

Removal of arsenic from drinking water by adsorption with amine modified polyketone



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Abstract

Removal of toxic arsenate from drinking water is a global problem affecting more than one hundred million people worldwide. Arsenate in water causes high rate of diseases even in low dosage. Arsenate should be removed from drinking water to a very low concentration below $10 \mu\text{g}/\text{L}$ according advice from the World Health Organization. Amine modified polyketone can be used as an adsorbant for this purpose. It should be known how high the arsenate uptake capacity to make comparison with other adsorbants and technologies possible.

To show functionality as an adsorbant for arsenates, amine modified polyketone was measured in a continuous flow adsorption column. These measurements were used in two different adsorption models to calculate adsorption capacity. Measurement and adsorption models show good agreement, thus adsorption models provide a reliable basis for comparing amine modified polyketone to other adsorption based technologies.

Adsorption experiments, and model results show that amine modified polyketone has high arsenate uptake capacity up to $190 \text{ mg}/\text{g}$ polyketone resin. This value is much larger than uptake capacity for competing technologies such as activated alumina and activated carbon which have capacities ranging from 10 to $50 \text{ mg}/\text{g}$. This high uptake capacity by itself makes amine modified an excellent adsorbant. Furthermore amine modified polyketone is shown to capable of regeneration, which makes repeated usage possible. Other advantages are also shown when comparison is made to competing technologies. Amine modified polyketone does not introduce contaminants to treatment systems, which is a disadvantage for ion-exchange and precipitative processes.

When production cost of amine modified polyketone can be as low as 15 \$ per kg, amine modified polyketone can compete with activated alumina and activated carbon on an economic basis.

Part I

Introduction and research Background

Resource usage roughly parallels prosperity and technological development of a country. Moreover, when prosperity increases, so do various quality and safety standards and requirements. Water as a resource is no exception to this case. Water usage in the industrialized world is around 250 to 575 liters of water per citizen per day. There are 1.1 billion people, usually in developing countries, who lack adequate water access and use less than 19 liters per day¹. As a source for consumption approximately two liter is used as drinking water per day (Anon, 2000a). If this water is contaminated a health risk can occur. One of this contaminants is Arsenic, an element occurring naturally in water, it leaches from the earth to the groundwater and rivers. Arsenic is known to be carcinogenic and increases the risk of various other diseases. The primary source of arsenic intake is through water. (Mohan and Pittman, 2007) report that 100 million people are consuming water with arsenic concentration up to 100 times the 10 $\mu\text{g}/\text{L}$ guideline of the World Health Organization. Risk from arsenic are strongly related to poverty and nutrition (Howard, 2003).

Various techniques for removing arsenic from water are available. One of these techniques is adsorption. From literature it is known that amine-functional groups are able to adsorb heavy metals (DeMarco et al., 2003; Iesan et al., 2008; Toncelli, 2013). The primary interest in polyketone as an adsorbant for arsenic comes from the fact that polyketone can be easily modified to contain amine-functional groups. Experiments performed at the RuG with amine modified polyketone to remove various heavy metals (Cr, Co, Fe, Ni, Cu, Hg, Ag) from water in a continuous column have proven that amine modified polyketone can be used as an adsorbant of heavy metals. Batch experiments have been performed for arsenic removal. These experiments show that amine modified polyketone can remove arsenic. Experiments with a continuous column have not been performed for arsenic removal. In order to determine if arsenic can effectively remove arsenic from water, adsorption experiments are performed. Furthermore regeneration experiments are performed to determine technical parameters and possible competitive advantages of polyketone adsorption to alternative techniques such as ion-exchange adsorption with activated carbon or activated alumina.

Previous investigations indicate that amine modified polyketone can compete with a range of available adsorbants on capacity. For example polyketone has an adsorptive capacity of $\sim 38\text{-}113\text{ mg/g}$ compared to $\sim 30\text{ mg/g}$ for activated carbon, $\sim 10\text{-}25\text{ mg/g}$ for activated aluminum (Oosterholt, 2010; Mohan and Pittman, 2007). However many adsorbants are used in batch operated systems. This implies solid waste streams, the need for replacement of adsorbant, the need for preconditioning and secondary processes such as filtration. A technique closely similar to adsorption is ion-exchange. However ion-exchange, exchanges the adsorbed ion with an ionic species present in the ion-exchange resin, resulting in the

¹<http://www.circleofblue.org/waternews/wp-content/uploads/2009/07/waterinfo.pdf>

introduction of new ionic species to the effluent. Furthermore ion-exchange often requires pretreatment to obtain satisfactory removal conditions ([Litter et al., 2010](#); [Kartinen Jr and Martin, 1995](#)). Polyketone is thought to have the advantage that it can be used in a continuous operated column, without the need for pretreatment of the influent stream. Amine modified polyketone can be used in natural pH conditions, therefore not introducing additional chemicals to the effluent. It is unknown if and how many times polyketone can be regenerated and how large its adsorption capacity is in continuous column operation. If polyketone can be regenerated, it could be a competitive technique for removal of arsenic from water. Using amine-modified polyketone for arsenic removal is a novel application of polyketone and a method that has not been reported in literature.

1 Research goals

This chapter will outline the research in more detail. Which research goals does this report address and what are the concepts that are used as a guide for the research.

(Voncken et al., 2004) define product technology as: “The science and art of developing and producing performance products to meet demands and requirements of society and achieve this by adding value to materials by improving existing and designing new products.” A distinction is made between bulk products such as gasoline, ammonia and ethylene. These products are made per required specification. On the other hand, the many small-scale products, which can vary from bread additives to special polymer coatings or drugs, may be called performance products. The latter are primarily produced and marketed because of their specific performance.

The definition of requirements and attributes usually start vague and is a process itself. Consumers and users usually do not define their requirements in such a way that the engineer can start with product development immediately (Voncken et al., 2004). Amine modified polyketone has not been used for arsenic removal, therefore specific attributes have not been defined. There are several relevant aspects that characterize how specification of requirements can be realized. These aspects originate from various stakeholders who can have different perspectives and further requirements.

One perspective applicable is to define stakeholder requirements from a problem situation perspective. A problematic situation is defined by (de Leeuw, 2002) as “any situation that causes to strive for improvement or renewal”. A problem situation is a system with one or more problems. An often used definition of a problem is a difference of a particular situation and a desired situation. Figure 1 shows this situation where a problem owner models goals from his reality or Real Life System. This model is a subjective perception of reality by the actor who judges his goals. There is a discrepancy in the model of the desired system (what the actor wants) and the perceived model of the system (what the actor thinks about the system). There are modeling and judgment elements which arise, which are used in diagnosis of the problem.

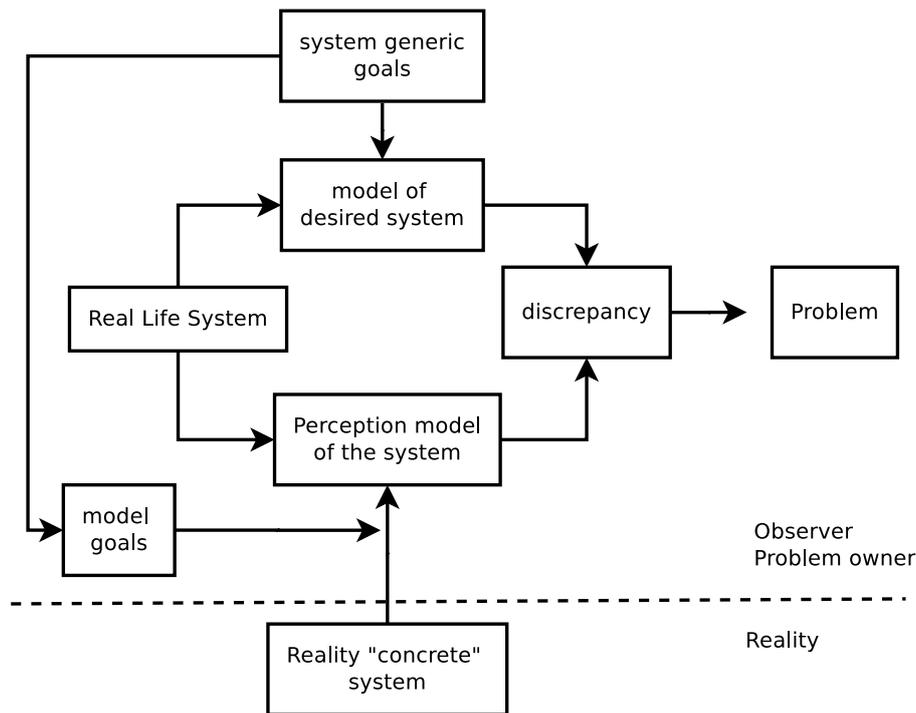


Figure 1 – Emergence of a problem (de Leeuw, 2002)

Standards and requirements for drinking water result in goals from a product technology perspective. Polyketone is researched for possible applications at the Rijksuniversiteit Groningen. Polyketone is currently not used in practical or commercial applications. When amine-modified polyketones' potential is considered as arsenic adsorbant, the required performance of amine-modified polyketone could be used to classify amine modified polyketone as a performance product as defined by (Voncken et al., 2004).

(Alvesson and Sandberg, 2013) state gap-spotting as the prevalent method of constructing research questions. Specifically application spotting can be used for this purpose. Application spotting is defined as searching for a shortage of a particular theory or perspective in a specific area of research. In this case the usage of amine modified polyketone as an adsorbant for arsenic. Gap spotting can additionally lead to research questions from problematization when different stakeholder perspectives conflict, and make it necessary to challenge existing knowledge. For example by examining cost effectiveness parallel to purely technical capability.

A gap between fundamental research of adsorption with amine modified polyketone and basic research knowledge on arsenic removal technologies places this research in an applied research scope. Applied research has the purpose of improving understanding of particular business or management problems, it has relevance to the specific problem, and provides practical relevance, value or solutions to managers in organizations (Saunders et al., 2009). The goal of this research is to show if amine modified polyketone is a material that can be used to remove arsenic from drinking water. And in what way it can be a competitive alternative to existing technologies.

Investigations done by the United States Environmental Protection Agency (US-EPA) provides insight of the scope and relevance of research on removal of arsenic with different

technologies, processes and scale sizes. Furthermore different stakeholders are considered in US-EPA research. This becomes clear from a statement in (Anon, 2003):

"As part of this Arsenic Rule Implementation Research Program, EPA's Office of Research and Development (ORD) proposed a project to conduct a series of full-scale, long-term, on-site demonstrations of arsenic removal technologies, process modifications, and engineering approaches applicable to small systems in order to evaluate the efficiency and effectiveness of arsenic removal systems at meeting the new arsenic MCL."

From an engineering and technical perspective the US-EPA investigations is very valuable. Because of its applied nature combined with scientific verification. EPA research does not include removal of arsenic with amine modified polyketone, however EPA research could be applied to amine modified polyketone specifically researched in this thesis. From a broader perspective the US-EPA documentation is valuable because of the information it provides information about other factors that are of importance for stakeholders (Condit and Chen, 2004):

"Many factors were considered in the selection process, including water quality, residual production and disposal, complexity of system operation, and costs..."

These factors influence the technical/engineering aspects of arsenic removal but can be considered on their own. As an example water quality can be of importance with respect to regulatory authorities only with respect to the question if the water is safe to drink. From a business perspective diagnosing the potential of polyketone can be based on comparison (de Leeuw, 2002) of other techniques for arsenic removal.

"On January 18, 2001, the U.S. Environmental Protection Agency (EPA) finalized the maximum contaminant level (MCL) for arsenic at $10 \mu\text{g}/\text{L}$ ($0.01 \text{ mg}/\text{L}$)" (Anon, 2003). Specifically arsenic levels above a level of $10 \mu\text{g}/\text{L}$ are considered a problem. The ability and capacity for adsorbing arsenic can therefore be viewed as specific performance requirements for amine modified polyketone. The reports by the US-EPA include field testing and measurements of technologies that are considered the best available technologies based results from comparing different technologies on a range of criteria. These criteria include arsenic concentration that can be treated, size of system in number of customers, geographical location (as an example: iron can be beneficial for removing arsenic), and cost effectiveness.

(Crawford and Di Benedetto, 2003) also recognize the need for value added attributes of new products. The number one cause of new product failure is "no need for the product" and number two is "there was a need but the new product did not meet that need". In other words the new product was not unique and superior.

From a developers point of view, considering amine modified polyketone is not used in any practical or commercial application. It can be considered a new product. (Crawford and Di Benedetto, 2003) recognize a conceptual framework by which a new product can be categorized. Three inputs are used in the classification process, these are: form, technology and need or benefit provided to fulfill a need by the product user. The conceptual framework for new product categorization is shown in figure 2.

