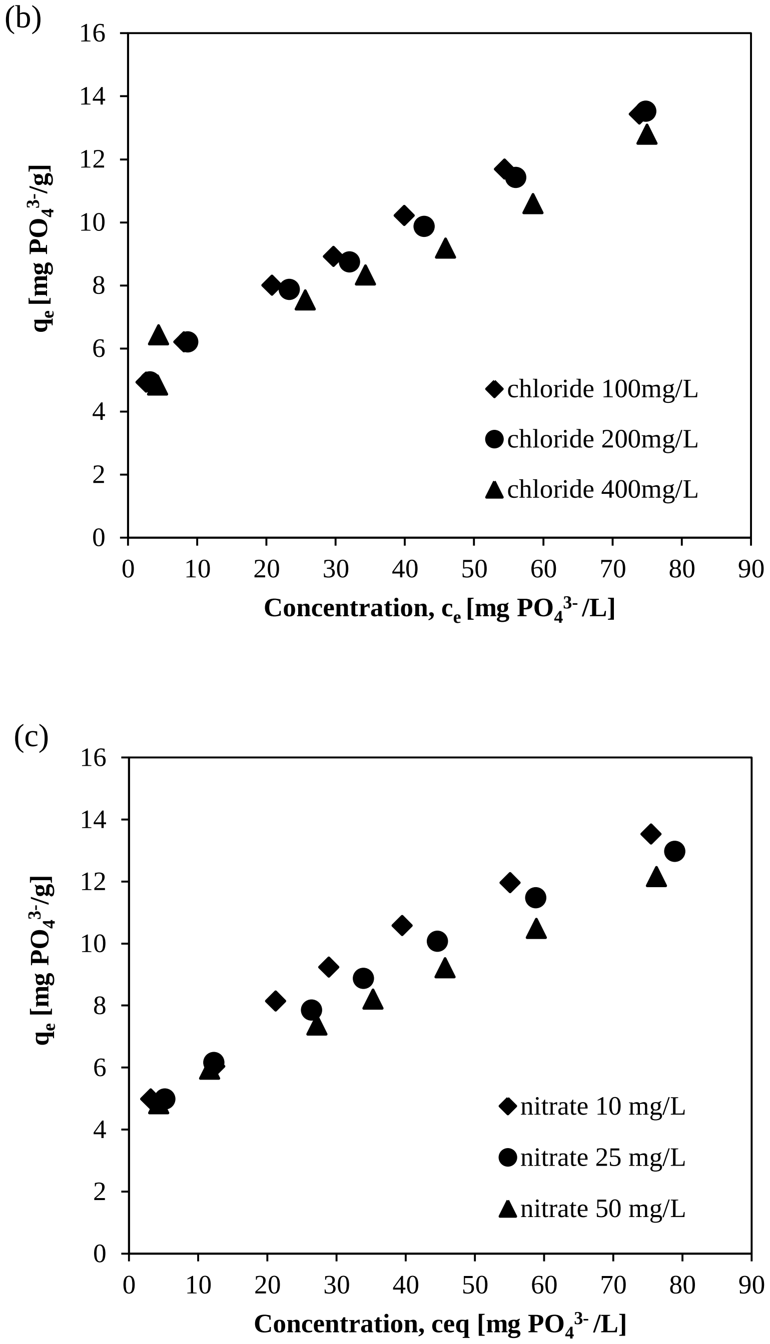
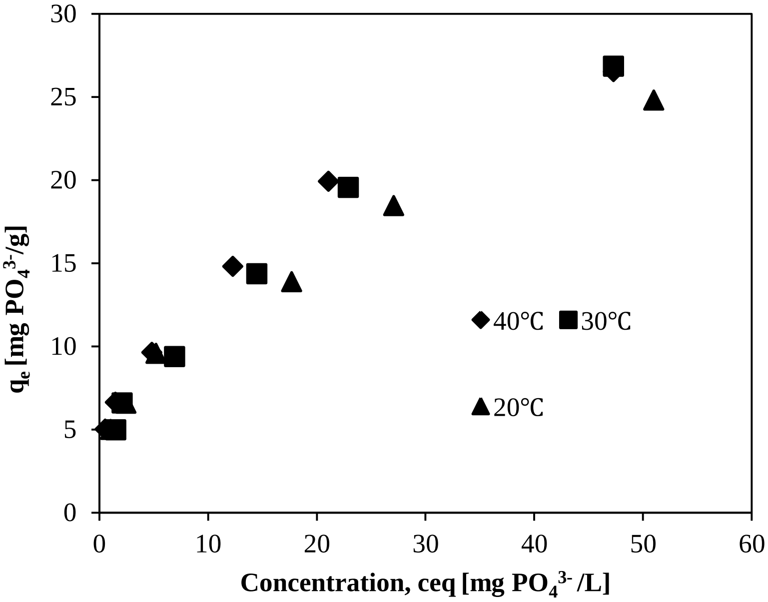


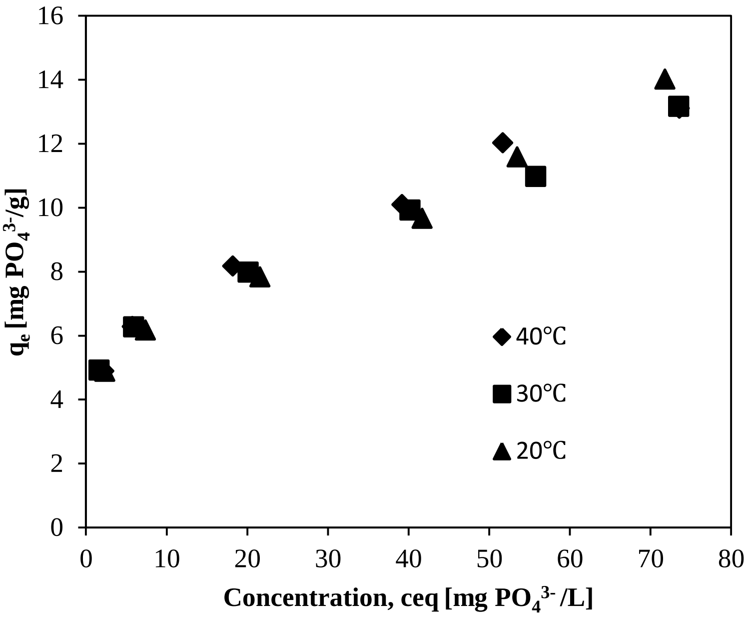
Figure 4.10: Influence of competing anions with different concentrations on phosphate sorption isotherms: (a) phosphate sorption in the presence of sulfate; (b) phosphate sorption in the presence of chloride; (c) phosphate sorption in the presence of nitrate.

4.2.6 Influence of temperature

Ambient temperature is usually a crucial factor of sorption processes. The effect of temperature on phosphate sorption by LayneRT was investigated by the isotherm experiments in the temperature range of 20-40 ^{o}C, since the temperature of digested sludge liquor normally ranges from 20 to 40 ^{o}C. Two different synthetic bulk solutions were prepared to, i.e. in the absence or presence of competing anions. In the pure solution of phosphate, the phosphate sorption capacities of LayneRT increased with an increase in temperature. On the contrary, phosphate adsorption seems to be independent upon the ambient temperature in the presence of sulfate at 100 mg/L, chloride at 200 mg/L and nitrate at 10 mg/L. These results may be attributed to different adsorption mechanisms in the absence or presence of the competing anions. Generally, phosphate sorption by LayneRT can be achieved not only by formation of the inner-sphere complexes with HFO, but also by an anion exchange process onto the porous matrix. Note that a simple anion exchange process driven by electrostatic or Coulombic interaction is an endothermic process in nature (Prevette et al., 2007), and higher ambient temperature is more favorable for phosphate sorption by LayneRT. As for the formation of the inner-sphere complexes, it is usually less dependent upon temperature than anion exchange or formation of outer-sphere complexes (Manjari and Kim, 2006). Without competing anions in solution, both adsorption mechanisms are operative, and the temperature-dependent phosphate adsorption is supposed to result mainly from the anion exchange process. When the competing anions are present at a high level, they compete for the anion exchange sites of LayneRT, and as indicated as Figure 4.11, most of the effective phosphate uptake relies on the dispersed HFO nanoparticles, and this part of P-sorption is less dependent upon the ambient temperatures.



(a) Temperature effect without competing anions



(b) Temperature effect with competing anions

Figure 4.11: Effect of ambient temperature on phosphate sorption by LayneRT: (a) temperature effect without competing anions (initial concentration of phosphate 100 mg/L); (b) temperature effect with competing anions (initial concentration of phosphate 100 mg/L, sulfate 100 mg/L, chloride 200 mg/L and nitrate 10 mg/L).

4.2.7 Molecular weight distribution of sludge liquor

The filtrate collected from the dewatering process of the digested sludge has a complex composition. Dissolved organic matter (DOM) is a complex mixture of many molecules and is usually operationally defined as the organic matter that passes a 0.45μm filter. DOM is usually highly heterogeneous, containing molecules of various molecular weights, ranging from the simple compounds like acetic acid, to more complex polymers like humic and fulvic acids. As already introduced in Chapter 3.1.3, fractionation of organic substances in classes of differdent molecular weight is a current way of characterization of the organic fractions in the sludge liquor.

Before the analysis of sample solutions, a calibration step is necessary. The elution volume of a given substance is dependent on its molecular weight. And for a certain gel bed the same substance is always eluted at the same elution volume (V_e). One may thus determine the molecular weight of an unknown substance from its elution volume. In the experiment described in Chapter 3.1.3 we used 3.53 g dry Sephadex G-50 to obtain a gel bed volume (V_t) of 41 mL. A set of standards with different molecular weights (MWs) were involved to calibrate the Sephadex size exclusion system. The substances used for calibration should be closely related to the substances to be studied. All standards selected (Müller et al., 2000), as shown in Table 4.5, were prepared with the solvent of 0.15 M

NaCl. As shown in Figure 4.12, the construction of an elution pattern was plotted on the ordinate the DOC concentration of fractionated effluents and on the abscissa the volume of the effluent. The effluent volume measured at the elution of a component in maximum concentration is known as the elution volume (V_e) for that component (Determann, 1969).

Table 4.5: Standards for calibration of size exclusion chromatography (SEC) (Müller et al., 2000)

Standard Unit	Molecular weight [Dalton]	Concentration [mg/L]	DOC* [mg/L]
Poly (sodium 4-styrenesulfonate)	~ 70000	600	209.8
Polyethylenglycol 4000	3500 - 4500	600	273.0
Polyethylenglycol 2000	1900 - 2200	600	270.3
NADP-dinatrium salt	787.4	600	165.1
Glucose	180	600	235,3

* tested by DIMA TOC 100

The standards eluted from the gel bed in order of decreasing molecular weight and at rates corresponding to the retention time in the stationary gel phase, which in turn is dependent on diffusion. The Sephadex G-50 column has a fractionation range between 500 and 10000 Dalton. Owing to its high molecular weight (~70000 Dalton), Poly (sodium 4-styrenesulfonate) did not diffuse into the gel grains, and this can represent the elution behavior of the substances, whose MWs are higher than 10000 Dalton. Only the space between the gel particles, i.e. void volume (V_o), is available for it. Glucose, on the other hand, owing to its low molecular weight, representing the elution behavior of low MW substances (<500), penetrated completely into the swollen Sephadex and therefore left the gel bed at last. By measuring the volume at which Poly (sodium 4-styrenesulfonate) was eluted from the gel, the volume outside the gel grains was determined as V_o = 18.2 mL. The elution of glucose, however, was expected to be capable of entering into all regions of the gel bed and as a result the sum of the void and inner volumes is required for its elution. The experimental elution volume for glucose was 42.2 mL, thus the inner volume (V_i) could be calculated to 24.0 mL.

The original experimental data from the size exclusion chromatography with standard solutions can be found in the Appendix 5. The elution behavior of a substance in the chromatography can be described by different variables which are derived from the elution volume V_e (Determann, 1969). As shown in Figure 4.13, the plot of logV_e against log$M$ presented a good linear relationship, which is evident to the dependence of the elution volume on the molecular weight (M). The relationship between the logarithms of the V_e and the M of standards was:

$$\log V_e = -0.3115 \ \log M + 2.4799 \tag{4.6}$$

and the correlation coefficient R^2 was 0.9647.

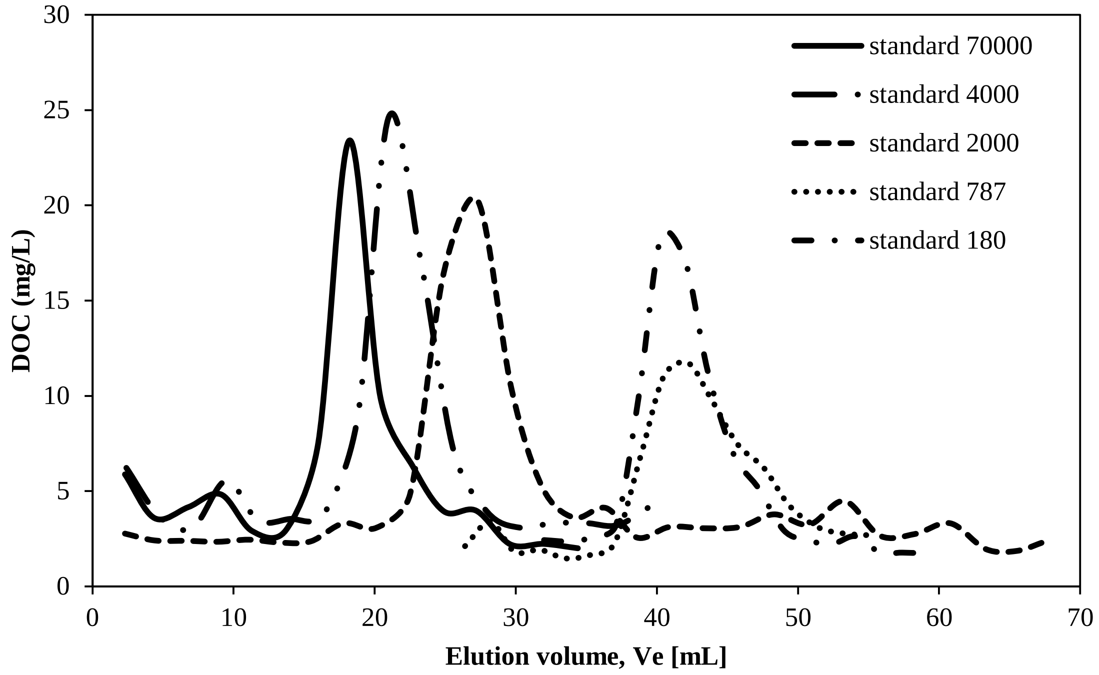


Figure 4.12: Calibration for the Sephadex size exclusion chromatography system with standard substrates: Poly (sodium 4-styrenesulfonate) (MW~ 70000), Polyethylenglycol 4000 (MW 3500- 4500), Polyethylenglycol 2000 (MW 1900- 2200), NADP-dinatrium salt (MW 787) and glucose (MW 180).