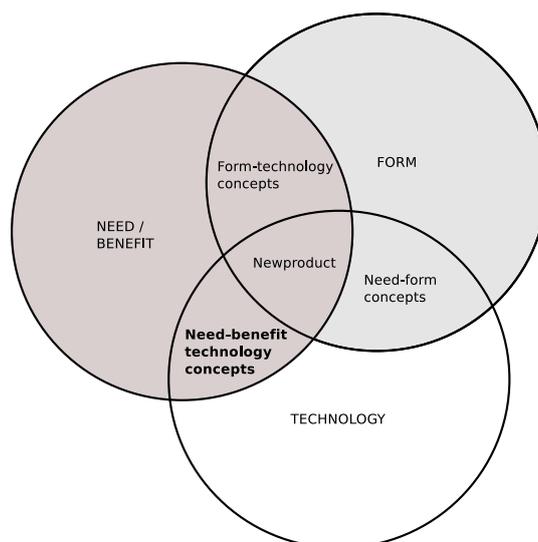


Figure 2 – New product concept (Crawford and Di Benedetto, 2003)

Amine modified polyketone is researched at the Rijksuniversiteit Groningen, it is an existing product, however it is not commercially available as it is discontinued from production ². Form and technology are set, however it's specific or potential application and required attributes are not known. Amine modified polyketone has been shown to have potential for heavy metal removal from aqueous solution (Alberts, 2010; Oosterholt, 2010; Toncelli, 2013). Potentially amine modified polyketone has benefits over other products and technologies. Technology and form in this case are closely related polyketone is a tangible product when modified with lysine, therefore amine modified polyketone should be placed as a need- or benefit-technology concept in figure 2.

Product requirements translate to attributes for amine modified polyketone (Voncken et al., 2004). These attributes may yield value added properties for amine modified polyketone when comparing to competing technologies. An example of a value added property could be specified by an operator of a drinking water processing plant, this requirement could also originate from rules or regulations stated by law.; For application in drinking water purposes it is required that an amine-modified polyketone adsorption process does not add chemicals or toxicity to water. Therefore comparison with ion-exchange could yield beneficial properties as ion-exchange adds new ionic species as an inherent side effect to its process. Other benefits or value added properties could be cost, capacity or re-usability of polyketone compared to other techniques. When comparing competing technologies the combination of capacity and regeneration potential determines advantageous attributes that are unique or beneficial for amine modified polyketone.

From an engineering perspective the goal of the research is to determine adsorption properties of polyketone for the removal of arsenic in a continuous column and determination of the regeneration potential of polyketone in continuous column for arsenic removal.

From a business perspective the goal of the research is a cost/benefit comparative analysis for a small drinking water system, equivalent to transition model 2, table 2 (10.000 or

²<http://matweb.com/search/datasheettext.aspx?matid=27909>

fewer people served). With comparison being made with an adsorption system using lysine modified polyketone compared to other Best Available Techniques as tested by the Environmental Protection Agency.

These goals result in the formulation of research questions.

2 Research questions

The main research question resulting from research goals can be defined as follows:

What are the relevant qualitative and quantitative performance characteristics for amine-modified polyketone with respect to functioning as a suitable adsorbant for arsenic in drinking water treatment systems?

The main research question can be subdivided in relevant technical and a business related research questions. These questions can be split into parts as to address specific factors relevant to the main question.

Technical perspective

1. *Does amine modified polyketone effectively adsorb arsenic from the aqueous phase?*
 - (a) *What is the adsorption capacity of amine modified polyketone for arsenic in the aqueous phase?*
 - (b) *What general observations does this provide for adsorption-speed, -capacity and workability?*
2. *Can amine modified polyketone adsorbant be regenerated for repeated usage?*
 - (a) *How large is the desorption rate compare to adsorption rate?*
 - (b) *Does adsorption capacity diminish over time?*

Business perspective

1. *Can amine-modified polyketone be a competitive technology to remove arsenic from drinking water?*
 - (a) *What are advantages of amine modified polyketone over other technologies?*
 - (b) *How many times can polyketone be regenerated before it has to be replaced?*
 - (c) *How many time should polyketone be able to be regenerated to be competitive with other Best Available Techniques?*
 - (d) *What should the price of polyketone be to be competitive with other adsorbants?*

3 Research setup and methods

The following steps will be performed in this research to answer research questions :

1. Column measurements with amine-modified polyketone to measure column adsorption parameters and predict breakthrough curve from regression of data
2. Comparison of measurements with three reference models. First being the Bed Depth Service Time model (BDST). The second model is the Thomas Model. The third model is the Yoon-Nelson model. These models are used to calculate uptake capacity for amine-modified polyketone.
3. Column regeneration measurements.
4. Comparative literature review of other arsenic removal techniques, and comparative literature review of small system Best Available Technologies (BAT) demonstration projects performed by the Environmental Protection Agency to produce benchmark data for further analysis of polyketone potential performance.
5. Scaling-up calculations of PK-adsorption on a scale similar to transition 2 model (table 2).
6. Cost/benefit comparison with real world applied techniques, and analysis of economic viability based on scale-up calculation results

3.1 Limitations

This study will focus on the removal of pentavalent arsenic, As(V). The removal of As(III) is recognized by various authors to be less efficient for most removal technologies. Column experiments are performed with arsenic concentrations ranging from 10 to 50 mg/L . This concentration is much higher than the WHO limit for arsenic of 10 $\mu g/L$, however column measurements by conductometry require higher concentration. Furthermore the concentration range is within range of concentrations occurring in drinking water systems, therefore this is deemed acceptable.

4 Thesis outline

The structure of the thesis report will follow the research flow. This is depicted in figure 3. The research divided in two phases the diagnostic phase where the information is obtained that is needed to make a conceptual design (design phase) of a process for arsenic removal with amine-modified polyketone. The “boundaries” of the design phase are placed on the simulation stage of the research. This boundary should be considered soft, because of the iterative nature of process simulation and sensitivity analysis that is needed obtain a conceptual design.

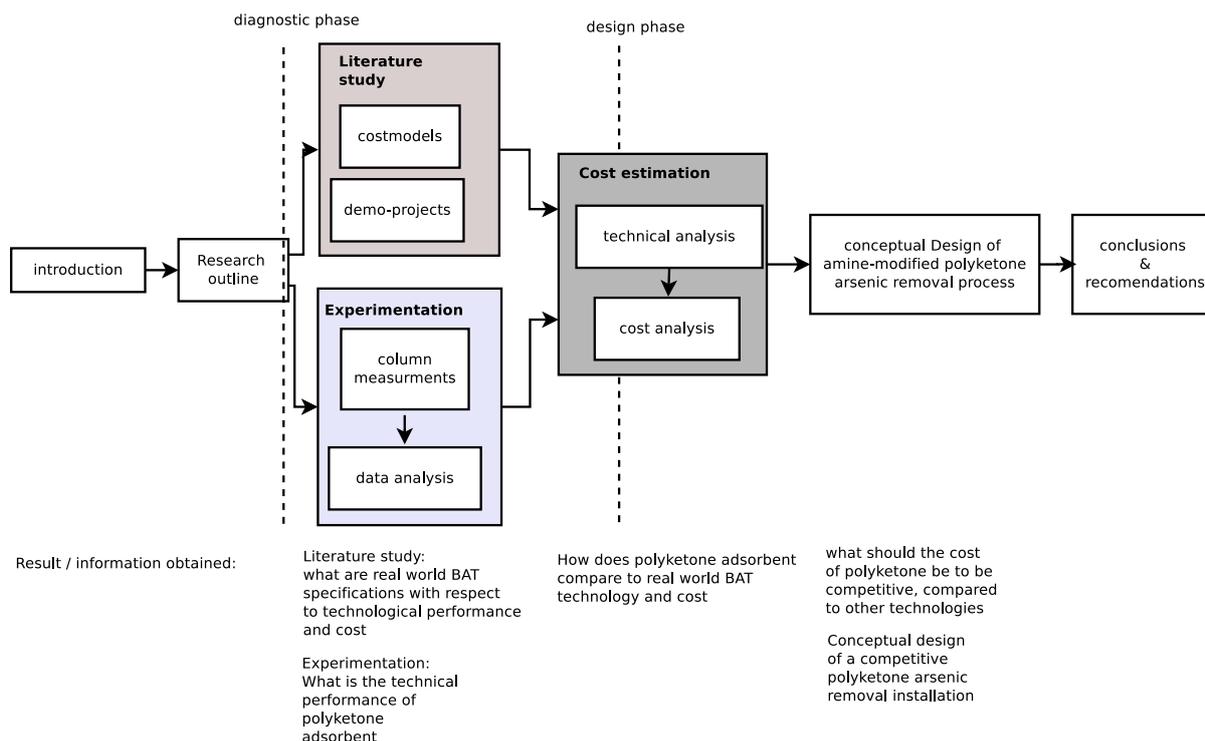


Figure 3 – Research flow and thesis outline

The contents of the thesis will be:

- Introduction to the subject of arsenic in (drinking)water; Why is arsenic in water a problem and what does this research contribute to the subject.
- Research goals, research questions and research setup will outline the research in more detail. Which research questions will be answered and what methods will be used to obtain these answers. What are the concepts that are used as a guide for the research.
- Literature research on information that is available with respect to technology and cost in real world “large-scale ” implementations of arsenic removal technologies.
- Detailing of experimental work with a small column containing amine-modified polyketone. Experimental work will be aimed at examining the regeneration charac-

teristics of amine-modified polyketone. Details of experimental work will be addressed, and results of analysis of data is reported.

- Simulation modeling with a monte-carlo technique is performed with information from literature and measurements as input. The result will be a description and model of a technological process that could be used to remove arsenic from drinking water. The cost of this process is calculated from on basis of this technology comparison.
- The last part of this thesis is used for reporting conclusions to the findings of the research.

Part II

Literature review

5 Occurrence toxicity and health hazards

Arsenic occurs in drinking water through human activities such as mining, use of arsenic pesticides and wood preservative agents (Choong et al., 2007). The presence of arsenic in natural water is mostly related to the process of weathering and leaching from arsenic containing rocks and sediments (Jain and Ali, 2000; Anon, 2003). Because of the natural occurrence of arsenic in groundwater at various locations in the world, arsenic is also encountered in drinking water in these areas. Exposure is predominately caused by drinking water that has been sourced from groundwater, arsenic exposure through food is relatively low. Humans ordinarily cannot detect arsenic in water without testing through appropriate technologies. We neither see, taste, or smell the presence of arsenic whether the water we drink is contaminated with arsenic compounds (Roy, 2008).

Arsenic rarely occurs in free state, it is largely found in combination with sulfur, oxygen and iron. Arsenic cannot be destroyed and can only be converted into different forms or transformed into insoluble compounds in combination with other elements, such as iron (Choong et al., 2007).

Inorganic arsenic generally exists in two predominant valence states, arsenite (As(III)) and arsenate (As(V)). The valence in aqueous media depends on local oxidation reduction conditions. Groundwater generally has reducing conditions, therefore arsenite occurs. Surface water has aerobic, oxidizing properties thus arsenate is found. Arsenite and arsenate are toxic to man and plants. Both arsenite and arsenate occur in four different species. The speciation of these molecules changes by dissociation and is pH dependent. The kinetic of dissociation for each are nearly instantaneous. The pH dependencies of arsenite and arsenate are depicted in figure 4 and figure 5 respectively.

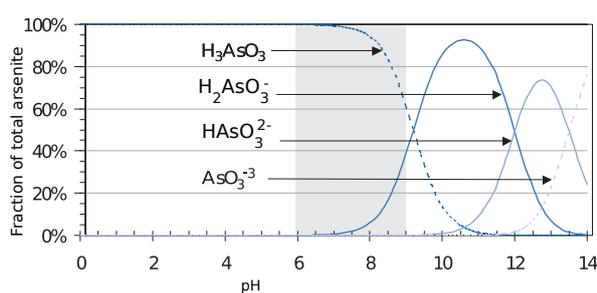


Figure 4 – Dissociation of arsenite [As(III)] (Anon, 2003)

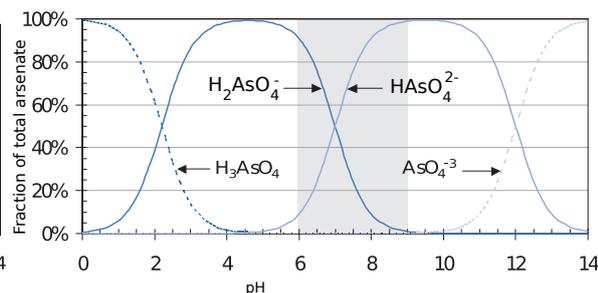


Figure 5 – Dissociation of arsenate [As(V)] (Anon, 2003)

Chemical speciation is a critical element of arsenic treatability. Negative surface charges facilitate removal by adsorption. The net charge of arsenite is neutral at natural pH levels (pH 6-9), therefore it is not easily removed. The net molecular charge of arsenate

is negative (-1 or -2) at natural pH levels, making removal more efficient. Conversion to arsenate is a critical element of treatment. Conversion can be accomplished by adding oxidizing agent such as chlorine, ozone or permanganate (Anon, 2003). Direct aeration is slow, only 0.25% of arsenite is converted to arsenate in 5 days by direct aeration of groundwater containing 200 $\mu\text{g/L}$ As(III) (Bissen and Frimmel, 2003).

Arsenic removal with amine functional polymers relies on chelation of arsenate species. The mechanism is further described in Chapter 8.

Organic arsenic is recognized to be less toxic than inorganic arsenic (Mandal and Suzuki, 2002; Jain and Ali, 2000; Sharma and Sohn, 2009). Arsenic can also occur in organic molecules for example through bacterial activity, but it occurs much less than inorganic arsenic. Inorganic arsenic is about 100 times more toxic than organic arsenic. For inorganic arsenic the toxicity of As(III) is 60 times greater than As(V) (Jain and Ali, 2000). Exposure to arsenic trioxide by ingestion of 70-80 mg has been reported to be fatal for humans (Sharma and Sohn, 2009). The LOAEL (lowest observable adverse effect level) is estimated to be between 10 and 20 $\mu\text{g/kg/day}$, the NOAEL (no observable adverse effect level) is estimated to be between 0,4 and 0,9 $\mu\text{g/kg/day}$ (DOHAHS, 2000).

The clinical manifestations of chronic arsenic poisoning (arsenicosis) in humans include non-cancer effects of skin pigmentation, hardening of the skin, hypertension, cardiovascular diseases diabetes (Ng et al., 2003), weakness, anaemia, burning sensation in the eyes, solid swelling of legs, liver fibrosis, chronic lung disease, gangrene of the toes and neuropathy (Choong et al., 2007). Cancer usually manifests typically as skin-, lung- and bladder cancer, however other cancers can occur.

Arsenic level in tap water $\mu\text{g/L}$ (parts per billion)	Approximate total cancer risk (assuming 2 liter consumed per day)
0,5	1 in 10.000
1	1 in 5.000
3	1 in 1.667
4	1 in 1.250
5	1 in 1.000
10	1 in 500
20	1 in 250
25	1 in 200
50	1 in 100

Table 1 – lifetime risks of cancer from arsenic in tap water (Anon, 1999), values above WHO limit (10 $\mu\text{g/L}$) in red

It has been estimated that about 60-100 million people in India and Bangladesh are currently at risk as a result of drinking arsenic-contaminated waters (Ng et al., 2003; Mandal and Suzuki, 2002; Sarkar and Biswajit, 2016). At present 2 million people in mainland China are exposed to high amounts of arsenic, and 20.000 cases of arsenicosis are confirmed (Mandal and Suzuki, 2002).

As an example in Antofagasta, Chili, over 12% of the 130.000 inhabitants exhibited dermatological manifestations related to arsenic due to consumption of water that contained

0,8 mg/L arsenic (Mandal and Suzuki, 2002). According to some estimates, arsenic in drinking water will cause 200.0000-270.000 deaths from cancer in Bangladesh alone (Choong et al., 2007).

The proportion of a population exposed to elevated arsenic from drinking-water that will go on to develop arsenicosis is unknown. The World Health Organization have modeled the progression of arsenicosis using data from Samta, Bangladesh. The range of those affected over 30 years was 15,75% in the lowest estimate scenario to 29,25% in the highest estimate scenario. Variation in estimates of mortality from cancers was between 5,0 and 6,5%. This implies a significant overall health burden for those affected. (Howard, 2003).

5.1 Occurrence in drinking water systems

The US-EPA publishes reports on various aspects of arsenic in drinking water. The occurrence in drinking water systems is described in a report by (Anon, 2000b). Arsenic occurs more frequent and with a slightly higher concentration in groundwater systems than in surface water systems. Furthermore about 99% of the systems have an arsenic concentration lower than 50 $\mu\text{g/L}$. Approximately 8% of the systems has an arsenic concentration higher than 10 $\mu\text{g/L}$.

Arsenic occurs in water in several different forms depending upon the pH and oxidation potential of the water, both parameters are routinely measured in water treatment processes, as pH and ORP (Oxidation Reduction Potential). It is found both in the trivalent, As(III) and pentavalent As(V) form.

Groundwater is often reducing (negative ORP). Arsenic occurs primarily in the trivalent, As(III) form. Experience has shown that As(III) is difficult to remove using the normally available processes, an oxidizing pre-processing step is often employed in treatment (Kartinen Jr and Martin, 1995).

Pentavalent arsenic species predominate and are stable in oxygen rich aerobic environments such as surface water. The oxidation of As(III) to As(V) is slow in air, the oxidation is in the order of 0,25% in 5 days. Therefore using groundwater that contains arsenic to produce drinking water involves more than simple aeration. Oxidizing agents such as chlorine, ozone and hydrogen-peroxide oxidize arsenic to the pentavalent form much more rapidly, oxidation time is usually around 30 minutes (Bissen and Frimmel, 2003).

5.2 Economic benefits of arsenic removal

Few studies evaluate the cost benefit of arsenic contamination and removal. (Roy, 2008) evaluate the economic benefit of reduction of arsenic in drinking water to a level of 50 $\mu\text{g/l}$. According to the study the chance of a person living in the West Bengal area getting an arsenic-related disease is "quite low" at 4,7%. Despite the fact that people are exposed to arsenic in 50% of the West Bengal districts. The economic benefit of arsenic reduction to a West Bengal household is 7 dollars per month, with an associated cost of 3 dollars per month per household. According to the authors a relevance to policy making is noteworthy when the probability of getting an arsenic-related disease, is considered to be low. Policy

makers may not feel compelled to act. However when the monetary valuation of welfare loss shows that value addition can result from arsenic removal. Policy makers may feel inclined to act.

6 Removal technologies

The environmental protection agency in the United States (US-EPA) has made a number of reports available on the subject of arsenic in drinking water ³. These reports include demonstration projects to test Best Available Technologies (BAT) to reach a maximum contaminant level (MCL) of 0,010 *mg/L* or less. The size of these demo projects is stated as *small system* which is defined as a system serving 10.000 or fewer people, this is normally less than 1,4 million gallons/day ($\pm 5300 \text{ m}^3/\text{day}$). The following section gives a description of alternative technologies for removal of arsenate from water streams. Appendix A contains a tabulated summary of compared technologies.

Furthermore the US-EPA has also reported on detailed cost estimation models for a range of treatment technologies at specific treatment scale ranges, these ranges are shown in table 2.

scale of treatment	capacity range m^3/day	
	lower	upper
VSS	57	378
Transition 1	378	1.022
water model	1.022	3.785
Transition 2	3.785	37.854
W/W cost model	37.854	757.082

Table 2 – Scale size of cost estimation models US-EPA

These treatment scale ranges are used as a reference for comparing technologies that are implemented by the US-EPA with a modeling study that is to be done on amine-modified polyketone.

The US-EPA uses the Empty Bed Contact Time (EBCT) and number of Bed Volumes to exhaustion (BV_e) to estimate installation size, cost and operating conditions such as run and regeneration times on various operating scales (table 2). From this data optimal run times can be determined.

Technology tree The existing technologies for arsenic removal can be roughly classified in four categories. Ion-exchange, sorption processes, membrane processes and precipitative processes. Figure 6 lists the technologies that are discussed most in the literature from the US-EPA with respect to actual field testing. Furthermore treatment is aimed at reducing the concentration of arsenic below 10 $\mu\text{g/l}$. This level can in some situations be obtained

³<http://epa.gov/nrmrl/wswrd/dw/arsenic/publications.html>

by blending water with concentrations above the 10 $\mu\text{g}/\text{l}$ threshold with water containing less than the threshold. Reducing the need for full capacity water treatment.

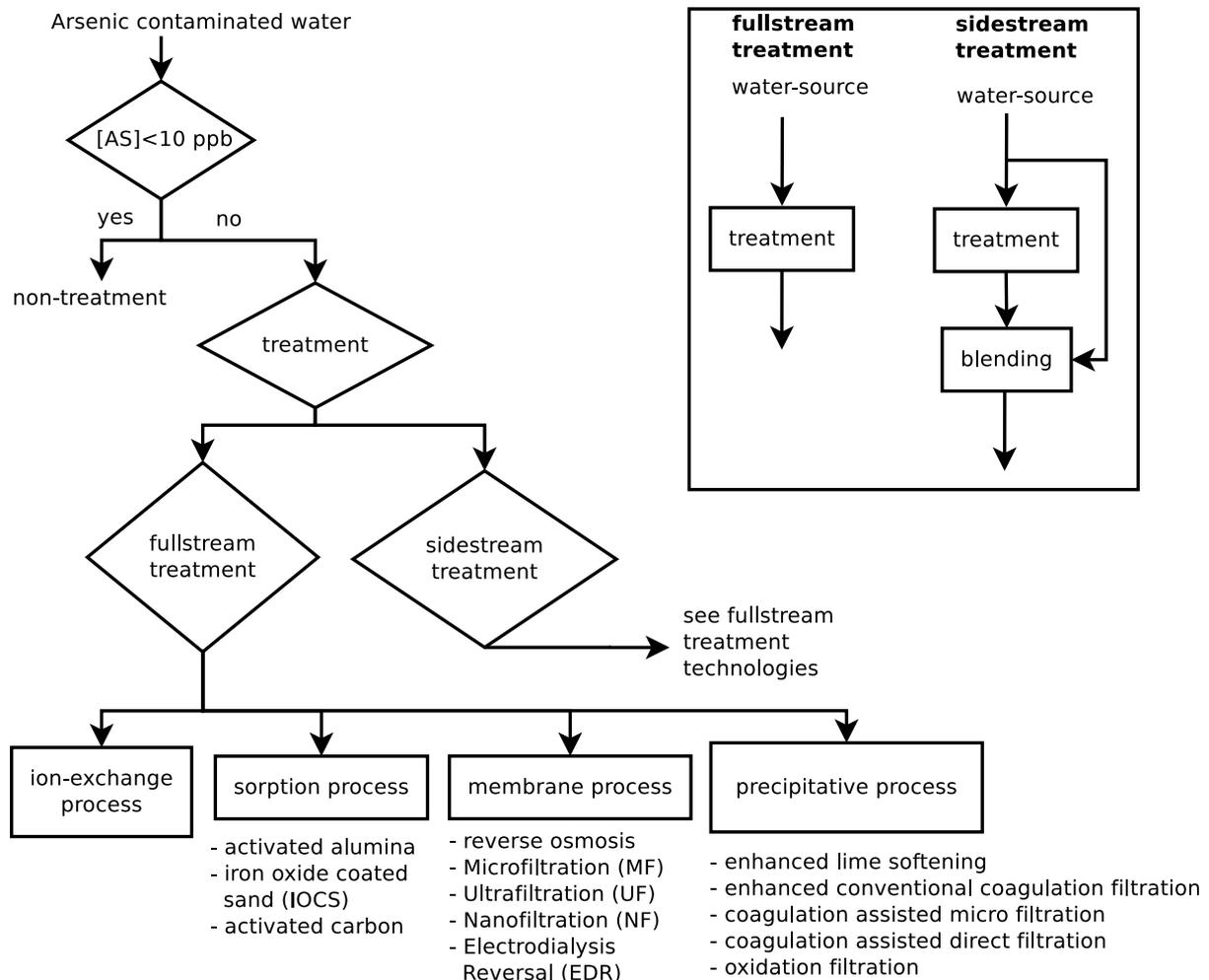


Figure 6 – Technology-tree

Treatment of arsenic contaminated water is aimed at making water safe to drink. There is little commercial interest in recovery of arsenic and arsenic compounds as there is a very limited market for the recovered material. Safety in handling and storage has made it even less practical to recover arsenic.

It is widely recognized that As(III) should be oxidized to As(V) independent of the removal technology that is used (Bissen and Frimmel, 2003; Dambies, 2005)

6.1 Sorption processes

Adsorption is one of the most widely applied unit operations used to separate molecules that are present in a fluid phase (adsorbate) using a solid surface (adsorbant). This process can be carried out in batch- or continuous mode. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or

concentration at the surface of another. Figure 7 shows process in which water is fed at steady rate, and the contaminant is adsorbed from the water onto the adsorbate, producing contaminant free water. However adsorbant particles become progressively more saturated with contaminant from the inlet end towards the outlet end, until at some specified point there occurs a breakthrough of contaminant in the outlet water stream. Further use eventually results in complete saturation and effluent contaminant concentration becomes equal to the influent concentration.

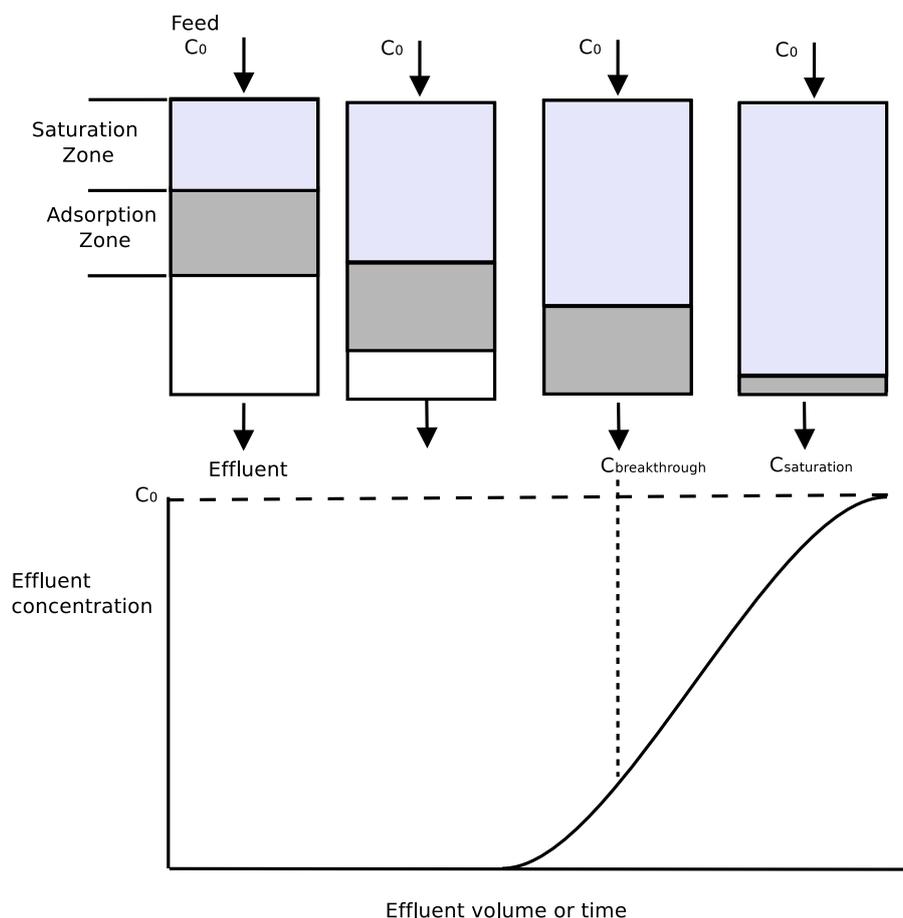


Figure 7 – Progression of the adsorption zone through a fixed-bed adsorber (Cooney, 1999)

Adsorption is used extensively in waste- and drinking water treatment. The nature of adsorption is an attractive interaction of contaminants with the surface of an adsorbant. In aqueous media this interaction can consist of various ionic interactions. One form of interaction is complexation this is further discussed in chapter 8.