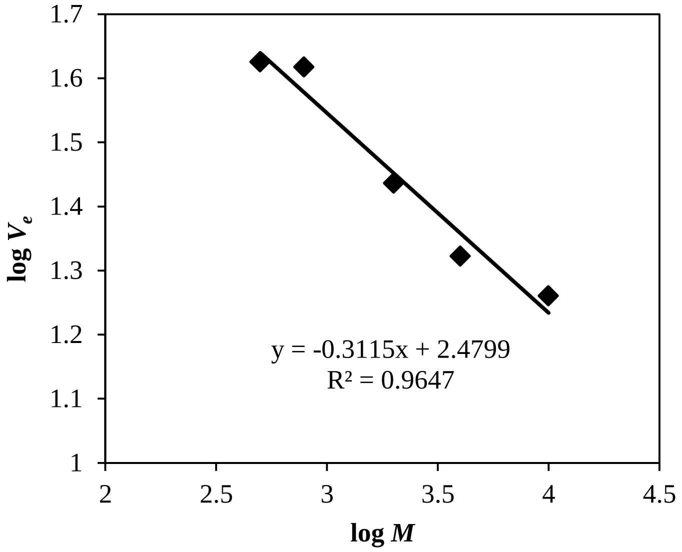


Figure 4.13: The relationship between the logarithms of the elution volume (V_e) and the molecular weight (M).

Based on the equation 4.6, the molecular weight distribution of an unknown substrate can be calculated according to the elution volume of the substrate from the SEC test. The limit of fractionation of this SEC ranged from 500 to 10000 Da, which was determined by the property of the chromatography gel.

After the calibration, the sample of 1.0 mL digested sludge liquor was injected into the Sephadex-50 column to investigate its molecular distribution of dissolved organic matter. The concentration of dissolved organic carbon (DOC) of the sludge liquor is 645 mg/L, thus the amount of DOC that was injected into the column was 645 μg. As a result, depicted in Figure 4.14 and Appendix 6, a small portion (3.5%) of the molecules eluted between the V_e of 15.7 and 21.6 mL, and the majority (95.72%) eluted between the V_e of 31.8 and 59.5 mL. The recovery ratio of DOC in the sample was over 98%. According to the calibration and the equation 4.6, the molecular weight of the early elution could be calculated higher than 6500 Da; and the molecular weight of the majority fraction was lower than 1300 Da. This result of the fractionation indicated that the low molecular weight organic matter was the predominant group, of DOM in the digested sludge liquor.

The second fractionation experiment was performed after the reaction of phosphate sorption by LayneRT from the digested sludge liquor. The concentration of DOC in the sludge liquor after sorption decreased to 453 mg/L, since a portion of DOM in the sludge liquor was removed by the sorbent. The 1.0 mL sample containing 453 μg DOC was fractionated, and the result was presented in Figure 4.14 and Appendix 6. Compared with the fractionation result before the sorption process, the second sample has almost the same molecular weight distribution, as the molecule elution occurred in the same ranges of the elution volumes. From Figure 4.14, one can see that the amount of low molecular organic matters was reduced obviously, while the organic matters with high molecular weight remained as before the sorption. The total amount of DOC fractions eluting between the V_e of 32.3 and 58.2 mL decreased to approximate 400 μg after sorption, compared with the total amount of DOC, 617 μg in this range before sorption.

It could be inferred that the low molecular weight volatile fatty acids contributed predominantly to the concentration of DOC in the sludge liquor. Significant amounts of these fatty acids are produced during the hydrolysis and acidogenesis stages of the anaerobic digestion for sludge. Normally they are further converted to methane and carbon dioxide. The individual acids are seldom determined separately; nevertheless they have some common characters that they all have short chain of six carbon or few and they are usually negatively charged. The relatively small size of molecules and the negatively charged surface make them easily be adsorbed onto the sorbent, compete sorption sites with phosphate ions and consequently reduce the capacity for phosphate sorption.

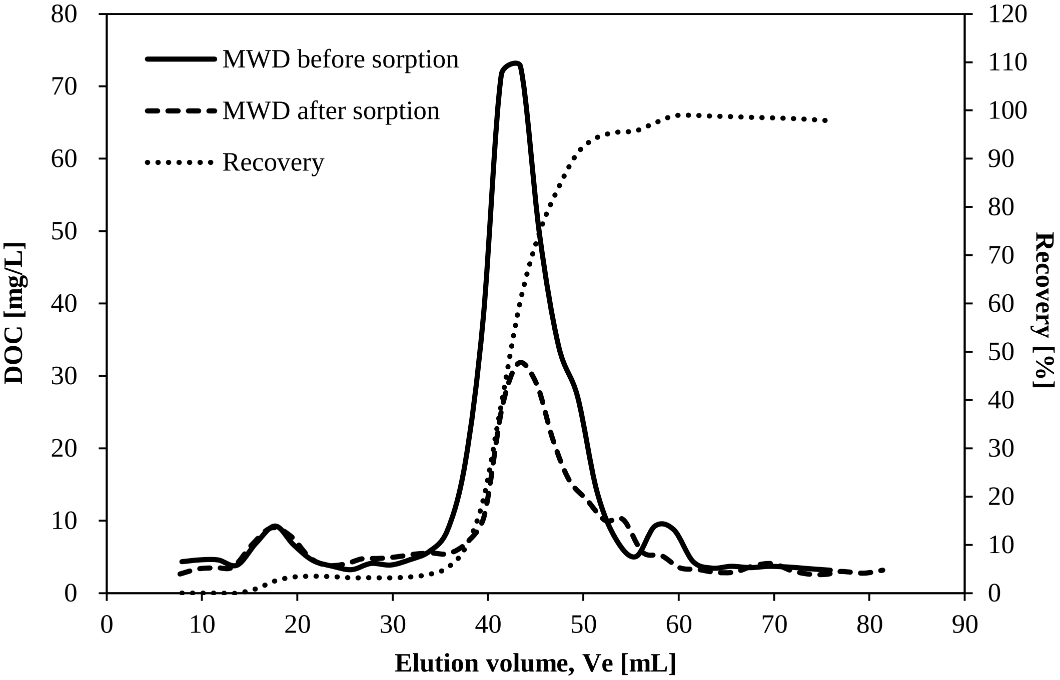


Figure 4.14: Molecular weight distribution of filtrated sludge liquor before and after LayneRT sorption.

4.3 Continuous experiments in fixed-bed column

Successful design of a column sorption process requires a description of the dynamic behavior of sorbate in the column. Continuous experiments of the phosphate sorption by LayneRT were operated in a fixed-bed column, as described in Chapter 3.4. Synthetic and actual sludge liquor solutions were fed from the bottom, percolated through the LayneRT granules in the fixed-bed, and subsequently discharged from the top of the column. The effluent was collected at regular intervals with an automatic sampler and afterwards analyzed to gather information of the sample fractions. The performance of the LaynerRT column for phosphate sorption was presented under different operation conditions. Each run of the column was operated until no further phosphate was sorbed, i.e. phosphate concentration in the effluent $C \approx$ phosphate concentration in the influent C_0. The breakthrough curve for a column run was determined by plotting the ratio of C/C_0 against the number of bed volumes.

4.3.1 Influence of flow rate

The flow rate affects the retention time of the sorbate in the column, during which the solution being treated is in contact with the sorbent and hence, affects the sorption performance, especially if the sorption is diffusion controlled (Ho et al., 1991). A synthetic solution with a concentration of phosphate of approximately 350 mg/L was used for the tests of flow rate. The flow rate of each run was controlled with the peristaltic pump at 4 mL/min, 8 mL/min and 12 mL/min, respectively, and thus, the corresponding retention times in the column ranged approximately 18 min, 9 min and 6 min.

The breakthrough curves were slightly influenced by the flow rates as depicted Figure 4.15, where it is apparent that the highest flow rate results in an earlier breakthrough and a reduction in the bed capacity (Ko et al., 2001). This effect is probably because at high flow rates homogenous distribution is hardly achieved, the decrease in residence time restricted the contact of phosphate ions to the sorbent. The phosphate ions did not have enough time to diffuse into the pores of the sorbent and they exited the column before equilibrium occurred. As also shown in Figure 4.15, the breakthrough curves of the two runs with lower flow rate presented similar breakthrough points around 45 bed volumes. However, the breakthrough curve getting from the 8 mL/min operation has a sharper front compared with the breakthrough curve of the 4 mL/min operation. This sharpness of the curve represented a preference of reaching equilibrium status and a high efficiency of phosphate sorption as well. Thus the flow rate of 8 mL/min was selected to be the operating flow rate in the following continuous experiments in the fixed-bed column.

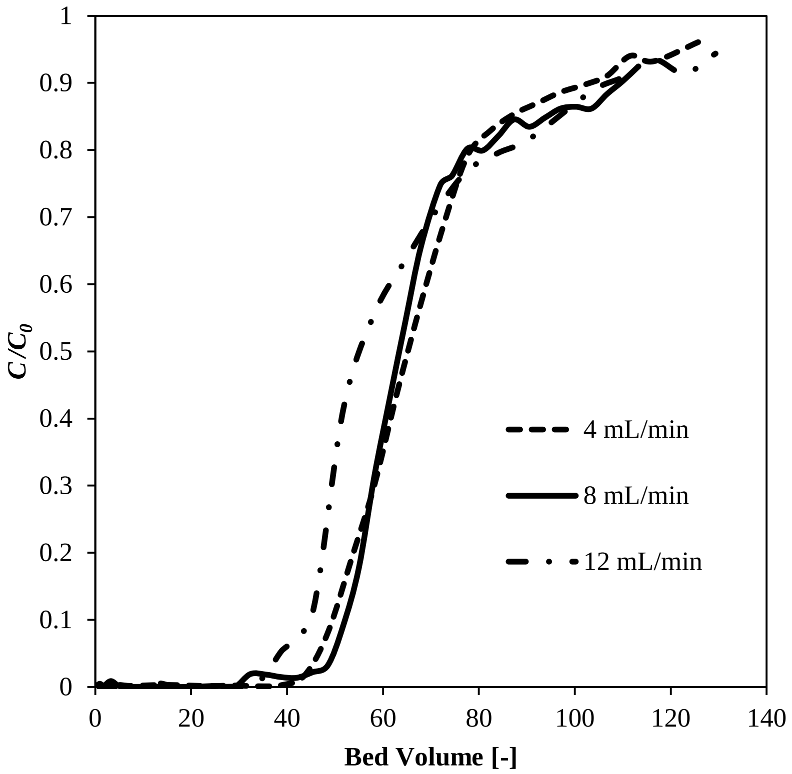


Figure 4.15: Influence of flow rate on the phosphate breakthrough of the column (pH 8.15, phosphate concentration of model solution ~ 350 mg/L).

4.3.2 Performance with model solution

The model solution for the continuous operation was prepared with K_2HPO_4 for the initial phosphate concentration of 338 mg/L, at pH 8.12. The operation flow rate was controlled consistantly at 8 mL/ min. The phosphate breakthrough of the column with the model solution and the phosphate accumulating progress in this column run were depicted in Figure 4.16 and more information were presented in Appendix 7. The software TableCurve 2D was applied to simulate the non-linear breakthrough curves. On basis of the best fit equation that was generated by TableCurve 2D, the phosphate loading on the sorbent in column at the time t, i.e. q_t (mg/g), could be calculated via the equation 2.25.

In this study the breakthrough point is considered at where the ratio C/C_0 reached 0.05, i.e. the effluent concentration is about 5% of the influent concentration. The breakthrough point emerges after the running of 40 bed volumes (V_b). And the phosphate loading at this breakthrough point is called the breakthrough capacity (q_b) , which equals to 20 mg/g in this run. After the running of approximate 120 bed volumes (V_x), the ratio C/C_0 reached 0.95, i.e. the effluent concentration is about 95% of the influent concentration, that indicated the sorbent in the column is almost exhausted. The phosphate loading at this exhaustion point is defined as the amount of phosphate sorbed by unit weight of the sorbent at saturation status, that is the exhaustion capacity (q_x) over 30 mg/g in this run. The degree of column utilization is another important feature, which is defined as the ratio between the breaktrhough capacity and the exhaustion capacity, i.e. q_b/q_x, which is about 0.65 in this run of the column.

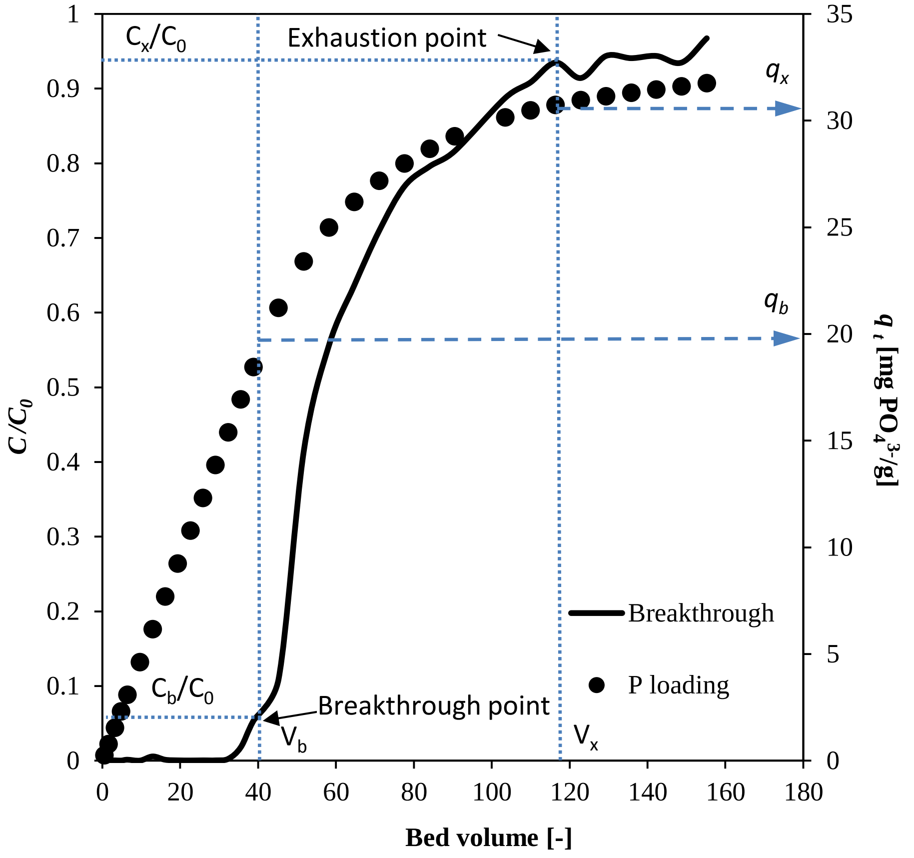


Figure 4.16: Phosphate breakthrough of the column with the model solution at pH 8.12.