6.1.1 Activated carbon

Activated carbon (AC) is one of the well known adsorbants. Many activated carbons are available commercially but few are selective for heavy metals (Mohan and Pittman, 2007). They are also expensive, and large quantities are needed for water purification. Results regarding removal of arsenic are controversial but most of them show that activated carbon

can remove As(V) but not As(III). However As(V) uptake capacities were low, reaching 30 *mg/g* on granular activated carbon (Dambies, 2005).

The performance of activated carbon depends on its chemical composition. (Lorenzen et al., 1995) demonstrated that the fly ash content of activated carbon was a critical parameter in arsenate removal. Arsenic adsorption can be improved chemically by pre-treating activated carbon with Cu(II), ferric hydroxide or tartaric acid (Choong et al., 2007).

Activated carbon is usually regenerated by heating up in a furnace when adsorbates are of organic origin, adsorbate is desorbed and combusted. Activated carbon is reactivated usually with high temperature steam. For arsenic this is not possible and spent carbon is stored, usually in a landfill (Cooney, 1999).

6.1.2 Activated alumina

Activated alumina (AA), commonly named aluminum oxide (Al_2O_3), is prepared by the thermal dehydration of aluminum hydroxide. Activated alumina has a high surface area (few hundred m^2/g) and a distribution of both macro and micro-pores. Activated alumina is classified by the US-EPA as among the best available technologies for arsenic removal in drinking water (Dambies, 2005). It is believed the arsenic adsorbs into the surface of the activated alumina. Eventually, the alumina surface becomes sufficiently saturated with arsenic that adequate removal is no longer accomplished. It then becomes necessary to regenerate the alumina. This is done by subjecting the alumina to a caustic bath, which appears to remove the surface layer of alumina, and the arsenic adsorbed into that layer. The alumina is then neutralized with an acid rinse, and put back into service. Regeneration of alumina is not complete, the alumina loses about 30-40% of its capacity each regeneration so it must be replaced after three or four cycles. However, its low cost and relatively high capacity keeps cost at an acceptable level (Kartinen Jr and Martin, 1995). Arsenic adsorption occurs mostly between pH 6 and 8, where AA is predominantly positively charged. As pH increases, the AA surface is less and less positive and As(V) sorption decreases.

At low residual arsenic concentration, AA performs better than other adsorbents with uptake capacities of a few *mg/g*. The arsenic uptake capacity varies with AA grade and is between 0,68 and 25 *mg/g* at a As(V) concentration of 1-100 $\mu g/L$, however a typical value would be around 10-15 *mg/g*. Fluoride-, sulfate-, chloride- and phosphate-ions decrease the arsenate removal efficiency by as much as 50% (Bissen and Frimmel, 2003; Dambies, 2005). AA has a low affinity for As(III), with a very low capacity of 0-0,8 *mg/L* at arsenic levels of 400 $\mu g/L$ (Dambies, 2005). (Kartinen Jr and Martin, 1995) showed several cases where the number of treated bed volumes that could be treated was a factor 20-80 higher if chlorine was used to oxidize arsenic to As(V) prior to adsorption.

6.1.3 Iron based sorbents

Iron oxides have been widely used as sorbents to remove contaminants from waste water and liquid hazardous wastes. Removal has been attributed to ion-exchange, specific adsorption to surface hydroxyl-groups or co-precipitation (Choong et al., 2007). Arsenic removal

technology by adsorption with a commercial granular ferric hydroxide (GFH) has been developed in the early 1990s (Jekel and Seith, 2000; Driehaus et al., 1998). It can be applied in simple fixed bed reactors, similar to those for activated alumina or activated carbon. Simplified operation is a key benefit of the system, which will operate without the need for chemical pre-feed or pH correction. GFH has a high adsorption capacity in natural waters (Choong et al., 2007). The work carried out by (Driehaus et al., 1998) shows that GFH possesses a high treatment capacity of 30.000 to 40.000 bed volumes. (Jekel and Seith, 2000) compared precipitation/flocculation by iron (III)-chloride and iron(II)sulphate as well as adsorption on GFH in a full scale water treatment plant. Their findings show that adsorption on granulated iron hydroxide has proven to be the method which will provide greater operational reliability with least maintenance and monitoring efforts.

Bayer AG together with Severn Trent Water developed a system of granular ferric oxy-hydroxide called the SORB33 system. It is claimed that the arsenic removal can be below the drinking water standard of $\mu\text{g}/\text{L}$. The only factor which needs monitoring is the pressure drop of water through the adsorbant bed. However under high pH conditions high levels of vanadium, phosphate and silica can reduce the adsorption of arsenic, requiring more frequent changing (Choong et al., 2007). (Deliyanni et al., 2003) synthesized akaganéite in laboratory conditions ($\beta - \text{FeO}(\text{OH})$) which has a high surface area of $330 \text{ m}^2/\text{g}$ and narrow pore size distribution. The maximum sorption capacity was found to be of the order of 120 mg As(V) per g of akaganéite.

6.1.4 Ion-exchange

Ion-exchange resins linked to charged functional groups, can be applied for As removal. Quaternary amine groups $-N^+(\text{CH}_3)_3$ are the preferred groups. Arsenate removal is efficient, producing effluents with less than $1 \mu\text{g}/\text{L}$ of arsenic, while arsenite, being uncharged, is not removed, and an oxidation step is necessary (Litter et al., 2010).

Arsenic ions can be removed by ion-exchange resin usually loaded with chloride ions at the exchange sites. The resin is placed in a column, water is passed over the resin and the arsenic exchanges for the chloride ions. The water exiting the vessel is lower in arsenic but higher in chloride than the water entering the vessel.

The effect of the presence of sulfate, competition with other anions, is an important factor to ion-exchanger treatment of arsenic. Sulfate levels can limit the applicability of ion-exchanger as arsenic treatment (Choong et al., 2007; Kartinen Jr and Martin, 1995).

(Korngold et al., 2001) used strong base anion-exchange resins for the removal of As(V). They observed competing reactions between SO_4 , NO_3 , Cl and arsenic ions so that the efficiency of arsenic decreased in the presence of these anions. More than 99% of arsenic was removed by the resins at an initial concentration of $600 \mu\text{g}/\text{L}$.

For ion-exchange it is important that arsenic has a pentavalent oxidation state and the pH should be at least 7,5 in order to achieve the best removal rates. Since oxidation of As(III) to As(V) is often done with chlorine there is a risk of degradation of the exchange resin (Kartinen Jr and Martin, 1995).

Strong base anion exchange resins have quaternary ammonium groups connected to the polymer matrix and differ by the nature of the group attached to the nitrogen. Anion

exchange resins have more affinity for divalent anions than monovalent anions, therefore $HAsO_4^{2-}$ will be preferentially adsorbed over $H_2AsO_4^-$ therefore arsenate removal is expected to increase between pH 6 and 9 (Dambies, 2005).

On the other hand, due to its weak dissociation constant, As(III) cannot be removed. A pre-oxidation step is necessary to treat an arsenite solution with ion-exchange technology (Dambies, 2005)

6.2 Membrane processes

Membrane separation is a pressure driven process. Pressure driven processes are commonly divided into four overlapping categories of increasing selectivity with respect to the size of particle rejection: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and hyper-filtration or reverse osmosis (RO). As selectivity increases driving pressure needed to force water through the membrane increases, this also increases energy cost Anon (2003). Separation is accomplished by MF and UF membranes via mechanical sieving, while capillary flow or solution diffusion is responsible for separation in NF and RO membranes (Wiesner et al., 1992).

Trivalent and pentavalent arsenic can be effectively removed from water by RO and NF over a range of operating conditions. For NF rejection rates can be as high as 95-99%. Some authors suggest that removal of As(V) and As(III) is comparable, with no preferential rejection of As(V) over As(III). This suggests that size exclusion governs their separation behavior and not the charge interaction. Other researchers have found a much lower rejection rate of As(III). Reverse osmosis membranes reject As(V) much more than As(III) in a pH range of 3-10, arsenic in the high oxidation states As(V) is very effective for RO (Choong et al., 2007; Bissen and Frimmel, 2003). (Han et al., 2002) studied the feasibility of a combination of flocculation and microfiltration for arsenic removal from drinking water. Microfiltration of the flocculated water had resulted in rejection of arsenic and lower turbidity. (Shih, 2005; Brandhuber and Amy, 1998) show that membrane technologies to be sufficiently effective to remove arsenic from water and meet the arsenic MCL standard. However, the effectiveness of membrane technologies is sensitive to a variety of source water characteristics, water contaminants, arsenic species, and membrane characteristics. No one-membrane material, membrane type and membrane process can be used in all the possible environments and requirements of different arsenic removal applications.

Pre-oxidation of As(III) to As(V) followed by NF may achieve high rates of arsenic removal. If arsenic is present in the particulate form, membranes of relatively large pore size may be effective for arsenic removal. The drawback of using membranes in arsenic removal are:

- The systems are more costly than other treatment methods.
- The discharge of the concentrate can be a problem
- Membrane fouling and flux decline

The membranes are justified when the total dissolved solids due to the presence of sulphates, nitrates and carbonates is important and require a treatment.

6.3 Precipitative process

Precipitative processes depend on formation of solid insoluble particles. Usually this process is induced by adding chemicals to the aqueous stream that is to be treated. Usually a second processing step such as filtering or settling is employed to remove formed particles. Four precipitation processes are reported in literature to be most useful in removing arsenic from water; alum coagulation, iron coagulation, lime softening and a combination of iron (and manganese) removal with arsenic (Choong et al., 2007).

6.3.1 Precipitative softening

Lime softening commonly is used to reduce hardness in source waters. Hardness is due primarily to the presence of calcium and magnesium ions. The lime provides hydroxide ions that increase pH, which results in calcium and magnesium removal due to the formation of CaCO_3 and Mg(OH)_2 precipitates. Lime softening can be used for removal of heavy metals through adsorption and occlusion with calcium and magnesium precipitate. The typical softening treatment process includes rapid mixing of the lime, flocculation of solids, and sedimentation (Fields et al., 2000).

The primary mechanism of arsenic removal is through co-precipitation with Mg(OH)_2 . The presence of iron promotes the formation of Fe(OH)_3 which can dramatically increase arsenic removal. The co-precipitation with CaCO_3 is low (<10%) furthermore carbonate interferes with removal by iron (McNeill and Edwards, 1997).

Disadvantages of lime-softening are that pre-oxidation of arsenite to arsenate is necessary (Rivas et al., 2011). Furthermore the effluent has a very high pH (>10.5), a very high dose of coagulant is needed and arsenic concentrations less than 1 mg/L are not achieved. Implying the need for secondary treatment (Litter et al., 2010).

6.3.2 Coagulation-Flocculation

Coagulation and flocculation are two of the most employed methods for removing arsenic. The principle removal mechanism is to create larger particles that can be better removed by filtration or sedimentation. The terms coagulation and flocculation are often used interchangeably. They are in fact, two distinct processes. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart, as a result the particles collide to form larger particles. Flocculation is the action of polymers to form bridges between the larger mass particles or flocs and bind the particles into larger agglomerates or clumps. It is not unusual to coagulate particles and apply flocculation to the coagulated particles. The general approach for this technique includes pH adjustment and involves adding a coagulant, often in the form of ferric/alum salts. (Kurniawn et al., 2006; Choong et al., 2007)

6.3.3 Oxidation filtration

Oxidation is a previously required step to transform As(III) species in more easily removable As(V) species. Direct aeration is slow (Bissen and Frimmel, 2003), but a number of

chemicals, including chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide, manganese oxide and Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) can be employed to accelerate oxidation. Chlorine is a rapid and effective oxidant, but it may react with organic matter, producing toxic and carcinogenic trihalomethanes as by-products. Potassium permanganate effectively oxidizes arsenite, and it may be a widely available inexpensive reagent suitable for developing countries. Hydrogen peroxide can be an effective oxidant if the raw water contains dissolved iron, which often occurs in conjunction with arsenic contamination. Ultraviolet radiation alone or with suitable light adsorbers such as TiO_2 can also be convenient options for As(III) oxidation.

7 Prospective technologies

Various literature sources shows that other technologies for arsenic removal exist that are either exotic, i.e. based on rarely used technologies, or that only have been tested on laboratory or small scale. These technologies include electro dialysis, electrocoagulation, metal loaded-, inorganic- or pure polymer sorbants.

Electrodialysis is a type of membrane process. Electric current is applied to draw the ions through the membranes leaving the fresh water behind. Electrodialysis cannot effectively treat water with metal concentrations higher than 1000 mg/L , and is more suitable for water with a metal concentration less than 20 mg/L . Since electro dialysis is a membrane process it requires a clean feed, careful operation, periodic maintenance to prevent damages to the stack (Kartinen Jr and Martin, 1995; Kurniawn et al., 2006).

(Balasubramanian and Madhavan, 2001) found that arsenic can be removed by electrocoagulation effectively. A coagulation agent is produced in-situ at the surface of the electrodes. For initial arsenic concentrations of 100 mg/L in industrial waste water 90% and 100% arsenic is removed at $0,5 \text{ A/dm}^2$ and $1,25 \text{ A/dm}^2$ with an electrolysis time of 12 hours.

(Dambies, 2005) describe the use of metal loaded polymers for arsenic removal. Metal loaded polymers are usually prepared by passing a metal ion solution through a packed column of resins. Table 3 shows examples of metal loaded polymer types used for arsenic removal.

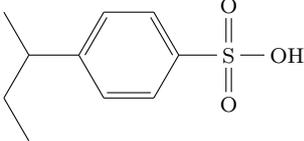
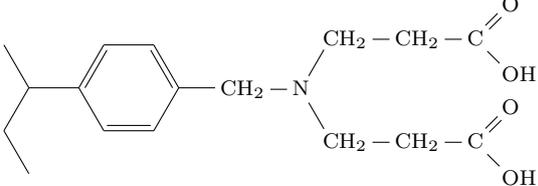
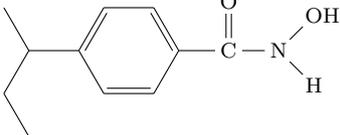
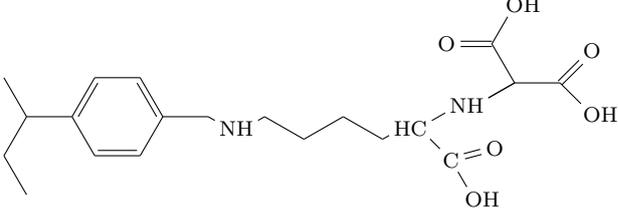
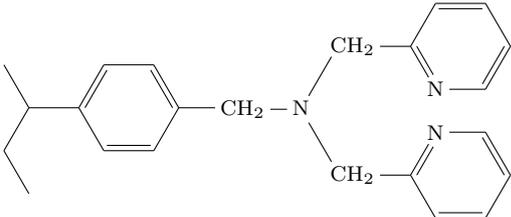
Type of resin	Metal loading	Capacity As(V) at concentration	Structure
sulfonic acid	Fe	not reported	
iminodiacetic (IDA)	Fe	49mg/g, Ceq=150mg/L, pH=2	
polyhydroxamic (PHA)	Fe	86,2mg/g, Ceq=2,2mg/L, pH=2-4, interference of F, Se, P ions	
lysinediacetic (LDA)	0,89 mmol/g Fe of wet sorbent	27,2mg/g, Ceq= 1 / 0,1mg/L, pH=3,5	
bis(2 picolylamine)	0,65 mmol/g Fe	63,6mg/g , Ceq = 15mg/g, pH=5-10	

Table 3 – Metal-loaded polymers ([Dambies, 2005](#))

The uptake capacity of these resins is influenced negatively by phosphate ions because of chemical similarities to arsenates. Regeneration of metal loaded polymers can be problematic as the impregnated metal can leach out of the resin along with arsenate. This would make repeated impregnation with metal necessary.

The metal loaded polymers saturation capacities are between 74,9 and 112,4 mg/g. However these capacities can drastically decrease at low residual arsenic concentration, making

them inefficient for drinking water treatment.

(DeMarco et al., 2003) report on a polymeric/inorganic hybrid sorbent that is capable of selectively removing arsenic(III) and arsenic(V). The sorbent particles consist of spherical macro-porous cation exchanger within which agglomerates of nanoscale hydrated Fe oxide (HFO) particles have been uniformly and irreversibly dispersed using a simple chemical-thermal treatment. This sorbent is referred to as hybrid ion-exchanger (HIX). The

(Awual and Jyo, 2009) report on the performance of cross-linked polyallylamine (PAA) resin as arsenate adsorbant using a packed column. PAA has a high amino group content of 14.6 mmol/g in free amine form. A breakthrough capacity of $0.8 - 3.52 \text{ mmol/g}$ dependent on flowrate and pH. A lower pH and flowrate resulted in higher breakthrough capacities. Furthermore the polymer can be regenerated by elution with 2M HCl. The report states that the adsorbant can be regenerated many times without loss of performance. Competitive uptake of arsenate and phosphate revealed that PAA slightly preferred phosphate to arsenate.

(Rivas et al., 2011) combined water soluble polymers with one or more amine, amide, carboxylic acid, hydroxyl, phosphonic acid, quaternary ammonium salts, and sulfonic acid groups at the backbone or side chain to form complexes of arsenate and polymer. The arsenate complex that is formed is subsequently removed by ultrafiltration. Two polymers are mentioned specifically for arsenic retention capacity. Poly[2-(acryloyloxy) ethyl] trimethylammonium chloride, P(CIAETA) has a capacity of 142 mg/g and poly[2-(acryloyloxy) ethyl] trimethylammonium methyl sulphate, P(SAETA) has a retention capacity of 75 mg/g . To remove As(III) species an additional electro-oxidation step is proposed. It is unclear what the benefit of electro-oxidation is compared to other oxidation techniques as these are not considered in the article.

8 Complexes

A complex is a compound that exists of a central metal ion attached to a number of ligands. Ligands are molecules or ions that are held by the metal ion by overlap of an empty orbital (d- and sometimes f- orbitals) on the metal with a filled orbital on the ligand. Sometimes there is overlap of a filled orbital on the metal with an empty orbital on the ligand. The bond therefore can be considered to be covalent with varying degrees of ionic character depending on positive and negative charges on the metal and surrounding ligands. Ligands are able to chelate, meaning more than one ligand interacts with a central metal ion. Chelating ligands are more stable than complexes formed by binding of analogous separate ligands (Morrison, 1992). Lysine modified polyketone contains amine and carboxylic acid groups that can form complexes with metal anions. An example of this interaction is given in figure 8.

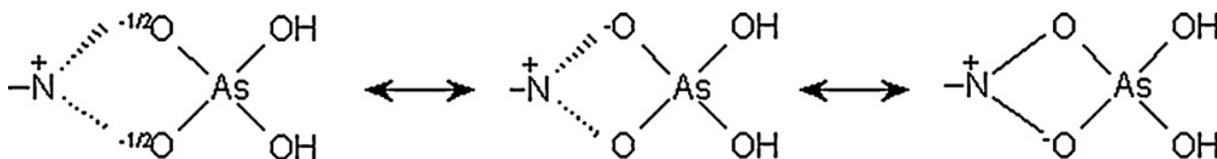


Figure 8 – Electrostatic interaction of ammonium groups with oxy-anion arsenate (Rivas et al., 2011)

Arsenic is dissociated in aqueous solution into various oxy-anions.

Arsenic dissociation into oxy-anions in aqueous solution	pK value
$H_3AsO_4(aq) \leftrightarrow H^+ + H_2AsO_4^-$	$pK_1 = 2, 22$
$H_2AsO_4^- \leftrightarrow H^+ + HAsO_4^{2-}$	$pK_2 = 6, 98$
$HAsO_4^{2-} \leftrightarrow H^+ + AsO_4^{3-}$	$pK_3 = 11, 4$

Table 4 – Arsenic dissociation in atmospheric oxidizing aqueous environment (Vatutsina et al., 2007)

Under atmospheric or more oxidizing environment, the predominant species is As(V), which, in the pH range of 6–9, exists predominantly as deprotonated oxy-anions, namely, $H_2AsO_4^-$ or $HAsO_4^{2-}$. (DeMarco et al., 2003; Vatutsina et al., 2007).

Parent oxyacid	pKa values	Predominant dissolved species at pH 6.0	Predominant dissolved species at pH 8.0	sorption interaction
As(V): H_3AsO_4	pKa1 = 2,20 pKa2 = 6,98 pKa3 = 11,60			As(V) can undergo Coulombic (ion-exchange) as well as Lewis acid-base interaction.

Table 5 – Oxyacids and conjugate anions of As(V) (DeMarco et al., 2003)

Table 4&5 show that arsenic oxyanions under atmospheric conditions disassociate into oxyanions therefore these species can be adsorbed by lysine functionalized polyketone.

9 Polyketone with lysine functional groups

Polyketone is a polymer consisting of perfectly alternating copolymers of carbon monoxide (CO) with ethylene (a) and/or propylene (b) groups (Hamarneh, 2010). Figure 9 shows alternating groups in the polyketone backbone to be either a hydrogen or a methyl group depending on the ethylene (a) or propylene (b) chain in the polyketone backbone.

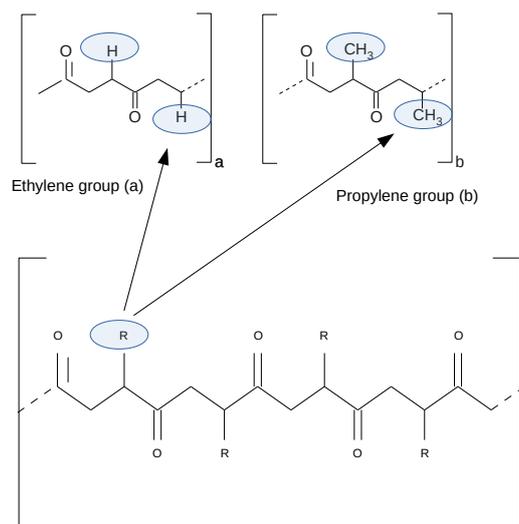


Figure 9 – possible alternating groups of polyketone: ethylene (a) or propylene (b)

There are a number of available polyketone types. Each with a different ratio of a or b, ethylene or propylene, in the polymer backbone. Three types of polyketone were prepared for experimentation. With ratio's a/b of 0/100, 30/70 and 50/50 (Hamarneh, 2010).

A wide variety of synthetic methodology is available for polyketone modification. Well known products are polypyrroles, polyalcohols, polyamines, polyphenols and polythiols (Hamarneh, 2010). Polypyrrole formation involves the reaction of two adjacent carbonyl groups (1,4-dicarbonyl moiety) on the polyketone backbone with a primary amine to form a pyrrole ring and water as a side product.

Amino acid and carboxylic acid functional groups are introduced by reacting polyketone with lysine. Three molar ratio's are prepared previously for experimentation, with PK:lysine molar ratio's of 0,2 0,4 and 0,6. In total three alternating group polyketone ratio's are reacted with three molar ratio's of polyketone:lysine, resulting in nine different lysine modified polyketone types. A summary of available lysine modified polyketone types is given in table 6 along with its corresponding sample code.

% ethylene/propylene (a/b) groups	Nitrogen groups measured <i>N</i> % and (expected <i>N</i> %) for [sample code]		
	PK:lysine ~0,2	PK:lysine ~0,4	PK:lysine ~0,6
0/100	18,75 (18,64) [PB2209]	34,49 (37,03) [PB2709]	48,24 (55,15) [PB2809]
30/70	21,99 (20,40) [PB2408]	44,09 (40,22) [PB3008]	59,68 (61,30) [PB0109]
50/50	28,66 (20,10) [PB0709]	48,76 (40,10) [PB0909]	56,91 (60,10) [PB1509]

Table 6 – Characterization of polyketone samples

The reaction occurs via the Paal-Knorr reaction. It involves the reaction of two adjacent carbonyl groups. This yields a pyrrole ring with both an amine and carboxylic acid side-group. Literature suggests there is also a possibility of cross-linking between pendent amine groups to form a further pyrrole ring or an imine group (Hamarneh, 2010). This removes amine groups, however carboxylic acid functional groups remain which can contribute to adsorption of metal ions via complex formation.

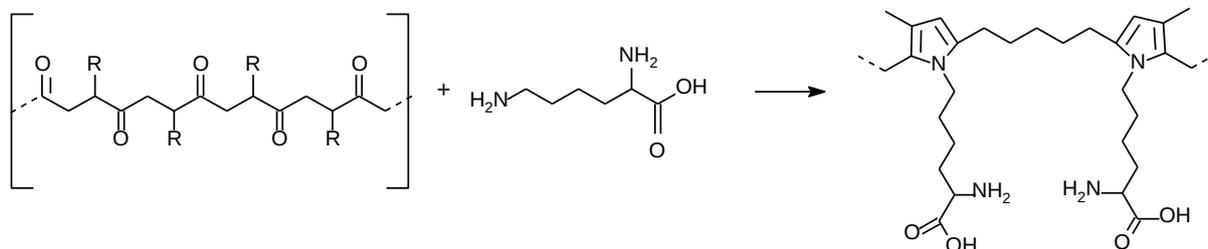


Figure 10 – Functionalization of polyketone via 'Paal-Knorr' reaction with lysine

The amine- and carboxylic acid groups are capable of forming complexes with arsenate species. Thus function as an adsorbant for arsenates.

10 Adsorption models for column measurements

Successful design of a column adsorption process requires prediction of the concentration-time profile or breakthrough curve for the column effluent. The maximum adsorption capacity of an adsorbant is also needed in design. Three models are relevant in these respects.

The Bed Depth Service Time (BDST) model gives the relationship between the service time (i.e. how long a column can be used before saturation) and the packed bed depth of the column. This is expressed as:

$$BDST \text{ model : } \quad C_0 t = \frac{N_0 h}{u} - \frac{1}{K} \ln \left(\frac{C_0}{C_t} - 1 \right) \quad (1)$$

Where C_0 = influent concentration (mg/L), t = service time to breakthrough (min), N_0 = adsorption capacity (mg/g), h = bed depth of fixed bed (cm), u = linear flowrate (cm/min) and K = adsorption rate constant ($L/(mg \ min)$) and C_t = effluent concentration at time t (mg/L).