Compared with the result of sorption capacity of LayneRT that was obtained from batch experiments, the breakthrough capacity was accordance to the batch capacity (~ 20 mg/g), while the exhaustion capacity was higher. Similar results were reported by Tor et al. (2009) and Gupta et al. (2001). The difference in maximum sorption capacity between batch and column studies may be that the sorbent has pores that favor enhanced the diffusion in solid phase relative to the batch tests (Chen et al., 2011).

The data of operational parameters obtained in this investigation gives an idea of the running time for breakthrough emerging, and helps to determine how much sample solution could be treated before the complete exhaustion of the sorbent in column. These data can also be useful for the design of fixed-bed reactors that would be applied for sorption reactions in larger scales.

4.3.3 Performance with actual sludge liquor

After the determination of operating parameters in the continuous experiment with model solution, actual digested sludge liquor was used to assess the column performance under more complicated conditions. The sludge liquor from sewage treatment plant Rastatt had initial concentrations of 170 mg/L phosphate, 10.6 mg/L sulfate, 304 mg/L chloride and 745 mg/L COD. The pH value was 8.17. Breakthrough curves of each component in the sludge liquor were depicted in Figure 4.17 and more information were presented in Appendix 8. The breakthrough point of phosphate appeared after elution of around 20 bed volumes. After elution of 45 bed volumes, the value of C/C_0 reached 95%, which means the sorbent LayneRT in the column was almost exhausted. The phosphate loading on the sorbent along with the continuous operation could be calculated with the help of the software TableCurve 2D. As shown in Figure 4.17, the maximum bed capacity for phosphate in this case was 7 mg/g, which is much lower Compared with the bed capacity of 30 mg/g in the experiment with phosphate model solution (Figure 4.16). The interfering anions and dissoloved organic matter (DOM) could be the main cause of this capacity reduction.

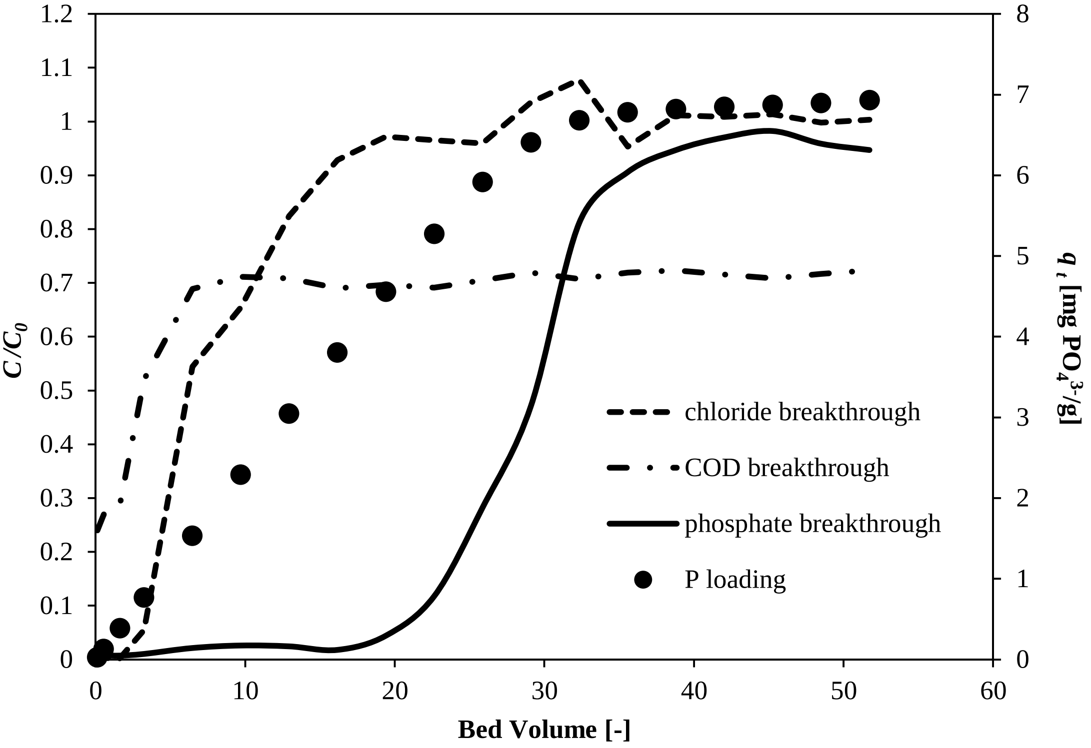


Figure 4.17: Breakthrough of the column for each component in filtrated sludge liquor at pH 8.17, with the initial concentration of phosphate 170 mg/L, sulfate 10.6 mg/L, chloride 304 mg/L and COD 745 mg/L.

The behavior of anions during the column operation were tested because they may hinder the phosphate sorption efficiency. This effect is probably due to competition between the phosphate and the other anions. However, compared with the amount of phosphate, the amount of sulfate and nitrate is relatively low, thus the effects of the ions are limited. On the other hand, the chloride concentration in sludge liquor is normally higher than the concentration of phosphate. As a result of the previous batch tests, we know that the presence of chloride reduced the sorption capacity for phosphate from 20 mg/g (Figure 4.4a) to 14 mg/g (Figure 4.10b), that is a reduction of 30%. For this reason, in the contineous test, the chloride is also accountable to the bed capacity reduction. It is noticeable in Figure 4.17 that the ratio C/C_0 of the chloride breakthrough curve is in excess of a unity between 29 and 45 bed volumes. This phenomenon is caused by the chromatographic elution effect of chloride ions, that some chloride anions initially loaded on LayneRT are replaced by phosphate ions due to their different sorption preferenc when insufficient sites are available (Pan et al., 2009).

The abundance of DOM in sludge liquor is another negative factor for phosphate sorption. The competitive relation between phosphate and DOM on different sorbent materials has been extensively studied before. As discussed in Chapter 4.2.7, low molecular weight organic acids are the main constituent of the DOM in sludge liquor. In this column test, the amount of DOM was represented by the parameter COD, mg/L. As shown in Figure 4.17, it is apparent that the COD started breaking through the sorbent bed with the ratio of C/C_0 around 0.25 from the very beginning of the operation. After the running for 8 bed volumes, the value of C/C_0 reached 70% and kept constant throughout the trial until the exhaution of the column. This indicated that DOM is another main cause of the dramatic reduction of the phosphate sorption capacity, since over 30% of the DOM remained in the column and occupied sorption sites on sorbent. The negative charged DOM would also contaminate the sorbent media and affect the mass flux of the column.

Other researchers (Guan et al., 2005) elucidated that the presence of small DOM such as humic acids with concentrations of 15 and 30 mg C/L suppressed phosphate adsorption by 21-46 and 48-66%, respectively on aluminum hydroxide surface. Previous studies (Nordin et al., 1997) also indicated that aromatic carboxylic acids were predominantly adsorbed on metal hydroxides by forming outer-sphere complexes. The presence of low molecular weight organic acids decreased the affinity of phosphate for adsorption on the sorbent; therefore, it is essential to take the competitive interaction of phosphate and organic matters into account in the column design and operation as well as in predicting the yield of phosphate recovery from sludge liquor.

4.3.4 Influence of pH value

Since the complex composition is a great hindrance for phosphate recovery with the sorbent column, reasonable modification of the column influent is needed. Among the various boundary conditions of the sorption process, pH value is the most important single parameter affecting the sorption capacity of the sorbent LayneRT. The initial pH value also reflects the nature of the physicochemical interaction of the species in solution and the adsorptive sites of adsorbent. The effect of pH on the breakthrough curves was tested at pH values of 6.5 and 5.5. The pH value of inlet sludge liquor was adjusted with HCl solutions prior to the column tests. The operation flow rate was kept constant at 8 mL/min.

Figure 4.18 and 4.19 presented the breakthrough curves of each component in sludge liquor at two different pH values. Detailed experimental data can be found in Appendix 9 and 10. In the case of pH 6.5 shown in Figure 4.18, the breakthrough of phosphate appeared around 48 bed volumes, while the exhaustion appeared around 70 bed volumes, where the value of C/C_0 reached 95%. The maximum bed capacity for phosphate in this trial was achieved over 10 mg/g, which is still lower than the ideal bed capacity but higher than the one achieved in the trial of original sludge liquor at pH 8.17 (Figure 4.17).

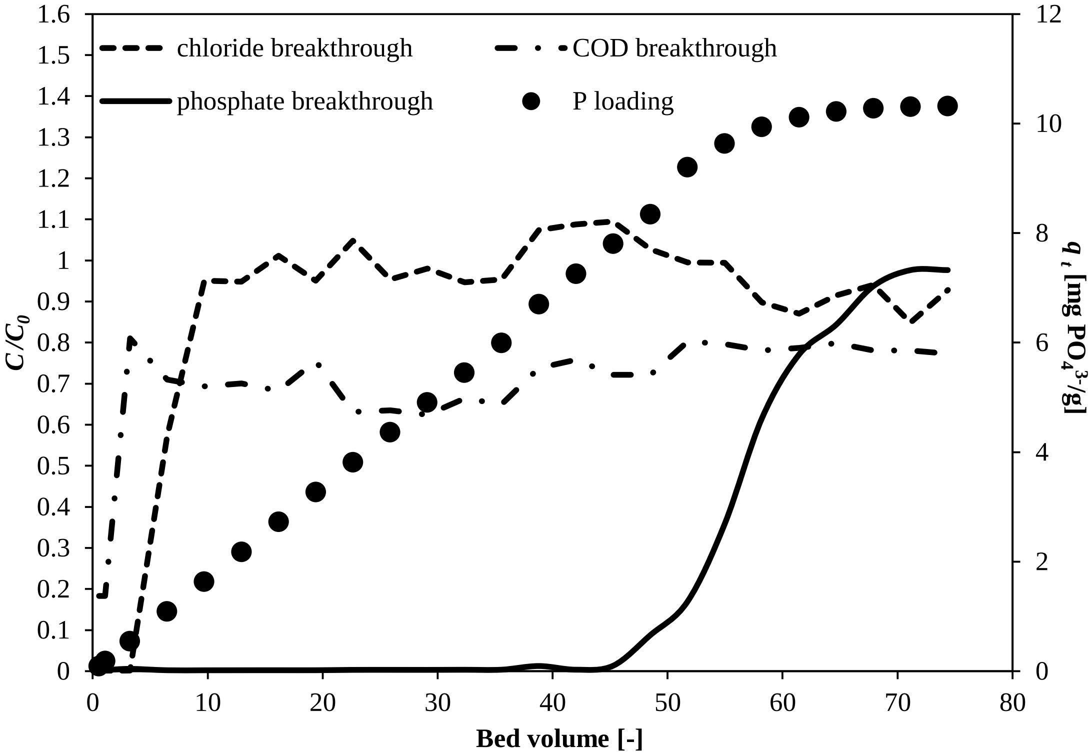


Figure 4.18: Breakthrough of the column for each component in filtrated sludge liquor at pH 6.5, with the initial concentration of phosphate 120 mg/L, sulfate 11.3 mg/L, chloride 2861 mg/L and COD 548 mg/L.

Since an HCl solution was used for pH adjustment, the chloride amount in this test is massive, i.e. 2861 mg/L. However, more than 90% of the chloride was eluted from the column and did not aggravate the reduction of phosphate sorption. This means around 280 mg/L chloride were adsorbed by the sorbent, which is in accordance with the results of the competing tests in batch experiments. This also implies that although the presence of chloride had negative effects on phosphate sorption the increase of chloride amount did not aggravate the reduction of phosphate sorption capacity. The behavior of DOM was similar to that at pH 8.17, but a higher elution ratio of 70-80% was observed, which implies less DOM was remained in the column at pH 6.5.

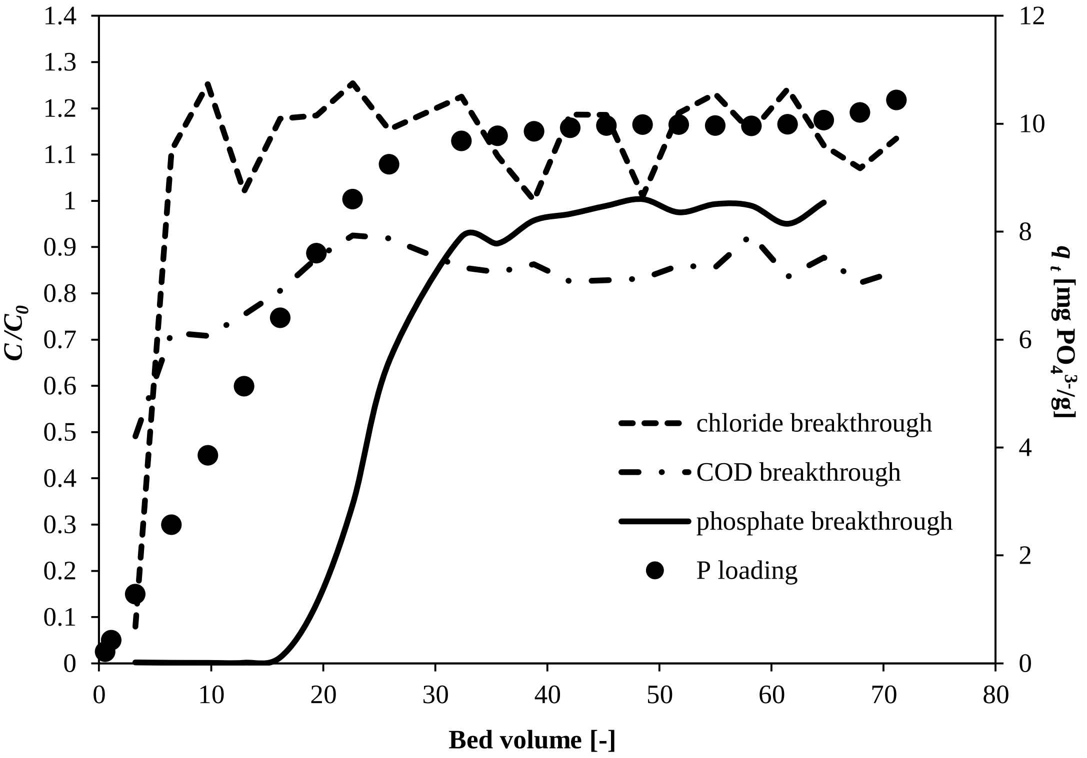


Figure 4.19: Breakthrough of the column for each component in filtrated sludge liquor at pH 5.5, with the initial concentration of 282 mg/L phosphate, 20.6 mg/L sulfate, 4466 mg/L chloride and 750 mg/L COD.