The Thomas model determines the maximum solid phase concentration of solute on the adsorbant and the adsorption rate constant for an adsorption column. This model is expressed as:

$$Thomas \text{ model : } \quad \ln \left(\frac{C_0}{C_t} - 1 \right) = \frac{k_{Th} q_0 m}{Q} - \frac{k_{th} C_0 V_{eff}}{Q} \quad (2)$$

Where k_{Th} = Thomas rate constant ($ml/(min \ mg)$), q_0 = equilibrium As(V) uptake (mg/g), m = amount of resin in the column (g), Q = volumetric flowrate (ml/min), V_{eff} = volume of effluent.

The Yoon-Nelson model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbant (Chun Yang Yin and Dead, 2009). The Yoon and Nelson model is not only less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbant, and the physical properties of the adsorption bed (Ozturk and Kavak, 2005). The linearized model for a single component system is expressed as:

$$Yoon - Nelson \text{ model : } \quad \ln \left(\frac{C_0}{C_0 - C_t} \right) = k_{YN} t - \tau k_{YN} \quad (3)$$

Where k_{YN} is the rate constant (min^{-1}) and τ is the time required for 50% adsorbate breakthrough (min).

Linear plots of $C_0 t$ against $\ln[(C_0/C_t) - 1]$, and $\ln[(C_0/C_t) - 1]$ against V_{eff}/Q (or t) have to be made to calculate the values of N_0 and k_{Th} from the intercept and K and q_0 from the slope of the linear plots. The Yoon-Nelson model can be fitted by a linear plot of $\ln[(C_0/C_0 - C_t)]$ against sampling time (t). Alternatively, τ can also be obtained at the adsorption time when $\ln[(C_0/C_0 - C_t)]$ is zero because of the fact that by definition τ is the adsorption time when C_t is one-half of C_0 .

All three models are mathematically equivalent. One single fitting can be obtained from model equations (1 , 2 and 3).

The fitting equation is expressed as:

$$\ln \left(\frac{C_0}{C_t} - 1 \right) = A - Bt \quad (4)$$

where:

<i>BDST Model</i>	<i>Thomas Model</i>	<i>Yoon – Nelson Model</i>
$A = \frac{KN_0h}{u}$	$A = \frac{k_{Th}q_0m}{Q}$	$A = \tau k_{YN}$
$B = KC_0$	$B = k_{Th}C_0$	$B = k_{YN}$

from A and B relevant parameter can be calculated:

<i>BDST Model</i>	<i>Thomas Model</i>	<i>Yoon – Nelson Model</i>
$K = \frac{-B}{C_0}$	$k_{Th} = \frac{-B}{C_0}$	$\tau = \frac{A}{B}$
$N_0 = \frac{A * u}{K * h}$	$q_0 = \frac{A * Q}{k_{Th} * m}$	$k_{YN} = B$

(6)

$$q_0 = \frac{1}{2}C_0Q(2\tau) = C_0Q\tau$$

The derivation for q_0 for the Yoon-Nelson model is based on the definition that 50% breakthrough occurs at τ . Accordingly, the bed should be completely saturated at 2τ (Ozturk and Kavak, 2005).

To facilitate direct visual comparison of models with breakthrough measurement curves (where C_t/C_0 is plotted against time) all three equations can be rewritten into the following equation:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp(A - B * t)} \quad (7)$$

Which is for the BDST model expressed as:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp \left(\frac{KN_0h}{u} - KC_0t \right)} \quad (8)$$

for the Thomas model as:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp \left(k_{Th} \frac{q_0m - C_0m}{Q} \right)} \quad (9)$$

and for the Yoon-Nelson model as:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp \left[k_{YN} - (\tau - t) \right]} \quad (10)$$

Part III

Experimental

11 Methods

Continuous measurement over time of arsenic removal from an aqueous solution is needed to calculate adsorption rate constants according to both the BDST, Thomas and Yoon-Nelson model of adsorption. Accurate measurement of very low concentrations of arsenic in the range the of the guideline of the World Health Organization; $10 \mu\text{g}/\text{L}$ require techniques such as atomic-absorption or atomic-emission spectrophotometry (Fields et al., 2000; Awual and Jyo, 2009). These methods are not suitable for continuous monitoring of effluent arsenic concentration. As these methods require sampling, combined with short experiment run length this would be impractical. Given the fact that literature reports concentrations of arsenic in the range up to $100 \text{mg}/\text{L}$ as typical for exposure and measurement of adsorption methods, conductometry is suitable for continuous measurement of arsenic concentration in column effluent. Conductometry is used to measure the total ion concentration in a solution. A calibration range of known arsenic concentrations is measured to determine the relation of conductivity and arsenic concentration in solution. Conductometry can then be used to determine the concentration over time of arsenic in the effluent from the adsorption column. These measurements provide the basis for calculation of BDST, Thomas and Yoon-Nelson adsorption models.

12 Calibration

Arsenic is not directly measured in the column setup. It is measured with a conductivity probe. To relate the conductivity with the arsenic concentration a calibration is done. Conductivity is measured for a range of known arsenic concentrations. This measurement gives the relation between conductivity and concentration. Linear regression is performed to obtain the following relationship between conductivity and arsenic concentration:

$$y = ax + b \quad (11)$$

With y being the measured response or conductivity ($\mu\text{Siemens}$), x the known predictor concentration (mg/L), a = slope coefficient, b = intercept coefficient.

From calibration measurements concentration can be predicted in adsorption experiments by calculating x (concentration of arsenic) from equation 11:

$$x = \frac{y - b}{a} \quad (12)$$

13 Materials

Lysine modified polyketone was provided for experimentation. Details of preparation can be found in Appendix B. Measurements are performed with amine modified polyketone that contain a high active lysine group ratios, PB1509 is used as it is expected to best perform as an adsorbant for arsenic. Increasing capacity with higher functionalization has been show for other heavy metals (Toncelli, 2013). An aqueous solution containing Sodium Orthoarsenate ($Na_2HAsO_4 * 7H_2O$) with a concentration ranging from 10 to 50 mg/L , is used for measurement.

All experiments were carried out at room temperature (293 K), without pH modification. Measurements are performed by pumping arsenic containing solute in a down flow direction through a stainless steel cylindrical shaped column, with a diameter of 0.5 cm and length of 16 cm filled with a lysine modified polyketone sample of interest. Flow is provided by a milipore Waters 510 HPLC pump with a flowrate up to 5 ml/min as maximum flowrate. Conductivity is measured with a B0382BT conductivity sensor. A computer with CoachlabII is attached to the conductivity probe which records measurements. This setup is shown in figure 11.

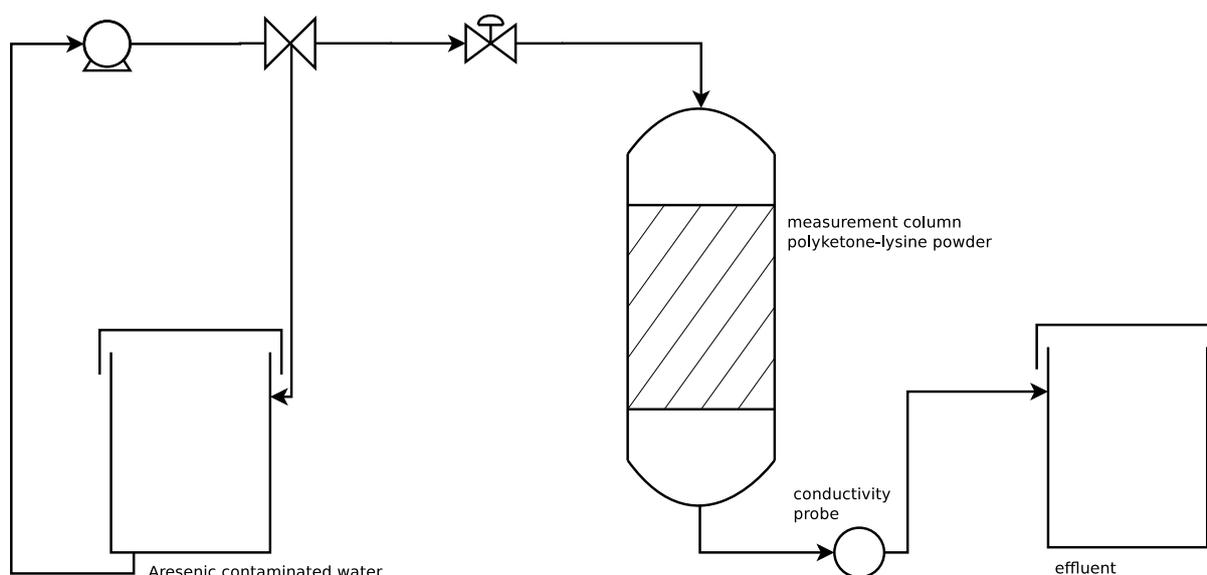


Figure 11 – Experimental setup

Before measurements the modified polyketone is flushed with demi-water to remove water soluble species from the polymer. To confirm that the polymer is no longer leaching to the water conductivity is measured. When the conductivity is not influenced by the polymer, measurements with arsenic can be performed.

Water containing As(V) is transferred through a column containing a sample of amine-modified polyketone. Arsenic will be adsorbed by the modified-polyketone. Conductivity measurements are performed of the effluent to monitor the concentration of arsenic in time. A computer records the conduction values at specific intervals. The capacity of the sample to adsorb arsenic becomes lower in time because of saturation, the arsenic concentration

of the effluent increases and subsequently conductivity increases. The measurement is complete when the conductivity of the effluent is equal to the conductivity of the inflow to the column i.e. $C_t/C_0 = 1$. The maximum amount of arsenic that is adsorbed and the adsorption rate can be determined from the measurements by application of adsorption models as shown in chapter 10.

Part IV

Results & Discussion

14 Column breakthrough models

Column measurements were performed for arsenic concentrations ranging from 10 to 50 mg/L . An example of a breakthrough curve and its fitting with two different models given in figure 12 (measurement without model) and figure 13 (Thomas- and Yoon-Nelson model).

Fitting was obtained by two methods; The first method is logarithmic transformation of response variable (y-axis) C_t/C_0 to $\ln[(C_0/C_t) - 1]$, followed by linear fitting. This method is valid because logarithmic transformation retains the value of the original measurement, i.e. exponentiation of the logarithmic transformation obtains the original measurement. The linearized Thomas model and Yoon-Nelson model result in distinct fitting models.

The second fitting method is obtained by direct non-linear regression fitting (Fan, 2012; Team, 2013). This method results in one single fitting equation as shown by equation 4 in chapter 10.

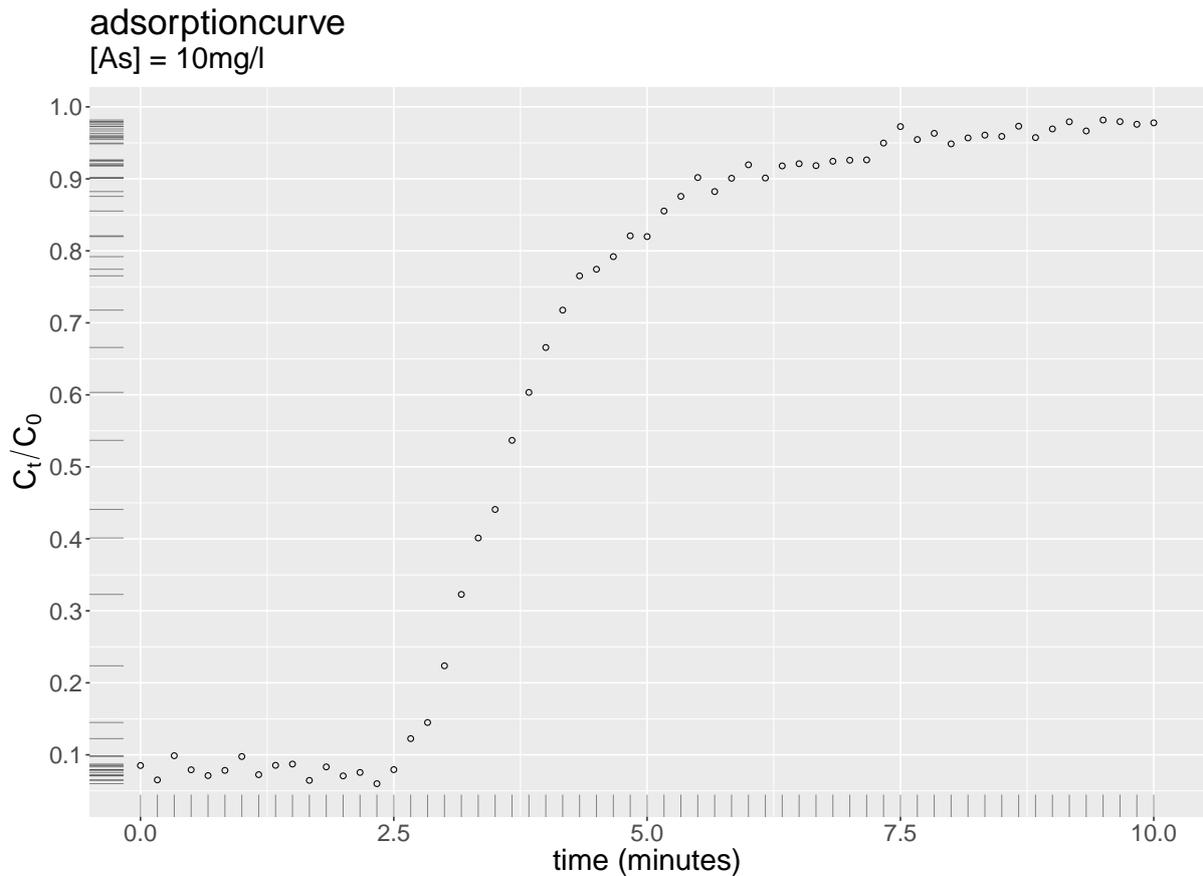


Figure 12 – Breakthrough measurement

Thomas & Yoon–Nelson Model fitting

[As] = 10mg/l

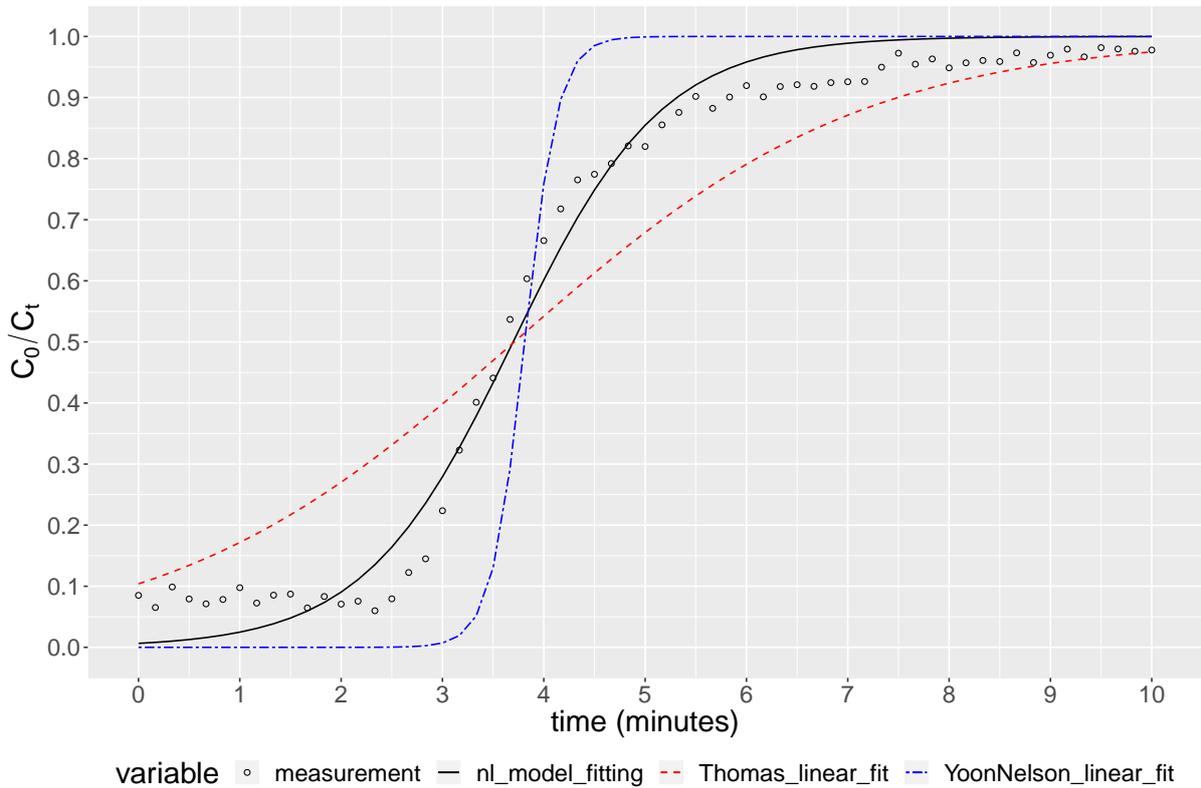


Figure 13 – Breakthrough measurement with Thomas and Yoon-Nelson model

Model fitting was performed for three models. Both Thomas and Yoon-Nelson models showed high R^2 values above 0,8 as shown in table 13 and 14 in appendix C. However the measurement showed poor correlation with the BDST model, these fittings resulted in models that deviated significantly from measurements. R-square values were below 0,55 for arsenic concentrations of 10 mg/L, and decreased for higher arsenic concentrations to below an R^2 value of 0,35. An explanation for this deviation can be found in the fact that amine-modified polyketone was found to show swelling behavior during measurement in aqueous media. As the BDST model includes a term h/u i.e. bed height and linear velocity, which both depend on volume of adsorbant, fitting the BDST model was not possible without large measurement errors. Therefore Bed Depth Service Time models are not used to estimate amine modified polyketone uptake capacity for arsenic.

Calculated adsorption capacities for Thomas and Yoon-Nelson models calculated from nonlinear fitting and linearized model fitting are shown in figure 14. It is observed that calculated adsorption capacity increases with higher influent arsenate concentration. This effect is known from literature (Ozturk and Kavak, 2005; Chun Yang Yin and Dead, 2009; Han et al., 2002). An explanation for this effect can be found in the fact that higher initial influent concentrations lead to higher mass transfer driving force, hence As(V) concentrations saturate the adsorbant more quickly.]

Difference in fitting method did not result in systematic under- or over estimation of

uptake capacity for either method. It is however observed that nonlinear fitting resulted in higher R^2 values indicating better fitting of model to data for nonlinear models.

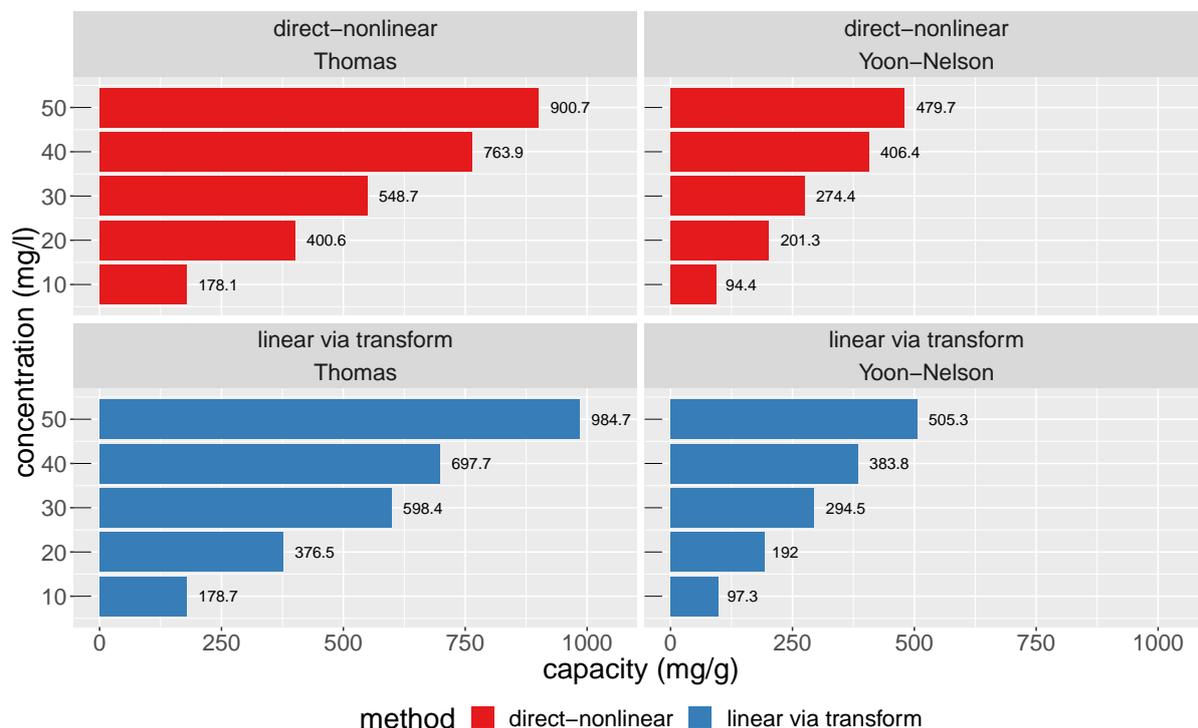


Figure 14 – Adsorption capacity compared by fitting model

Figure 13 and table 13 and 14 show better fitting by employing a nonlinear fitting method compared to linear fitting of logarithmic transformation of response variables. An explanation for this effect can be found in relatively large measurement error of conductivity measurements, a 1% measurement accuracy is reported by the manufacturer of the conductivity sensor. Therefore $C_t/C_0 < 0$ or $C_t/C_0 > 1$ could result from this error. For low concentration measurement this could result in errors when $C_t < 0$ is measured, as $\ln(C_0/$ a negative number) is not defined. For high concentrations logarithmic transformation results in error when $C_t/C_0 > 1$, as $\ln[(C_0/C_t) - 1]$ for $C_t > 1$ also results in an undefined value.

To make linear transformation possible it is necessary to remove measurements that give these errors. However removing systematic measurement errors is not an acceptable statistic procedure (Caulcutt, 1991). As a result a direct nonlinear fitting procedure with the Levenberg-Marquardt (Fan, 2012) method is more robust, because systematic measurement errors resulting in $0 > C_t$ or $C_t > 1$ do not have to be erroneously removed. Moreover fitting results are much less influenced by the number of measurements with high arsenic concentrations close to $C_t/C_0 = 1$, therefore manual defining when adsorption saturation is reached is not necessary.

15 Regeneration by desorption

The possibility of regenerating amine modified polyketone by desorbing arsenate ions was investigated. Washing amine modified polyketone resin saturated with arsenate with milli-q water (18 $M\Omega/cm$) at room temperature (293 K) removes arsenate from the column as shown in figure 15. Increased temperature of desorbent water could increase desorption time, however it was observed that increased temperature resulted in a decrease in flowrate, probably caused by swelling behavior of amine modified polyketone resin. At a modest temperature of 40 degrees Celsius, flow of fluid was stopped because of resin swelling. Previous research investigating heavy metal desorption from amine modified polyketone indicated that desorption kinetics were not markedly influenced by temperature (Roepers, 2013). Therefore further measurement of temperature effect on desorption was not attempted.

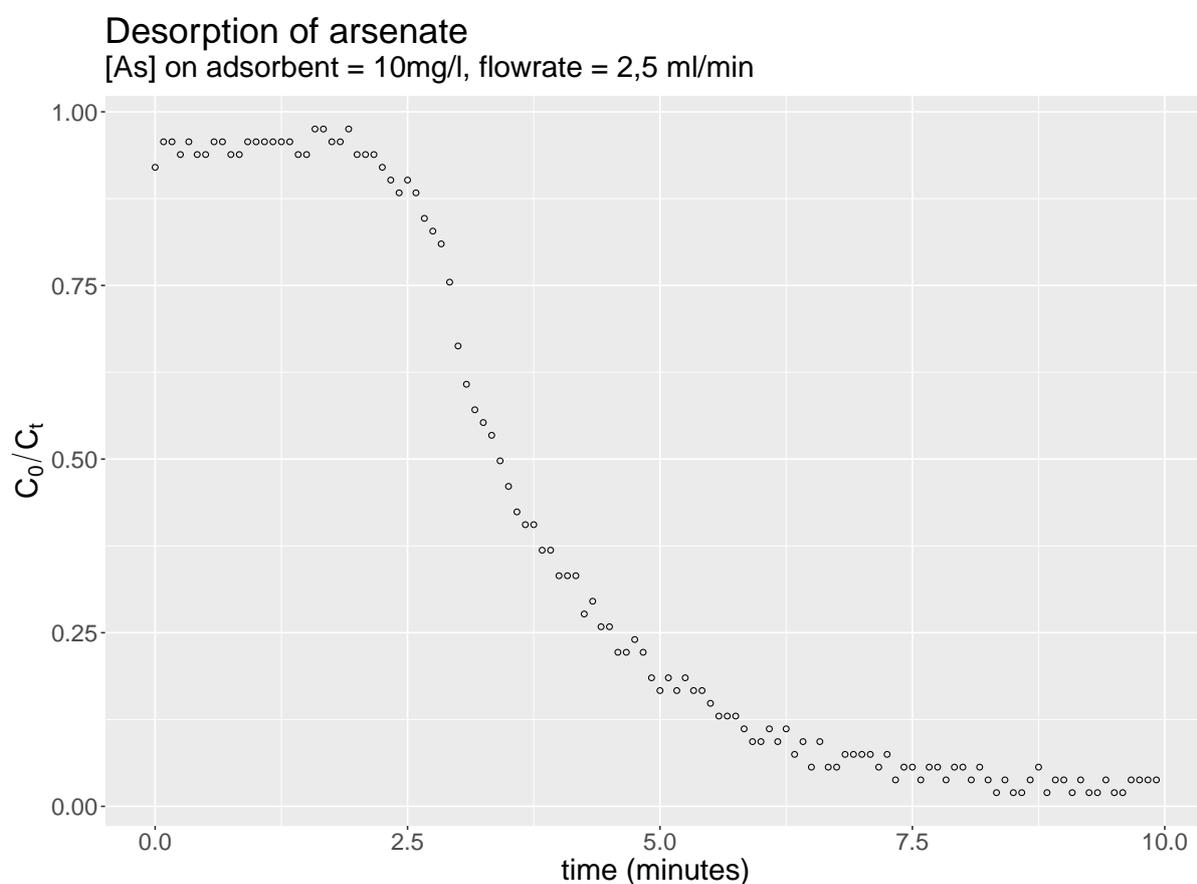


Figure 15 – Arsenate desorption from adsorption column

16 Cost estimation of amine modified polyketone adsorbant

In order to answer the business research question: Can amine-modified polyketone be a competitive technology to remove arsenic from drinking water? Cost is an essential

component of the answer to this question. It is very difficult to give an exact answer to the question what a particular technological solution to a problem would cost. Often times an estimation is made.