For the test at pH 5.5, the sludge liquor as influent had higher initial concentrations of phosphate (282 mg/L), sulfate (20.6 mg/L), chloride (4466 mg/L) and COD (750 mg/L). As shown in Figure 4.19, the breakthrough point of phosphate appeared early around 18 bed volumes, while the exhaustion appeared around 40 bed volumes. The maximum bed capacity for phosphate in this test was achieved over 10 mg/g in much the same as the bed capacity at pH 6.5. The breakthrough curve of chloride at pH 5.5 presented a complete elution of chloride, in which the value of C/C_0 stayed above 1.0 after the running of 5 bed volumes. This phenomenon may imply that at lower pH condition the chloride contributed less to the reduction of the phosphate sorption capacity, since it was not constantly retained in the sorbent bed but eluted out of the column. The elution ratio of DOM at pH 5.5 increased even above 90%, which implies the rational decreasing of pH value can diminish the negative affect on phosphate sorption from DOM.

Comparing the breakthrough curves in Figure 4.18 and 4.19, besides the influence of anions and DOM under different pH conditions, the influent concentration of phosphate affected the operating duration as well. The increase of initial concentrations of the phosphate influent accelerated the sorption rate of phosphate and consequently brought about an earlier leakage of phosphate ions from the column. However, the higher initial concentration did not reduce the maximum bed capacity for phosphate. This is because a higher concentration gradient promotes the molecule diffusion at the interface between the bulk solution and the sorbent, which is favorable for the ion sorption process. But this high concentration gradient does not change the properties of the sorbent material.

4.4 Regeneration of exhausted LayneRT

4.4.1 Regeneration in batch experiment

At the end of a complete sorption process, the equilibrium between liquid and solid phases is achieved and the sorbent is exhausted. Normally a regeneration process is followed to obtain desorption of adsorbed molecules from the sorbent media, and a regenerated sorbent for reutilization. The regeneration of LayneRT could be accomplished by a variety of techniques such as thermal desorption, steam washing, solvent extraction, etc. Each method has inherent advantages and limitations. 1.0M NaOH solution was used to elute and recover phosphate from the spent sorbent.

The regeneration efficiency of LayneRT was investigated by repetitive plotting of sorption isotherm of different batches of regenerated sorbent in a group of 10 centrifuge tubes. These tubes were dosed with identical amount of phosphate model solutions and gradient amout of LaynerRT for the isotherm plotting.

After one hour reaction for desorption, the phosphate concentration (C_r) in each tube was tested and compared with the initial phosphate concentration (C_0) of the treated solution, i.e. P-source solution. The concentration C_r represented the amount of phosphate that was recovered from the spent sorbent. The concentration ratio between C_r and C_0 indicated the recovery ratio of phosphate from the initial solution.

As shown in Figure 4.20, the sorbent LayneRT made a good performance for phosphate recovery in every batch of experiment. The phosphate recovery ratio after the regeneration was defined as the ratio between the equilibrium concentration of desorption and the adsorbed concentration of phosphate on the sorbent. It presented the degree of the phosphate desorption from the exhausted sorbent. After the first regeneration of the sorbent, the phosphate recovery ratio ranged at 83.7-100.3%; after the second regeneration, the recovery ratio ranged 94.1-100.1%. The phosphate desorption of the third regeneration was not tested because the spent sorbent in ten tubes was all mixed and regenerated all in one beaker flask. For the forth cycle of sorption, a new solution containing lower phosphate concentration (190 mg PO_4^{3-}/L) was used for isotherm plottings, and the gradient dose of sorbent was reweighed in each tube. However, this change of experimental set did not reduce the phosphate recovery efficency. The phosphate recovery ratio ranged at 96.6-99.1%. The product of phosphate recovery from this desorption process is high-purity sodium phosphate due to the regenerant NaOH.

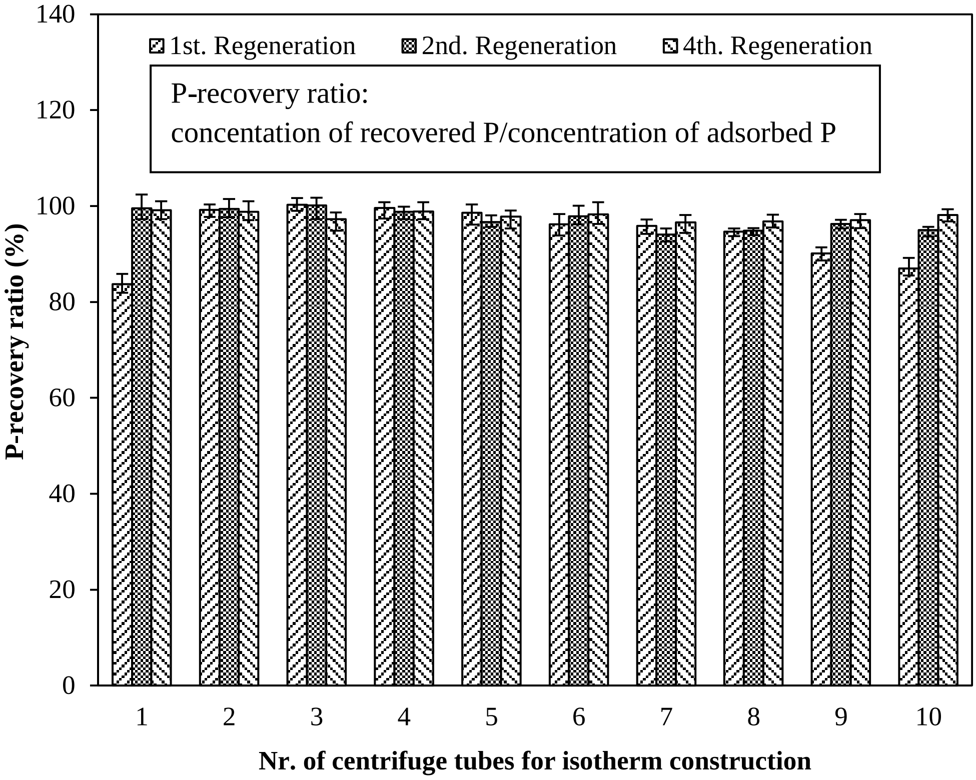


Figure 4.20: Regeneration efficiency of the sorbent LayneRT.

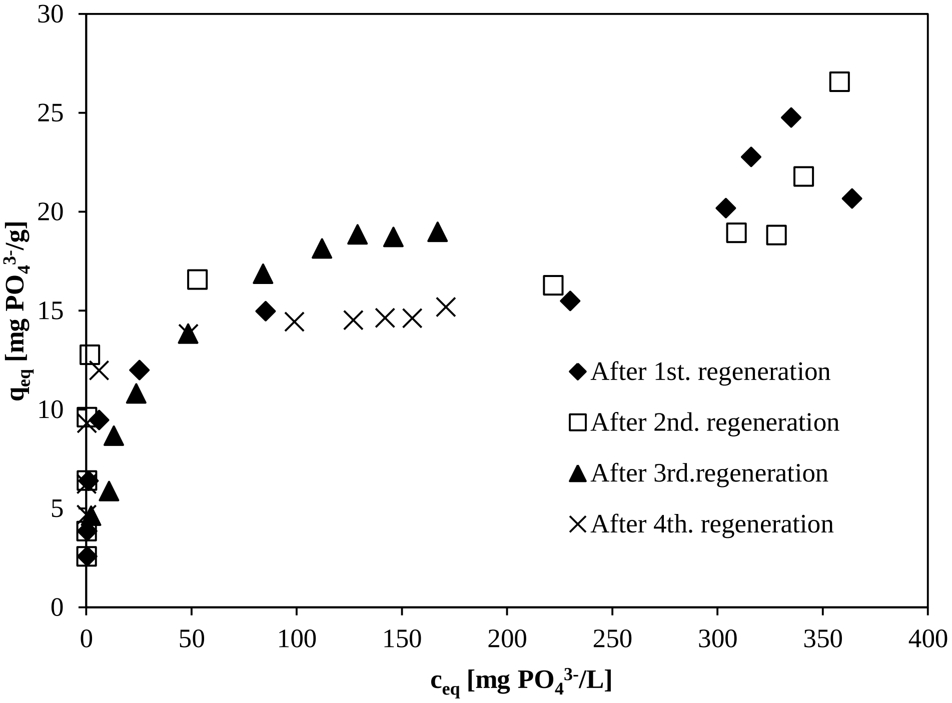


Figure 4.21: Phosphate sorption isotherms of regenerated LayneRT.

From the perspective of sorbent retrieving, the phosphate sorption isotherms of regenerated LayneRT in Figure 4.21 presented stable capacities for phosphate sorption after four cycles of regeneration. Compared with the phosphate sorption isotherm in Chapter 4.2.2, the regenerated LayneRT had even higher phosphate sorption capacities approching 25 mg/g than the capacity of virgin LayneRT (20 mg/g). It is postulated that after the regeneration with dilute NaOH, the active sites at sorbent surface were saturated by hydroxide ions, which is a preferable form for phosphate sorption.

4.4.2 Regeneration in continuous experiment

When the sorbent in the column was saturated with phosphate or the effluent coming out from the column reached the allowable maximum discharge level, the regeneration of the sorbent in column was quite necessary. In this study, in situ regeneration of the exhausted LayneRT granules was carried out in reverse directions of the sorption process by using 1.0M NaOH as the desorption regenerant, followed by rinsing with distilled water until the pH value of outflow was stable. The regenerated column was then used for the next cycle of column sorption.

After exhaustion of the column, it was first downwards washed with 2 bed volumes of distilled water to remove unsorbed phosphate from the sorbent bed. Then the desorption regenerant was pumped into the sobent bed at the flow rate of 8 mL/min. The effluent of desorption was collected in fraction of 10 mL at gradient time intervals. Phosphate concentrations of the effluent fractions were examined to determine the number of bed volume until all phosphate was desorbed and eluted out of the column.

The desorption curve of phosphate after the sorption operation with the sludge liquor at pH 6.5 was presented in Figure 4.22. The column regeneration was accomplished within 5 bed volumes. The total mass of phosphate uptake by the sorbent bed was estimated by multiplying the maximum bed capacity and the mass of exhausted sorbent. The percentage of phosphate recovered after desorption is roughly 95% from the actual sludge liquor at pH 6.5. This remarkable high phosphate recovery persentage suggests that the active binding sites on the hybrid sorbent LayneRT had a good affinity to the phosphate ions in aqueous system. On the other hand, through the operation of fixed-bed column, for instance, from the real sludge liquor at pH 6.5 with the initial concentration of phosphate 120 mg/L, phosphate could be concentrated from a sludge liquor volume of 70 bed volumes until the sorbent exhaustion (see Figure 4.18) and then be recovered from the exhausted column within 5 bed volumes by desorption with 1.0 M NaOH.

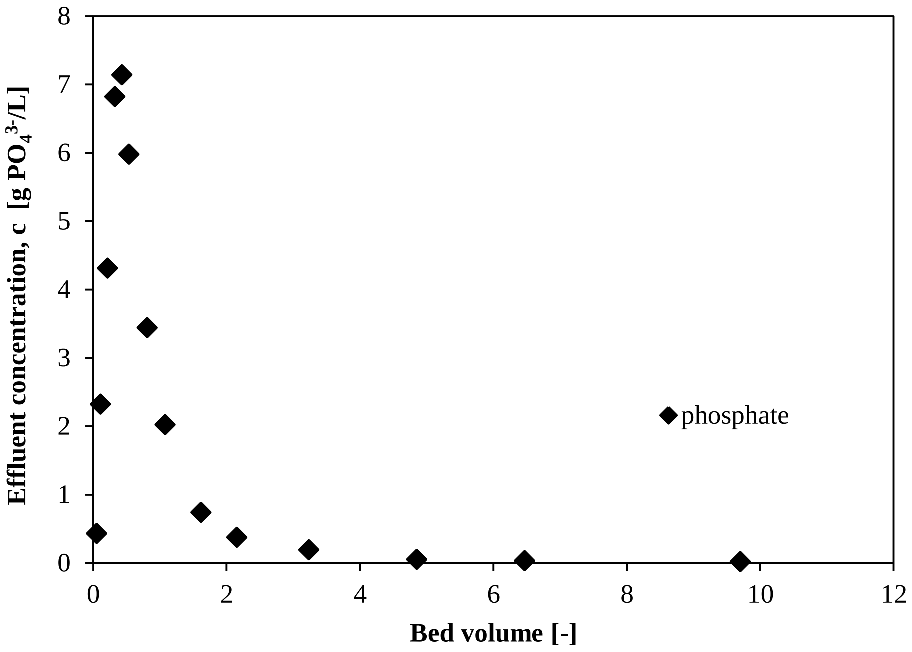


Figure 4.22: Desorption curve of the in situ regeneration of the exhausted LayneRT with 1.0 M NaOH.

The quality of the phosphate recovery product from the real sludge liquor has to be further controlled, however, because phosphate is not the unique ion species that LayneRT can take from the complex real sludge liquor. Interfering substances such as divalent/ multivalent anions and negative charged organic matter can also adhere to the sorbent. During the regeneration procedure of the sorbent, these interfering substances are eluted out of the column simultaneously with the desorption of phosphate. It is hence difficult to yield high purity liquid P-product from the real sludge liquor.

5 Discussion

5.1 The sorbent for P-recovery

The hybrid anion sorbent LayneRT was used for phosphate sorption in the first phase of the novel phosphate recovery technology named PHOSIEDI. This sorbent was fabricated by dispersing hydrated ferric oxide (HFO) nanoparticles into traditional polymeric anion exchanger resin; accordingly it has dual characteristics of ligand complexation and anion exchange.

To achieve good performance in the phosphate sorption process, a series of batch experiments were designed to characterize the sorbent, to investigate the sorption mechanism and finally determine the optimal boundary conditions for phosphate uptake.

For a phosphate sorption process, the pH variation is quite important that determines the species of phosphate in solution. In the range of pH 4-10, monovalent $H_2PO_4^-$ and divalent HPO_4^{2-} phosphate anions are selectively bound to HFO sorption sites. Among them, HPO_4^{2-} tends to form stronger bi-dentate complexes as shown in Figure 5.1, while $H_2PO_4^-$ tends to form mono-dentate complexes, which is weaker than the bi-dentate complexes. It is probably the reason why LayneRT presents higher sorption capacity for phosphate at pH around 7.0 where HPO_4^{2-} is the predominant species.

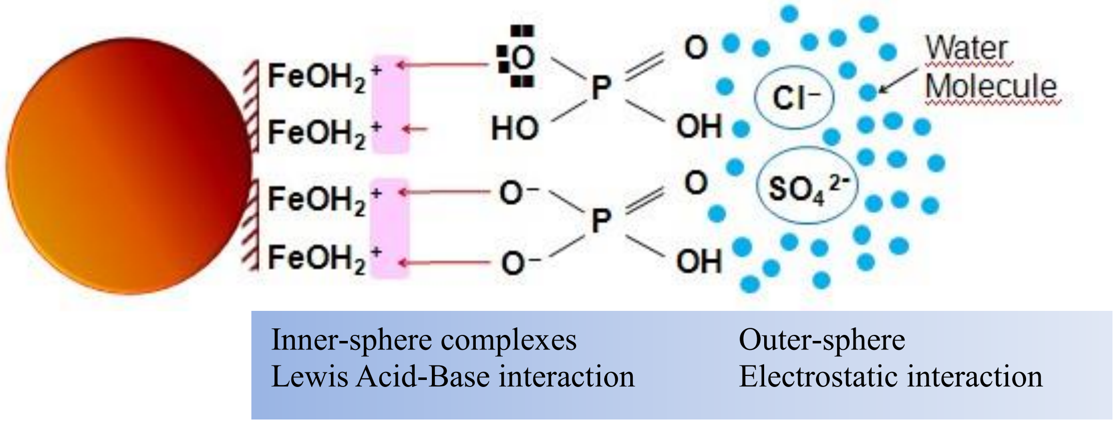


Figure 5.1: Schematic illustration of the formation of mono- and bidentate inner-sphere complexes between phosphate and HFO on the LayneRT surface; competing anions form only outer-sphere complexes.

The surface property of the sorbent LayneRT can also be affected by the pH value, since the dispersed HFO exhibits amphoteric character under different conditions. As shown in Figure 5.2, the electron activity ($\mathrm{pe} = -\lg[e^-]$) of HFO decreases as the pH value increases, which means at high alkaline pH the HFO tends to have high electron activity and acts as an electron donor in the system. This is not favorable for the Lewis-Acid-Base interaction between the HFO and phosphate. On the contrary, in the lower range of pH values, the HFO acts as an electron acceptor which will encourage the Lewis-Acid-Base interaction with the electron donator, i.e. phosphate species. Thus, the pH value of the phosphate sorption with LayneRT must be determined moderately from the perspective of both solid and liquid phases. As a result of batch experiments with phosphate model solutions at different pH value, the optimal working pH ranged from 6 to 8.2.

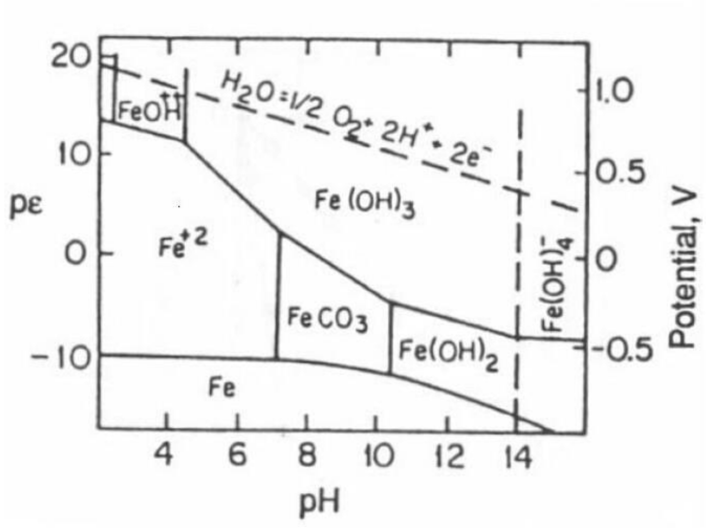


Figure 5.2: pe-pH diagram of iron in aqueous system (Fischer, 2002).

In order to obtain the maximum sorption capacity of LayneRT for phosphate, sorption isotherms were plotted in ideal conditions. As results of the experiment, the maximum capacity for phosphate in a one-component solution is 14.58 mg/g for Cl-form sorbent and 18.97 mg/g for OH-form sorbent. Both isotherms can be simulated by the Redlich-Peterson model, which is a three-parameter isotherm featuring both Langmuir and Freundlich models. The calculated capacities of phosphate are 13.42 mg/g for the Cl-form sorbent and 19.87 mg/g for OH-form sorbent, which are relatively close to the experimental results. The value of exponent β in the model equation indicated both forms of the sorbent have heterogeneous binding sites for phosphate sorption. Compared with the Cl-form sorbent, the OH-form sorbent, pretreated by NaOH, exhibited higher capacity for phosphate ions. It is postulated that after the pretreatment of regeneration with dilute NaOH, the active sites at sorbent surface were in the hydroxide ion form, which is a preferable form for phosphate ion exchange. Hence the OH-form LayneRT was selected for further P-sorption investigation, and dilute NaOH was used to regenerate the exhausted sorbent for recylcling.

Isotherms of OH-form LayneRT under non ideal conditions were also taken in consideration. In the multi-component solution with competing anions (see Table 4.4), i.e.

sulfate chloride and nitrate, the phosphate capacity decreased by around 30%. But the concentration increasing of competing anions did not aggravate the capacity reduction, because these competing ions can only compete for the outer-sphere ion exchange sites by electrostatic attractions. The majority of phosphate was combined with HFO through inner-sphere complexation, which follows the principle of Lewis-Acid-Base interaction.

The investigation of ambient temperature provided more evidence for the different mechanisms between phosphate sorption and competing ion sorption on LayneRT. Since the electrostatic interaction is more sensitive to the temperature variation than the Lewis-Acid-Base interaction (Prevette et al, 2007; Manjari and Kim, 2006), the changes of phosphate capacity in the presence of competing ions are less obvious than the changes without competing ions in the bulk solution. Without competing anions in solution, both electrostatic and Acid-Base interactions are operative for phosphate sorption, when temperature changes, the outer-sphere binding through electrostatic changes with it and results in the variation of phosphate sorption capacity. With competing ions in solution, the outer-sphere sites are occupied by the competing ions, phosphate can only combine with the sorbent through Lewis-Acid-Base interaction, which is relatively independent on temperature variation, and the phosphate capacity therefore also keeps constant under different temperature conditions.

The kinetics study reveals the sorption mechanisms through the fitting of kinetic models. The pseudo-second-order kinetic model and intra-particle diffusion model provided best match to the experimental data. The good agreement with pseudo-second order model implied that the rate limiting step could be the chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and phosphate. This deduction is in accordance with the outcomes from afore batch experiments that phosphate combines with HFO through Lewis-Acid-Base interaction. Since the pseudo-second-order kinetic model cannot figure out the rate-controlling step of the sorption process, the Weber’s intra-particle model was employed to describe the diffusion at the liquid-solid interface. The multi-linear plotting of the model indicated two sections of the diffusion. The rate of the first section was controlled by the boundary layer diffusion and the second section was controlled by the intra-particle diffusion.

During the regeneration under high alkaline condition with NaOH, HFO sorption sites on the sorbent surface are all deprotonated and negatively charged, so are the phosphate species. Donan co-ion exclusion is thus operative under this condition and results in efficient desorption of the negatively charged phosphate ions. And the sorbent LayneRT is regenerated simultaneously. The LayneRT granules presented strong mechanical and chemical resistance during the sorption and regeneration processes and did not show any sign of fragmentation or erosion throughout the reuse in experiments.

For comparison, phosphate uptake by other reported sorbents are summarized in Table 5.1. Due to the high specific surface areas, the sorbents in the form of powder presented high sorption capacities. However, they are hardly to be regenerated for reuse due to their fine or ultrafine particle size, which is a hinder for liquid-solid separation. The powder sorbents also cannot be directly employed in fixed-bed columns or any other flow-through systems because of the high hydraulic resistance that is caused by the compacted fine powders.

5.2 The solution as P-source

The digested sludge liquor collected at the effluent of dewatering centrifuge was selected as the source for phosphate recovery. As described in Chapter 3.1.1, the sludge liquor contains relatively high concentration of phosphate, low concentration of sulfate and scarcely any nitrate after the anaerobic digestion. Before the sorption process with LayneRT, the digested sludge liquor was filtrated through the 0.45 µm membrane to intercept microorganisms in the liquor. However, the dissolved organic matter (DOM) has not been removed from the sludge liquor before reaction.

According to the result of size-exclusion chromatography that presented in Chapter 4.2.7, the predominant fractions of DOM in sludge liquor are the low molecular organics at molecular weights lower than 1300 Da. After the reaction with LayneRT, the amout of DOM in this molecular range decreased by 35%, which means this portion of DOM brought negative effects to the phosphate uptake and reduced the sorption capacity of LayneRT.

In the present study, individual organic acids in sludge liquor were not determined separately. The most direct way to diminish the negative effect of DOM is eliminating it before the phosphate sorption process. The DOM removal efficiency through treatment options was dependent on the nature and amount of the individual fractions based on their hydrophobicity, molecular weight and fluorogenic nature (Ciputra et al., 2010). As mentioned in previous studies, activated carbon is widely used for DOM removal from different wastes. Activated carbon (AC) and modified activated carbon (MAC) can eliminate DOM efficiently (Cheng et al., 2005), and granular activated carbon (GAC) can be packed in columns for continuous operation (Schreiber et al., 2005). A magnetic ion exchanger named MIEX® was developed to remove a majority of small molecular weight organic matter (500 - 1000 Da). And it was specifically useful in removing the hydrophilic portion of DOC. At optimal concentration, the MIEX® process could remove as high as 60% of DOC in the wastewater. Combining MIEX® pretreatment with PAC adsorption, one could achieve more than 80% TOC removal (Zhang et al., 2005).

Besides the digested sludge liquor, other kinds of wastewater also can be used as the source solution for phosphate recovery. The maximum loading of phosphate on HAIX-Fe resin in O'Neal and Boyer's (2013) research was 10 mg P/g resin in fresh urine and 5-7 mg P/g resin in hydrolyzed urine. Pan et al. (2009) showed a maximum phosphate loading of 10 mg P/g resin for wastewater containing phosphate (approx. 80 mg P/L; initial concentration not reported), sulfate (500 mg/L), and pH 6.4-6.7. And Kumar et al. (2007) showed a maximum phosphate loading of 8-10 mg P/g resin for RO waste stream (12 mg P/L, 480 mg/L sulfate, 890 mg/L chloride, 234 mg/L nitrate and pH 8). HAIX resin containing Zr(IV) showed a maximum phosphate loading of 16 mg P/g resin for water containing 80 mg P/L at pH 6 (Zong et al., 2013). HAIX resin containing Cu(II) showed a maximum phosphate loading of 2 mg P/g resin for water containing 18 mg P/L and 200 mg/L sulfate at pH 7 (Zhao and SenGupta, 1998).

5.3 The application of sorbent for P-recovery

After the characterization of the sorbent LayneRT and the analysis of the P-rich sludge liquor, the fixed-bed column was built up for continuous operation of phosphate recovery. During the continuous operation, phosphate model solution or filtrated sludge liuqor was constantly pumped into the sorbent bed at the flow rate of 8 mL/ min. The phosphate sorption process ended when the effluent phosphate concentration approaching 95% of the inlet concentration. After saturation of the sorbent, distilled water was pumped in reverse direction, in order to wash out excessive phosphate that was not adsorbed by the LayneRT. Afterwards, the column was regenerated by 1.0 M NaOH at the flow rate of 8 mL/ min. By the massive amount of hydroxyl ion, the HFO sorption sites on the sorbent surface were all deprotonated and negatively charged, so are the phosphate species. The exclusion effect of co-ions was operative under this condition and resulted in efficient desorption of phosphate. Thus the regeneration effluent flows out of the column with extremely high concentration of Na_3PO_4, which can be considered as a high-purity liquid product of P-recovery.

In the case of treating phosphate model solution (sample Nr. 1 in Table 5.2), the LayneRT column exhibited long operation cycle for 120 bed volumes, and high sorption capacity over 30 mg/g for phosphate. The regeneration of sorbent was accomplished with 5 bed volumes. The total volume of treated solution was approximate 9.0 L; the total mass of phosphate recovered was approximate 1.6 g; and the volume of P-recovery product was around 0.375 L.

In the case of taking phosphate from actual sludge liquor, the performance of the LayneRT column depended on the conditions of the liquor. As listed in Table 5.2, for the original sludge liquor without any pretreatment (sample Nr. 2) at pH 8.17, the bed of sorbent was exhausted after 45 bed volumes, and the maximum sorption capacity decreased dramatically to 7 mg/g. About 0.38 g phosphate was recovered from 3.00 L sludge liquor in around 380 min. For the sludge liquor (sample Nr. 3) at pH 6.5, the bed of sorbent was exhausted after 70 bed volumes, and the maximum sorption capacity increased to 10 mg/g. About 0.54 g phosphate was recovered from 5.28 L sludge liquor in 660 min. For the sludge liquor (sample Nr. 4) at pH 5.5, the bed of sorbent was exhausted after 40 bed volumes, and the maximum sorption capacity was 10 mg/g. About 0.54 g phosphate was recovered from 3.00 L sludge liquor in 380min.

Comparing the yield efficiency of P-recovery from sludge liquor in different conditions, one can find that the pH value and the initial phosphate concentration are the predominant factors. The operation cycle using sludge liquor at lower pH range (6.5 and 5.5) presented higher bed capacity (10 mg/g) than the cycle at pH 8.17 (7 mg/g), since the decrease of pH value diminished the competing sorption of DOM. In the lower range of pH value, the negatively charged DOM was tending to be protonated, which is unfavorable for its competition on the surface of LayneRT. The initial concentration of phosphate in sludge liquor affected the phosphate recovery efficiency. Comparing sludge liquor Nr. 3 and Nr. 4, for the equal amount of P-production, the sludge liquor Nr. 4 with higher initial P-concentration shortened the operating duration and presented a high efficiency for P-recovery. The reason might be that higher concentration gradients promote molecule diffusion at the interface between the bulk solution and the sorbent, which is favorable for the ion sorption process. But this high concentration gradient does not change the intrinsic properties of the sorbent material, hence the bed capacity of the sorbent remains at 10 mg/g.

In the present study, only lab-scale fixed-bed column were set up for continueous P-sorption and recovery. And only the essential aspects of process optimization could be examined. Nevertheless, it has been possible to show the potential of the process for P-recovery from WWTPs. The production of sludge liquor is about 5 L/C·d, with the average phosphate concentration of 300 mg/L. According to the P-sorption capacity of 10 mg/g LayneRT in sludge liquor, the comsuption of LayneRT for P-recovery per capita per day is about 150 g. According to the results of regeneration tests and the supporting information from similar ion exchange products, LayneRT can be assumed to be reused for 1000 cycles (loaing and regeneration). The price of LayneRT is 20 €/kg, so the cost of the sorbent in this P-recovery process is about 0.003 €/C·d.

Pretreatment units for DOM elimination such as a flow-bed reactor of activated carbon, or a MIEX® process afore the phosphate sorption would diminish the negative effects from DOM and would therefore enhance the phosphate sorption performance of the LayneRT column. The P-product that yields from the integrated system would have relatively high purity, since the organic acids were removed before entering the column and would not appear in the P-product. Another bonus from the pretreatment might be the prolonging of the sorbent life, since the presence of DOM plays an important role of organic fouling in filtration systems such as the fixed-bed column for phosphate sorption and recovery.

Table 5.1: Sorbents for phosphate sorption from different P-rich wastewater.

Sorbent	Morphology	pH	Initial C_{PO43-} [mg P/L]	P-sorption capacity [mg/ g]	Literature
HFO-201	granule	6.5-8.0	10	50	Pan et al., 2009
Fe-EDA-SAMMS	powder	5.0	1.14	14.26	Chouyyok et al., 2010
Steel slag	unformed	5.5	22.79	5.30	Xiong et al., 2008
Ca-ZFA	powder	6.6-9.5	50	19.11	Guan et al., 2009
Crab shells	unformed	6.5	667	36.07	Jeon et al., 2009
Al-PILC	powder	3.0-4.0	99.2	20.46-26.97	Kasama et al., 2004
La(III)-chelex resin	granule	5.5	155	3.04	Wu et al., 2007
Calcined Mg-Al-LDHS	powder	6.0	50	44	Das et al., 2006
Dry iron oxide tailings	unformed	3.5	10	8	Zeng et al., 2004

Table 5.2: Comparison of continuous performance of column with sludge liquor under different conditions

			Initial concentrations								P-recovery	
	Nr.	pH	Phosphate mg/L	Sulfate mg/L	Chloride mg/L	COD mg/L	Breakthrough BVs	Exhaustion BVs	Bed capacity mg PO_4^{3-}/g	Treated volume L	P-production g	Operating time min
Model solution	1	8.12	338	-	-	-	40	120	30	9.0	1.6	1125
sludge liquor	2	8.17	170	10.6	304	745	20	45	7	3.0	0.38	380
	3	6.5	120	11.3	2861	548	48	70	10	5.28	0.54	660
	4	5.5	282	20.6	4466	750	18	40	10	3.0	0.54	380

6 Conclusions and Recommendation

6.1 Conclusions

As the first phase of the novel phosphate recovery technology that is named PHOSIEDI, the selective sorption of phosphate ions from P-rich solutions is a critical step for the overall system. The performance of an appropriate sorbent determines the quality of the final product and the productive efficiency of the technology. In the present study, a hybrid anion sorbent (LayneRT) was employed to catch phosphate ions from the digested sludge liquor.

Parameters affecting phosphate sorption were investigated in this study in order to determine the optimal boundary conditions for high performance. Among them, the pH value is a crucial parameter that determines not only the surface properties of the sorbent but also the existing forms of the components in aqueous systems. The sorbent LayneRT consists of a polymer resin matrix and nanosized hydrous ferric oxide (HFO). HFO exhibits an amphoteric character in aqueous systems, which is being proton a donor at acidic pH and being a proton acceptor at alkaline pH. The pH value also determines the amount of phosphate species in solutions. Since different phosphate species have different binding mechanisms with HFO, the pH value therefore affects the sorption behavior.

The sorption isotherms were plotted to figure out the relationship between the maximum phosphate loading on sorbent and the equilibrium phosphate concentration in bulk solution. The sorption capacity for phosphate can be determined through the isotherm batch experiments and with the help of isotherm models. In this study, the Redlich-Peter isotherm was applied. The model suggested a phosphate sorption capacity of LayneRT of 19.87 mg PO_4^{3-}/g, which is very close to the experimental data of 18.97 mg PO_4^{3-}/g.

The sorption kinetics describes the sorption procedure from the temporal perspective, and the suitable kinetic models can rationally clarify the sorption mechanism at the interface. The pseudo-second order model and the Weber’s intra-particle model provided best match with the experimental data. The good agreement of the pseudo-second order model implied that the rate limiting step could be the chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and phosphate. Weber’s intra-particle model indicated that phosphate sorption on LayneRT has two sections of diffusion, the initial phase controlled by external mass transfer, i.e. boundary layer diffusion and the later controlled by intra-particle diffusion.

The effect of competing anions and ambient temperature were also taken into consider. Although the sorption capacity for phosphate was decreased in the presence of competing ions, an increasing competing concentration did not aggravate the decline of phosphate capacity. This result elucidated that both, electrostatic (outer-sphere) and Acid-Base interactions (inner-sphere complex), were operative for phosphate sorption on LayneRT, while the other competing anions can only affect the part of outer-sphere sites through electrostatic interaction. Accordingly, phosphate exhibits selective priority over the other anions on this sorbent.

Performance of continuous operation for P-sorption and recovery was investigated in the fixed-bed column. Flow rates, pH value and the composition of sludge liquor were the predominant factors for continuous operation. A moderate flow rate ensured enough contact time and even hydraulic distribution for the phosphate sorption. The pH variation determined the major species of the polyatomic ions and the surface properties of dissolved organic matter. At low pH range, the negatively charged DOM was tending to be protonated and its competition on the sorbent was restricted. The inflow concentration of phosphate also affected the efficiency of P-recovery. Higher concentration gradient promoted the molecule diffusion at the interface between the bulk solution and the sorbent, which was favorable for the ion sorption process. But the concentration gradient did not change the intrinsic properties of the sorbent material such as the sorption capacity.

6.2 Recommendation

In order to overcome the negative effects from DOM and to achieve a high quantity of P-product through the sorption-regeneration cycle, specific pretreatment for DOM removal is recommended. At the current stage, both, powered and granule activated carbon are the most common and economic options for DOM elimination. Specific anion exchange resins such as MIEX® were developed for DOM removal. Higher removal efficiency can be achieved via the combination of different methods. Furthermore, ultrafiltration can also be applied for removal of DOM, but is not recommended due to the costs of operation.

In the perspective of sorbent materials, the hybrid anion sorbent in this study can be substituted by some other novel sorbents that were developed for phosphate removal. For instance, metal hydroxides such as goethite, hematite, gibbsite etc. can be modified for phosphate uptake. Some industrial by-products such as red mud from aluminum mining can also be modified for phosphate sorption. Granule sorbents are more operative than powered sorbents, since the former can be applied directly in fixed-bed reactors for continuous operation.

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Appendixes

Appendix 1: Literature review of adsorbents for P-removal and P-recovery.

Sorbent	Morphology	Optimum pH	Initial C_{PO43-}	Max. capacity	Literature
			[mg P/L]	[mg P/ g]	
Al-PILC	powder	3.0-4.0	99.2	20.46-26.97	Kasama et al., 2004
Aluminum oxide hydroxide	powder	4	100	35	Tanada et al., 2003
Aluminum hydroxide gel	granule	4.0-6.0	127	34.5	Kawasaki et al., 2010
Alunite	powder	< 5.0	200	106.6	Özacar, 2003
Blast furnace slag	Powder	9.8-11.7	200	6.5	Kostura et al., 2005
Calcined Mg-Al-LDHS	powder	6.0	50	44	Das et al., 2006
Ca-ZFA	powder	6.6-9.5	50	19.11	Guan et al., 2009
Crab shells	unformed	6.5	667	36.07	Jeon et al., 2009
Dolomite	powder	2	1000	227.3	Mangwandi et al., 2014
Dry iron oxide tailings	unformed	3.5	10	8	Zeng et al., 2004
Fe-Cu binary oxides	powder	5.0-7.0	5	35.2-39.8	Li et al., 2014
Fe-EDA-SAMMS	powder	5.0	1.14	14.26	Chouyyok et al., 2010
Fe-Mn binary oxides	unformed	5.6	35	36	Zhang et al., 2009
Fly ash	powder	11.5	130	71.87	Oguz, 2005
Goethite	powder	5.0	950	64.7	Wei et al., 2014
Hydrous niobium oxide	powder	2	50	13	Rodrigues et al., 2009
Iron oxide	powder	3	1600	4.6	Daou et al., 2007
Magnetic iron oxide	powder	< 6.0	20	5.03	Yoon et al., 2014
Activated red muds	powder	5.5	1	0.58	Huang et al., 2008
Activated red muds	granule	9.17	50	9.80	Yue et al., 2010

Steel slag	unformed	5.5	22.79	5.30	Xiong et al., 2008
Zirconium oxide	powder	2.0-6.0	2.0	12-50	Chitrakar et al., 2006
Zirconium oxide	unformed	6.2	50	99.01	Su et al., 2013

Appendix 2: Isotherms for P-sorption by Cl-form LayneRT, initial concentration of phosphate 385 mg/L, pH 8.12, at 25^{o}C.

m	equ. conc.	loaded conc.	qe	Langmuir			Freundlich			Redlich Peterson		
				1/c	1/qe	q(L)	lnc	lnqe	q(F)	lnc	ln(K_RCe/qe -1)	q(R)
g/L	mg PO_4^{3-}/L	mg PO_4^{3-}/L	mg PO_4^{3-} /g			mg PO_4^{3-} /g			mg PO_4^{3-} /g			mg PO_4^{3-} /g
10.02	239.00	146.00	14.58	0.00	0.07	8.34	5.48	2.68	12.26	5.48	11.40	13.42
20.04	158.00	227.00	11.33	0.01	0.09	8.30	5.06	2.43	10.87	5.06	11.24	11.49
30.02	110.00	275.00	9.16	0.01	0.11	8.25	4.70	2.21	9.78	4.70	11.09	10.03
40.05	74.00	311.00	7.77	0.01	0.13	8.16	4.30	2.05	8.71	4.30	10.86	8.64
60.13	30.10	354.90	5.90	0.03	0.17	7.81	3.40	1.78	6.70	3.40	10.23	6.17
100.08	3.67	381.33	3.81	0.27	0.26	5.10	1.30	1.34	3.62	1.30	8.57	2.80
149.98	0.98	384.02	2.56	1.02	0.39	2.44	(0.02)	0.94	2.46	(0.02)	7.64	1.70

Appendix 3: Isotherms for P-sorption by OH-form LayneRT, initial concentration of phosphate 187 mg/L, pH 8.11, at 25^{o}C.

m	equ. conc.	loaded conc.	q	Langmuir			Freundlich			Redlich Peterson		
				1/c	1/qe	q(L)	lnc	lnqe	q(F)	lnc	ln(K_RCe/qe -1)	q(R)
g/L	mg PO$_4^{3-}$/L	mg PO$_4^{3-}$/L	mg PO$_4^{3-}$ /g			mg PO$_4^{3-}$ /g			mg PO$_4^{3-}$ /g			mg PO$_4^{3-}$ /g
1.05	167.00	20.00	18.98	0.01	0.05	14.38	5.12	2.94	20.33	5.12	3.44	19.88
2.19	146.00	41.00	18.72	0.01	0.05	14.32	4.98	2.93	19.38	4.98	3.31	19.10
3.08	129.00	58.00	18.84	0.01	0.05	14.25	4.86	2.94	18.53	4.86	3.18	18.40
4.14	112.00	75.00	18.13	0.01	0.06	14.16	4.72	2.90	17.61	4.72	3.07	17.63
6.11	84.10	102.90	16.85	0.01	0.06	13.94	4.43	2.82	15.89	4.43	2.85	16.14
10.01	48.50	138.50	13.83	0.02	0.07	13.34	3.88	2.63	13.04	3.88	2.47	13.54
15.11	23.70	163.30	10.81	0.04	0.09	12.05	3.17	2.38	10.08	3.17	1.95	10.58
20.06	13.10	173.90	8.67	0.08	0.12	10.45	2.57	2.16	8.14	2.57	1.51	8.44
30.03	10.90	176.10	5.86	0.09	0.17	9.86	2.39	1.77	7.62	2.39	1.76	7.83
40.02	2.24	184.76	4.62	0.45	0.22	4.29	0.81	1.53	4.31	0.81	(0.26)	3.57

Appendix 4: P-sorption isotherms in the presence of competing anions.

Nr.	Dosage	Equlibrium concentration (ce)				P-elimination	Equilibrium loading (qe)			
	LayneRT	Phosphate	Sulfat	Chlorid	Nitrat		Phosphate	Sulfat	Chlorid	Nitrat
	g resin/L	mg/L	mg/L	mg/L	mg/L	%	mg PO$_4^{3-}$/g	mg SO$_4^{2-}$/g	mg Cl$^-$/g	mg NO$_3^-$/g
1	initial	101.00	51.50	207.90	10.40					
	2.07	69.70	71.80	204.30	8.34	30.99	15.15	-9.83	1.74	1.00
	4.00	53.80	57.60	186.90	7.01	46.73	11.80	-1.53	5.25	0.85
	6.02	39.70	59.50	172.90	6.29	60.69	10.19	-1.33	5.82	0.68
	8.01	29.20	60.30	164.70	5.28	71.09	8.96	-1.10	5.39	0.64
	10.04	21.00	62.60	155.80	4.93	79.21	7.97	-1.11	5.19	0.54

	15.06	12.80	65.40	141.10	3.94	87.33	5.86	-0.92	4.44	0.43
	19.99	3.13	69.20	128.20	3.40	96.90	4.90	-0.89	3.99	0.35
2	initial	107.00	94.10	207.50	10.30					
	2.02	82.30	98.80	195.90	8.46	23.08	12.24	-2.33	5.75	0.91
	4.01	63.80	93.00	187.40	7.46	40.37	10.77	0.27	5.01	0.71
	6.02	47.60	92.40	177.60	6.58	55.51	9.86	0.28	4.96	0.62
	8.00	37.30	96.00	175.60	6.04	65.14	8.71	-0.24	3.99	0.53
	10.04	28.40	92.10	163.70	5.38	73.46	7.83	0.20	4.36	0.49
	15.01	12.10	97.10	149.60	4.23	88.69	6.32	-0.20	3.86	0.40
	20.02	5.10	97.20	137.30	3.50	95.23	5.09	-0.15	3.51	0.34
3	initial	102.00	207.90	208.60	9.08					
	2.03	78.30	192.40	195.70	8.30	23.24	11.69	7.64	6.36	0.38
	4.01	60.60	189.20	192.30	6.92	40.59	10.33	4.67	4.07	0.54
	5.99	51.00	183.00	185.40	6.39	50.00	8.51	4.15	3.87	0.45
	8.01	38.30	174.20	175.20	5.58	62.45	7.95	4.21	4.17	0.44
	10.03	27.20	170.70	167.80	5.08	73.33	7.45	3.71	4.07	0.40
	14.99	11.70	163.60	155.10	4.43	88.53	6.02	2.95	3.57	0.31
	20.00	4.31	156.30	140.80	3.66	95.77	4.88	2.58	3.39	0.27
4	initial	101.20	97.70	104.70	9.33					
	2.03	73.90	84.90	93.20	7.28	26.98	13.44	6.30	5.66	1.01
	4.00	54.40	78.30	88.00	6.05	46.25	11.69	4.85	4.17	0.82
	6.00	39.90	76.00	79.70	5.08	60.57	10.21	3.61	4.16	0.71
	8.02	29.70	71.70	75.20	4.48	70.65	8.91	3.24	3.68	0.60
	10.04	20.80	66.80	73.50	3.85	79.45	8.01	3.08	3.11	0.55
	14.99	8.08	62.40	66.90	3.06	92.02	6.21	2.35	2.52	0.42
	20.01	2.63	63.00	60.50	2.58	97.40	4.93	1.73	2.21	0.34
5	initial	102.00	103.30	220.00	7.94					
	2.01	74.80	94.30	189.10	6.80	26.67	13.52	4.47	15.36	0.57
	4.03	56.00	92.70	179.10	5.59	45.10	11.43	2.63	10.16	0.58
	6.00	42.80	89.60	174.70	5.08	58.04	9.87	2.28	7.55	0.48

	8.01	32.00	88.80	159.50	4.51	68.63	8.74	1.81	7.55	0.43
	10.00	23.30	86.90	154.60	3.89	77.16	7.87	1.64	6.54	0.40
	15.04	8.63	83.50	136.30	3.13	91.54	6.21	1.32	5.57	0.32
	20.02	3.19	83.90	127.50	3.23	96.87	4.94	0.97	4.62	0.24
6	initial	101.00	95.90	408.40	9.09					
	2.03	75.00	91.85	395.00	7.72	25.74	12.80	-2.93	6.59	0.67
	4.01	58.50	95.80	381.00	7.43	42.08	10.59	-2.47	6.83	0.41
	6.00	45.90	102.10	364.30	6.52	54.55	9.18	-2.70	7.35	0.43
	8.01	34.30	103.10	353.00	5.89	66.04	8.33	-2.15	6.92	0.40
	10.01	25.60	103.00	335.40	5.06	74.65	7.53	-1.71	7.29	0.40
	15.03	4.40	108.20	298.30	4.53	95.64	6.43	-1.48	7.32	0.30
	20.01	4.30	113.80	277.90	3.88	95.74	4.83	-1.39	6.52	0.26
7	initial	103.00	97.70	207.90	10.40					
	2.03	75.50	84.90	204.30	8.34	26.70	13.53	6.30	1.77	1.01
	4.00	55.10	78.30	186.90	7.01	46.50	11.96	4.85	5.24	0.85
	6.00	39.50	76.00	172.90	6.29	61.65	10.58	3.61	5.83	0.68
	8.02	28.90	71.70	164.70	5.28	71.94	9.24	3.24	5.39	0.64
	10.04	21.20	66.80	155.80	4.93	79.42	8.15	3.08	5.19	0.54
	14.99	12.40	62.40	141.10	3.94	87.96	6.04	2.35	4.46	0.43
	20.01	3.15	63.00	128.20	3.40	96.94	4.99	1.73	3.98	0.35
8	initial	105.00	103.30	207.50	25.50					
	2.01	78.90	94.30	195.90	21.02	24.86	12.97	4.47	5.77	2.23
	4.03	58.80	92.70	187.40	17.46	44.00	11.48	2.63	4.99	2.00
	6.00	44.60	89.60	177.60	14.62	57.52	10.07	2.28	4.98	1.81
	8.01	33.90	88.80	175.60	12.51	67.71	8.88	1.81	3.98	1.62
	10.00	26.40	86.90	163.70	10.78	74.86	7.86	1.64	4.38	1.47
	15.04	12.30	83.50	149.60	8.95	88.29	6.16	1.32	3.85	1.10
	20.02	5.20	83.90	137.30	8.63	95.05	4.99	0.97	3.51	0.84
9	initial	101.00	102.90	208.60	50.90					
	2.03	76.30	91.85	195.70	45.30	24.46	12.16	5.44	6.35	2.76

	4.01	58.90	95.80	192.30	39.94	41.68	10.49	1.77	4.06	2.73
	6.00	45.70	91.10	185.40	35.39	54.75	9.22	1.97	3.87	2.59
	8.01	35.30	89.90	175.20	31.98	65.05	8.20	1.62	4.17	2.36
	10.01	27.20	93.00	167.80	29.08	73.07	7.37	0.99	4.08	2.18
	15.03	11.70	88.20	155.10	24.87	88.42	5.94	0.98	3.56	1.73
	20.01	4.31	83.80	140.80	23.66	95.73	4.83	0.95	3.39	1.36

Appendix 5: Calibration of Sephadex G-50 size exclusion column with standards of different molecular weights.

Chromatography and recovery of standard MW 70000 (c_0=209.8 mg/L, 0.5mL injection)

Sample Nr.	V(mL)	Ve (mL)	DOC(mg/L)	DOC (mg)	Σ DOC (mg)	Recovery (%)
1	2.3	2.3	5.88			
2	2.1	4.4	3.58			
3	2.4	6.8	4.16			
4	2.3	9.1	4.83			
5	2.2	11.3	2.91			
6	2.4	13.7	2.94			
7	2.3	16	7.53	17.319		
8	2.2	18.2	23.4	51.48		
9	2.2	20.4	9.94	21.868		
10	2.3	22.7	6.30	14.49	105.157	100.245
11	2.2	24.9	3.94			
12	2.3	27.2	3.97			
13	2.4	29.6	2.21			
14	2.4	32	2.23			
15	2.4	34.4	2.00			

Chromatography and recovery of standard MW 4000 (c_0=273 mg/L, 0.5mL injection)

Sample Nr.	V(mL)	Ve (mL)	DOC(mg/L)	DOC (mg)	Σ DOC (mg)	Recovery (%)
1	2.4	2.4	6.22			
2	2.4	4.8	3.62			
3	2.3	7.1	3.08			
4	2.4	9.5	5.56			
5	2.2	11.7	3.47			
6	2.3	14	3.54			
7	2.4	16.4	3.80			
8	2.4	18.8	8.91	21.384		
9	2.2	21	24.6	54.208		
10	2.3	23.3	17.0	39.008		
11	2.3	25.6	7.10	16.33	130.93	95.919414
12	2.4	28	3.89			
13	2.3	30.3	3.08			
14	2.3	32.6	3.32			
15	2.4	35	3.32			
16	2.2	37.2	3.21			
17	2.3	39.5	4.18			

Chromatography and recovery of standard MW 2000 (c_0=270.3 mg/L, 0.5mL injection)

Sample Nr.	V(mL)	Ve (mL)	DOC(mg/L)	DOC (mg)	Σ DOC (mg)	Recovery (%)
1	2.3	2.3	2.77			
2	2.1	4.4	2.41			
3	2.3	6.7	2.39			
4	2.2	8.9	2.34			
5	2.2	11.1	2.45			
6	2.3	13.4	2.29			
7	2.1	15.5	2.37			
8	2.3	17.8	3.31			
9	2.3	20.1	3.07			
10	2.4	22.5	4.82	11.568		
11	2.4	24.9	16.47	39.528		
12	2.4	27.3	20.26	48.624		
13	2.4	29.7	10.35	24.84		
14	2.2	31.9	5.17	11.374	135.934	100.5801
15	2.2	34.1	3.61			
16	2.3	36.4	4.11			
17	2.2	38.6	2.56			
18	2.3	40.9	3.12			
19	2.5	43.4	3.05			
20	2.5	45.9	3.12			

Chromatography and recovery of standard MW 787 (c_0=165.1 mg/L, 0.5mL injection)

Sample Nr.	V(mL)	Ve (mL)	DOC(mg/L)	DOC (mg)	Σ DOC (mg)	Recovery(%)
16	1.7	29.9	1.82			
17	1.8	31.7	1.92			
18	1.8	33.5	1.47			
19	1.7	35.2	1.63			
20	1.8	37	2.26			
21	1.9	38.9	6.97	13.243		
22	1.6	40.5	11.04	17.664		
23	1.7	42.2	11.73	19.941		
24	1.6	43.8	9.90	15.84		
25	1.9	45.7	7.48	14.212	80.9	98.001211
26	1.9	47.6	6.20			
27	1.8	49.4	4.23			
28	2	51.4	3.11			
29	1.8	53.2	2.78			
30	1.9	55.1	2.68			

Chromatography and recovery of standard MW 180 (c_0=235.3 mg/L, 0.5mL injection)

Sample Nr.	V(mL)	Ve (mL)	DOC(mg/L)	DOC (mg)	Σ DOC (mg)	Recovery (%)
19	1.8	32	2.43			
20	1.8	33.8	2.36			
21	1.6	35.4	2.57			
22	1.7	37.1	3.22			
23	1.6	38.7	9.90	15.84		
24	1.6	40.3	18.37	29.392		
25	1.7	42	17.10	29.07		
26	1.6	43.6	11.31	18.096		
27	1.8	45.4	7.00	12.6		
28	1.8	47.2	5.15	9.27	114.268	97.125372
29	1.8	49	2.94			
30	1.7	50.7	2.42			
31	1.7	52.4	2.22			
32	1.7	54.1	2.63			
33	1.7	55.8	1.78			
34	1.6	57.4	1.77			
35	1.8	59.2	1.73			

The relationship between the elution volume (V_e) and the molecular weight (M)

MW	M	log M	Ve	log Ve
70000	10000	4	18.2	1.2600714
4000	4000	3.60206	21	1.3222193
2000	2000	3.30103	27.3	1.4361626
787	787	2.8959747	41.4	1.6170003
180	500	2.69897	42.2	1.6253125

$$\log V_e = -0.3115 \ \log M + 2.4799$$

Appendix 6: Molecular weight distribution of DOM in digested sludge liquor.

Size-exclusion chromatography and recovery of DOM in original sludge liquor (DOC 645 mg/L, 1.0 mL injection)

Sample Nr.	V(mL)	Ve (mL)	DOC(mg/L)	DOC (mg)	Σ DOC (mg)	Recovery(%)
1	7.9	7.9	4.34			0
2	1.9	9.8	4.59			0
3	1.9	11.7	4.58			0
4	2	13.7	3.86			0
5	2	15.7	6.94	5.88	5.88	0.91
6	2	17.7	9.26	10.52	16.40	2.54
7	1.9	19.6	6.68	5.09	21.49	3.33
8	2	21.6	4.53	1.06	22.55	3.50
9	2.1	23.7	3.71	-0.61	21.94	3.40
10	2	25.7	3.24	-1.52	20.42	3.17
11	2	27.7	4.09	0.18	20.60	3.19
12	2.1	29.8	3.88	-0.25	20.35	3.16
13	2	31.8	4.61	1.22	21.57	3.34
14	2	33.8	5.71	3.42	24.99	3.87
15	1.9	35.7	8.52	8.59	33.58	5.21
16	1.9	37.6	17.9	26.39	59.97	9.30
17	1.9	39.5	38.0	64.52	124.49	19.30
18	1.9	41.4	71.6	128.46	252.95	39.22
19	2	43.4	72.8	137.56	390.51	60.54
20	2	45.4	49.6	91.20	481.71	74.68
21	2	47.4	34.2	60.30	542.01	84.03
22	2	49.4	27.1	46.22	588.23	91.20
23	2	51.4	14.2	20.36	608.59	94.36
24	2	53.4	7.50	7.00	615.59	95.44
25	2.1	55.5	5.03	2.16	617.76	95.78
26	2	57.5	9.25	10.50	628.26	97.40
27	2	59.5	8.74	9.48	637.74	98.87
28	2	61.5	4.37	0.74	638.48	98.99

Size-exclusion chromatography and recovery of DOM in treated sludge liquor (DOC 452.8 mg/L, 1.0 mL injection)

Sample Nr.	V(mL)	Ve (mL)	DOC(mg/L)	DOC (mg)	∑DOC (mg)	Recovery (%)
1	7.7	7.7	3.96			0
2	1.9	9.6	5.01			0
3	1.9	11.5	5.26			0
4	1.8	13.3	5.46			0
5	2	15.3	10.16	9.52	9.52	2.10
6	2	17.3	13.52	16.24	25.76	5.69
7	2	19.3	11.83	12.86	38.62	8.53
8	2	21.3	7.38	3.96	42.58	9.40
9	1.8	23.1	5.77	0.67	43.25	9.55
10	1.9	25	6.01	1.16	44.41	9.81
11	1.8	26.8	7.11	3.08	47.48	10.49
12	1.7	28.5	7.18	3.03	50.51	11.15
13	1.9	30.4	7.51	4.01	54.52	12.04
14	1.9	32.3	8.07	5.07	59.59	13.16
15	1.8	34.1	8.29	5.20	64.79	14.31
16	1.8	35.9	8.20	5.04	69.83	15.42
17	1.9	37.8	10.52	9.73	79.56	17.57
18	1.8	39.6	15.96	19.01	98.57	21.77
19	1.9	41.5	38.64	63.16	161.73	35.72
20	1.7	43.2	47.64	71.81	233.53	51.58
21	1.9	45.1	43.33	72.07	305.60	67.49
22	1.7	46.8	31.86	44.98	350.58	77.43
23	1.7	48.5	23.47	30.72	381.30	84.21
24	1.9	50.4	19.25	26.32	407.62	90.02
25	1.9	52.3	15.05	18.34	425.95	94.07
26	1.9	54.2	15.19	18.60	444.55	98.18
27	2	56.2	8.49	6.18	450.73	99.54
28	2	58.2	7.75	4.70	455.43	100.58
29	1.9	60.1	5.25	-0.29	455.15	100.52
30	1.9	62	4.90	-0.95	454.20	100.31
31	1.9	63.9	4.29	-2.11	452.09	99.84
32	2	65.9	4.36	-2.08	450.01	99.38
33	2	67.9	5.68	0.56	450.57	99.51
34	2	69.9	6.09	1.38	451.95	99.81
35	1.9	71.8	4.67	-1.39	450.56	99.51

Appendix 7: Phosphate breakthrough and P-loading calculation during the continuous operation with model solution at pH 8.12, initial concentration of phosphate 338 mg/L.

t [min]	BV	pH	Cond.[µS/cm]	C_{PO43-} [mg/l]	C/C_0	C_0*t [mg/l*min]	*integral [mg/l*min]	(C_0*t - Integral) [mg/l*min]	Loading $q_m(t)$ [mg/g]
0	0.00	8.12	203.00	338.00	0.00				
5.00	0.54	8.87	193.00	0.80	0.00	1690.00	0.00	1690.00	0.26
15.00	1.62	8.83	195.00	0.09	0.00	5070.00	0.00	5070.00	0.77
30.00	3.23	8.81	196.00	0.14	0.00	10140.00	0.00	10140.00	1.54
45.00	4.85	8.82	196.00	0.05	0.00	15210.00	0.00	15210.00	2.31
60.00	6.47	8.83	196.00	0.43	0.00	20280.00	0.00	20280.00	3.08
90.00	9.70	8.79	196.00	0.04	0.00	30420.00	0.00	30420.00	4.62
120.00	12.93	8.82	195.00	1.91	0.01	40560.00	0.00	40560.00	6.16
150.00	16.17	8.83	195.00	0.42	0.00	50700.00	0.00	50700.00	7.70
180.00	19.40	9.02	196.00	0.15	0.00	60840.00	0.00	60840.00	9.24
210.00	22.64	9.45	201.00	0.08	0.00	70980.00	0.00	70980.00	10.78
240.00	25.87	9.66	212.00	0.15	0.00	81120.00	0.00	81120.00	12.32
270.00	29.10	10.23	218.00	0.14	0.00	91260.00	0.00	91260.00	13.85
300.00	32.34	10.68	244.00	0.82	0.00	101400.00	0.00	101400.00	15.39
330.00	35.57	10.62	246.00	6.08	0.02	111540.00	6.38	111533.62	16.93
360.00	38.80	10.62	245.00	18.00	0.05	121680.00	182.66	121497.34	18.44
420.00	45.27	10.51	236.00	36.90	0.11	141960.00	2176.02	139783.98	21.22
480.00	51.74	10.11	225.00	140.00	0.41	162240.00	8078.02	154161.98	23.40
540.00	58.21	9.83	219.00	188.00	0.56	182520.00	17910.07	164609.93	24.99
600.00	64.67	9.62	218.00	215.00	0.64	202800.00	30255.17	172544.83	26.19
660.00	71.14	8.29	211.00	240.00	0.71	223080.00	44100.37	178979.63	27.17
720.00	77.61	9.28	211.00	260.00	0.77	243360.00	58985.83	184374.17	27.99

780.00	84.07	8.76	210.00	269.00	0.80	263640.00	74709.06	188930.94	28.68
840.00	90.54	8.26	210.00	276.00	0.82	283920.00	91159.02	192760.98	29.26
960.00	103.48	7.68	206.00	300.00	0.89	324480.00	125905.09	198574.91	30.15
1020.00	109.94	7.73	208.00	307.00	0.91	344760.00	144038.25	200721.75	30.47
1080.00	116.41	7.67	207.00	316.00	0.93	365040.00	162566.04	202473.96	30.74
1140.00	122.88	7.64	207.00	309.00	0.91	385320.00	181403.74	203916.26	30.96
1200.00	129.35	7.95	207.00	319.00	0.94	405600.00	200468.95	205131.05	31.14
1260.00	135.81	7.98	206.00	318.00	0.94	425880.00	219683.67	206196.33	31.30
1320.00	142.28	7.91	206.00	319.00	0.94	446160.00	238975.98	207184.02	31.45
1380.00	148.75	7.87	205.00	316.00	0.93	466440.00	258281.06	208158.94	31.60
1440.00	155.21	7.80	205.00	327.00	0.97	486720.00	277541.72	209178.28	31.76

* integral refers to $\int_0^{t_i} C_i dt$ in the equation 2.25 for the calculation of P-loading during the continueous operation

Appendix 8: Phosphate, chloride and COD breakthrough and P-loading calculation during the continuous operation with original sludge liquor at pH 8.17, with the initial concentration of phosphate 170 mg/L, sulfate 10.6 mg/L, chloride 304 mg/L and COD 745 mg/L.

t (min)	BV	pH	C_{PO43-} (mg/L)	C_{Cl-} (mg/L)	COD (mg/L)	C_{PO43-}/C_0	C_{Cl-}/C_0	COD /COD_0	integral [mg/l*min]	(C_0*t - Integral) [mg/l*min]	Loading q(t) [mg/g]
1.00	0.11	12.06	1.24	2.56	179.00	0.01	0.01	0.24	1.23	168.77	0.03
5.00	0.54	12.10	1.31	0.75	201.00	0.01	0.00	0.27	6.18	843.82	0.13
15.00	1.62	12.09	1.24	0.69	214.00	0.01	0.00	0.29	19.47	2530.53	0.38
30.00	3.23	9.90	1.76	16.73	388.00	0.01	0.06	0.52	44.23	5055.77	0.77
60.00	6.47	8.67	3.63	165.50	513.00	0.02	0.54	0.69	117.25	10082.75	1.53
90.00	9.70	8.43	4.42	199.00	530.00	0.03	0.65	0.71	218.58	15081.42	2.29
120.00	12.93	8.23	4.16	250.70	528.00	0.02	0.82	0.71	334.05	20065.95	3.05
150.00	16.17	8.26	3.04	282.30	514.00	0.02	0.93	0.69	447.93	25052.07	3.80
180.00	19.40	8.19	7.52	295.60	519.00	0.04	0.97	0.70	600.92	29999.08	4.55
210.00	22.64	8.19	20.00	293.60	515.00	0.12	0.97	0.69	965.91	34734.09	5.27
240.00	25.87	8.20	48.00	291.80	525.00	0.28	0.96	0.70	1837.79	38962.21	5.91
270.00	29.10	8.14	80.10	314.90	536.00	0.47	1.04	0.72	3699.14	42200.86	6.41
300.00	32.34	8.17	138.00	327.80	527.00	0.81	1.08	0.71	7014.53	43985.47	6.68
330.00	35.57	8.16	154.00	289.90	536.00	0.91	0.95	0.72	11457.10	44642.90	6.78
360.00	38.80	8.12	161.00	307.60	539.00	0.95	1.01	0.72	16283.43	44916.57	6.82
390.00	42.04	8.21	165.00	306.70	533.00	0.97	1.01	0.72	21194.39	45105.61	6.85
420.00	45.27	8.10	167.00	308.20	528.00	0.98	1.01	0.71	26138.92	45261.08	6.87
450.00	48.50	8.10	163.00	303.50	534.00	0.96	1.00	0.72	31084.76	45415.24	6.89
480.00	51.74	8.13	161.00	305.20	539.00	0.95	1.00	0.72	35967.54	45632.46	6.93

Appendix 9: Phosphate, chloride and COD breakthrough and P-loading calculation during the continuous operation with original sludge liquor at pH 6.5, with the initial concentration of phosphate 120 mg/L, sulfate 11.3 mg/L, chloride 2861 mg/L and COD 548 mg/L.

t (min)	BV	pH	C_{PO43-} (mg/L)	C_{Cl-} (mg/L)	COD (mg/L)	C_{PO43-}/C_0	C_{Cl-}/C_0	COD /COD_0	integral [mg/l*min]	(C_0*t - Integral) [mg/l*min]	Loading q(t) [mg/g]
5.00	0.54	11.91	0.52	1.79	100.40	0.00	0.00	0.18	2.49	597.51	0.09
10.00	1.08	11.92	0.34	1.90	100.20	0.00	0.00	0.18	4.92	1195.08	0.18
30.00	3.23	10.04	0.67	5.32	444.00	0.01	0.00	0.81	14.00	3586.00	0.54
60.00	6.47	6.71	0.26	1639.00	389.00	0.00	0.57	0.71	25.90	7174.10	1.09
90.00	9.70	6.60	0.26	2719.00	380.00	0.00	0.95	0.69	36.08	10763.92	1.63
120.00	12.93	6.54	0.27	2713.00	384.00	0.00	0.95	0.70	45.00	14355.00	2.18
150.00	16.17	6.61	0.27	2893.00	374.00	0.00	1.01	0.68	53.14	17946.86	2.72
180.00	19.40	6.53	0.27	2719.00	414.00	0.00	0.95	0.76	61.07	21538.93	3.27
210.00	22.64	7.02	0.37	2999.00	346.00	0.00	1.05	0.63	69.37	25130.63	3.82
240.00	25.87	6.90	0.38	2729.00	348.00	0.00	0.95	0.64	78.59	28721.41	4.36
270.00	29.10	6.91	0.37	2805.00	342.00	0.00	0.98	0.62	89.27	32310.73	4.91
300.00	32.34	6.86	0.40	2708.00	364.00	0.00	0.95	0.66	101.92	35898.08	5.45
330.00	35.57	6.85	0.43	2728.00	356.00	0.00	0.95	0.65	117.24	39482.76	5.99
360.00	38.80	6.66	1.53	3056.00	366.00	0.01	1.07	0.74	137.14	44142.86	6.70
390.00	42.04	6.63	0.44	3097.00	376.00	0.00	1.09	0.76	167.99	47802.01	7.26
420.00	45.27	7.01	1.63	3117.00	358.00	0.01	1.10	0.72	230.67	51429.34	7.81
450.00	48.50	7.13	10.80	2924.00	358.00	0.09	1.03	0.72	388.46	54961.54	8.34
480.00	51.74	6.52	21.70	3273.00	410.00	0.17	0.99	0.80	807.69	60632.31	9.20
510.00	54.97	6.48	45.90	3271.00	407.00	0.36	0.99	0.80	1804.39	63475.61	9.64
540.00	58.21	6.50	78.80	2954.00	399.00	0.62	0.90	0.78	3663.40	65456.60	9.94
570.00	61.44	6.84	98.70	2863.00	402.00	0.77	0.87	0.79	6319.50	66640.50	10.12

600.00	64.67	6.62	108.00	3009.00	408.00	0.84	0.91	0.80	9489.28	67310.72	10.22
630.00	67.91	6.60	120.00	3095.00	399.00	0.94	0.94	0.78	12957.34	67682.66	10.28
660.00	71.14	6.60	125.00	2792.00	399.00	0.98	0.85	0.78	16604.87	67875.13	10.30
690.00	74.37	6.67	125.00	3053.00	395.00	0.98	0.93	0.77	20349.51	67970.49	10.32

Appendix 10: Phosphate, chloride and COD breakthrough and P-loading calculation during the continuous operation with original sludge liquor at pH 5.5, with the initial concentration of 282 mg/L phosphate, 20.6 mg/L sulfate, 4466 mg/L chloride and 750 mg/L COD.

t (min)	BV	pH	C_{PO43-} (mg/L)	C_{Cl-} (mg/L)	COD (mg/L)	C_{PO43-}/C_0	C_{Cl-}/C_0	COD /COD_0	integral [mg/l*min]	(C_0*t - Integral) [mg/l*min]	Loading q(t) [mg/g]
5.00	0.54	12.20	0.52	4.33	186.00	0.00	0.00	0.25	0.00	1410.00	0.21
10.00	1.08								0.000	2820.00	0.43
30.00	3.23	10.33	0.56	356.00	368.00	0.00	0.08	0.49	0.00	8460.00	1.28
60.00	6.47	6.61	0.36	4953.00	536.00	0.00	1.11	0.71	0.00	16920.00	2.57
90.00	9.70	5.57	0.31	5593.00	531.00	0.00	1.25	0.71	0.00	25380.00	3.85
120.00	12.93	5.67	0.37	4555.00	565.00	0.00	1.02	0.75	3.91	33836.09	5.14
150.00	16.17	6.04	3.65	5258.00	604.00	0.01	1.18	0.81	118.32	42181.68	6.40
180.00	19.40	5.70	36.20	5289.00	657.00	0.13	1.18	0.88	694.27	50065.73	7.60
210.00	22.64	5.69	96.90	5603.00	694.00	0.34	1.25	0.93	2560.64	56659.36	8.60
240.00	25.87	5.52	184.00	5155.00	689.00	0.65	1.15	0.92	6777.55	60902.45	9.25
300.00	32.34	5.50	260.00	5472.00	642.00	0.92	1.23	0.86	20821.99	63778.01	9.68
330.00	35.57	5.72	256.00	4898.00	634.00	0.91	1.10	0.85	28668.38	64391.62	9.78
360.00	38.80	5.70	270.00	4472.00	647.00	0.96	1.00	0.86	36593.28	64926.72	9.86
390.00	42.04	5.85	274.00	5299.00	619.00	0.97	1.19	0.83	44614.74	65365.26	9.92
420.00	45.27	5.82	279.00	5296.00	621.00	0.99	1.19	0.83	52785.01	65654.99	9.97

450.00	48.50	5.81	283.00	4513.00	624.00	1.00	1.01	0.83	61126.52	65773.48	9.99
480.00	51.74	5.73	275.00	5314.00	645.00	0.98	1.19	0.86	69612.35	65747.65	9.98
510.00	54.97	5.67	280.00	5500.00	642.00	0.99	1.23	0.86	78163.83	65656.17	9.97
540.00	58.21	5.77	279.00	5133.00	695.00	0.99	1.15	0.93	86659.85	65620.15	9.96
570.00	61.44	5.99	268.00	5545.00	627.00	0.95	1.24	0.84	94955.84	65784.16	9.99
600.00	64.67	5.52	281.00	5001.00	658.00	1.00	1.12	0.88	102908.20	66291.80	10.06
630.00	67.91	5.62	237.00	4780.00	617.00	0.84	1.07	0.82	110397.00	67263.00	10.21
660.00	71.14	5.61	213.00	5067.00	636.00	0.76	1.13	0.85	117339.60	68780.40	10.44

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Adenauerring 20

76131 Karlsruhe

Tel.: 0721/608-42457

Fax: 0721/608-44729

E-Mail: irmtraud.kaupa@kit.edu