A technique that is suitable and intuitive in this regard is monte-carlo simulation. Monte-Carlo simulation relies on estimation of realistically possible starting conditions (distributions) of input variables that result in representative output variables (Llopis-Albert et al., 2016). Possible starting conditions represent all variations of best estimates known to the researcher. Output variables use all input variables and thus give a distribution of possible outcomes which are the best representation of knowledge available to the researcher regarding input variables. Outcome estimates can therefore be considered the best estimate available given estimated input variables.

For comparison of amine modified polyketone two technologies are considered as an alternative. Activated Carbon adsorption and activated alumina adsorption. Both technologies are considered best available technologies in studies conducted by the US-EPA (Anon, 2000a, 2003; USEPA, 2000). Usually adsorption is performed with two separate columns (Cooney, 1999), these can be placed in parallel or series configuration, figure 16 shows a simplified schematic of adsorption column operation (series operation is depicted).

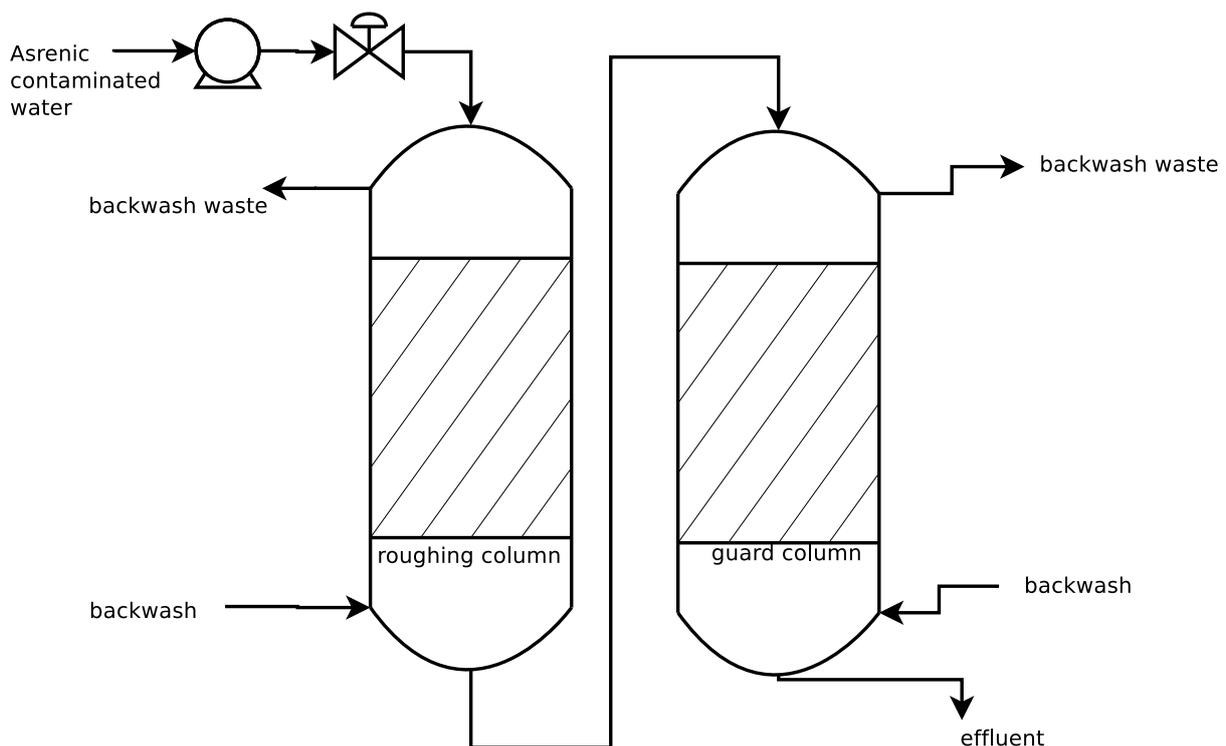


Figure 16 – Industrial column adsorption setup (simplified)

Some assumptions have to be made regarding performance of amine modified polyketone adsorbant. These assumptions are based on figures from literature (Anon, 2000c,a; USEPA, 2000; Bissen and Frimmel, 2003; Dambies, 2005; Mohan and Pittman, 2007). Estimates for polyketone adsorbant are obtained from measurements and adsorption models:

- Cost comparison is made on a basis of material cost only, installed equipment is considered as similar.
- 100% arsenate is adsorbed until breakthrough capacity.
- Adsorption of influent arsenate concentration in the range of 50- to 100 $\mu\text{g}/\text{L}$ is adsorbed at the same rate as the experimentally measured influent concentration of 10 mg/L .
- Estimates are drawn from a uniform distribution with a lower and upper bound

Aspect	lower bound	upper bound
Influent arsenate concentration $\mu\text{g}/\text{L}$	50	100
Treated volume of effluent (m^3/day)	3785	37854
Wastewater to treated water ratio %	0,5	1,00
Waste cost per ton	160	250
Activated alumina adsorbant		
Activated Alumina uptake capacity (mg/g)	5	25
Times regeneration possible	6	8
Replacement activated alumina %	10	30
kg NaOH regenerant / m^3 Treated volume	0,03	0,04
kg H_2SO_4 / m^3 Treated volume	0,0264	0,0352
NaOH cost per kg	0,35	0,40
H_2SO_4 cost per kg	0,10	0,20
Media cost \$ per kg	0,70	3,20
Activated carbon adsorbant		
Activated Carbon uptake capacity (mg/g)	10	50
replacement activated carbon	100	100
Media cost \$ per kg	1,4	2,7
Amine modified polyketone adsorbant		
Polyketone-lysine uptake capacity (mg/g)	100	180
Times regeneration possible	6	8
replacement amine modified polyketone %	10	30
Media cost \$ per kg	15	25

Table 7 – Assumptions for comparison of amine modified polyketone with activated alumina- and carbon adsorbant

Based on assumption in table 7 calculations can be made to estimate cost and cost per m^3 of treated water. For activated alumina, activated carbon and amine modified polyketone.

The following calculations, based on mass balance are relevant:

- $\text{Amount of Arsenate to Adsorb} = \text{Treatment Volume} * \text{Arsenate Concentration}$
- $\text{Adsorbate mass needed} = \frac{1}{\# \text{ regen possible}} * \frac{\text{Amount of Arsenate to Adsorb}}{\text{Adsorbent uptake capacity}} / 1000$

- $Adsorbate\ Cost = Adsorbate\ mass\ needed * Cost\ of\ Adsorbent$
- $Regeneration\ Wastewater = Wastewater\ to\ treated\ water\ ratio * Treatment\ Volume$
- $Solid\ Waste = Adsorbate\ mass\ needed * Adsorbent\ Replacement\ \%$
- $Adsorbent\ replacement = Adsorbate\ mass\ needed * Adsorbent\ Replacement$
- $\sum Adsorbent\ cost = Adsorbate\ cost * (Adsorbent\ needed + Adsorbent\ replacement)$
- $Solid\ waste\ cost = waste\ cost * Solid\ Waste$
- $regenerant = Treatment\ Volume * (NaOH\ needed + H_2SO_4\ needed) * Treatment\ ratio$
- $regenerant\ cost = regenerant * regenerant\ cost$
- $total\ cost = \sum Adsorbent\ cost + Solid\ waste\ cost + Water\ waste\ cost + regenerant\ cost$

Calculation based on assumptions listed in table 7 results in a range of values for each aspect. Figure 17 shows how costs are distributed across variables for Activated alumina (AA), Activated carbon (AC), and amine modified polyketone (PK-Lys). Table 8 shows distribution statistics for these calculations.

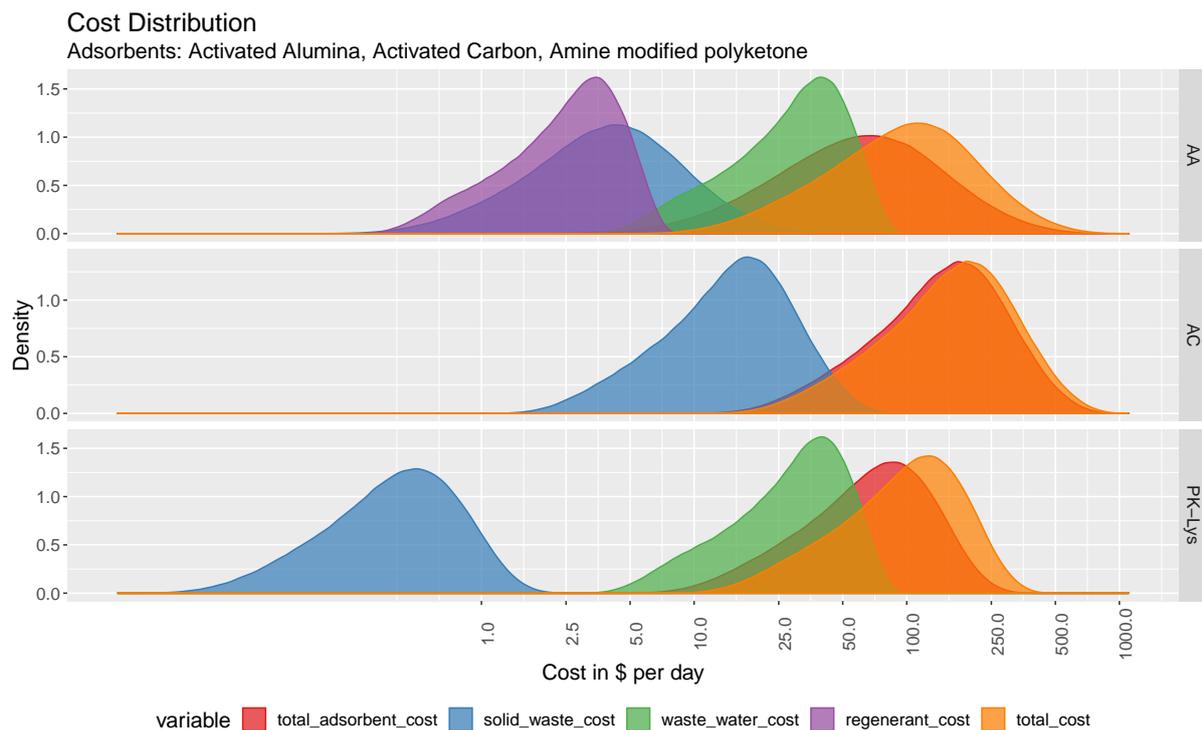


Figure 17 – Cost distribution based on comparison of amine modified polyketone with activated alumina- and carbon adsorbent

variable	adsorbent	value.min	value.max	value.mean	value.median
total_adsorbent_cost	AA	1.45	971.23	84.41	60.55
total_adsorbent_cost	AC	9.62	955.37	175.87	150.44
total_adsorbent_cost	PK-Lys	4.33	416.63	78.88	69.23
solid_waste_cost	AA	0.14	50.62	5.16	3.91
solid_waste_cost	AC	1.14	90.31	17.58	15.25
solid_waste_cost	PK-Lys	0.02	2.57	0.47	0.40
waste_water_cost	AA	3.11	93.73	32.04	30.32
waste_water_cost	PK-Lys	3.12	93.78	32.00	30.25
regenerant_cost	AA	0.26	8.58	2.77	2.62
total_cost	AA	4.96	1124.16	124.38	97.40
total_cost	AC	10.76	1045.67	193.45	165.68
total_cost	PK-Lys	7.46	512.98	111.35	99.89

Table 8 – Results of calculation based on comparison of amine modified polyketone with activated alumina- and carbon adsorbant.

16.1 Accuracy of cost estimation

The accuracy required for a cost estimation is defined by the American Association of Cost Engineers, five types are defined (Perry, 1999):

Type	Description	Probable error
Order-of-magnitude estimate (ratio estimate)	Rule-of-thumb method based on cost data for previous similar types of plant	10-50 %
Study estimate (factored estimate)	Requires knowledge of major items of equipment; used for feasibility surveys	≤ 30 %
Preliminary estimate (budget-authorization estimate)	Requires more detailed information than study estimate	≤ 20 %
Definitive estimate (project-control estimate)	Based on considerable data prior to preparation of completed drawings and specifications	within 10 %
Detailed estimate (firm or contractor's estimate)	Requires complete drawings, specifications, and site surveys	within 5 %

Table 9 – cost estimate types

It is assumed that calculated estimates are in the range of order of magnitude estimates

i.e. 10-50% probable error, because assumptions are made that are substantiated by literature but are not confirmed by measurement results. It is not known how efficient regeneration of amine modified polyketone can be, compared to activated alumina. To make comparison possible, regeneration characteristics were assumed equal. However amine modified polyketone does not require strong base for regeneration as activated alumina does, amine modified polyketone is regenerated with demineralized water.

Part V

Conclusions and recommendations

This chapter will describe the conclusion of this research. After an answers to the research questions has been given, some suggestions for further research are given.

Measurements show that amine modified has a high uptake capacity ranging from 100 to 190 *mg* arsenate per gram of resin in aqueous media. Uptake capacity of amine modified polyketone is 3-20 times higher, compared to adsorbants such as activated alumina and activated carbon. Literature describes metal loaded polymers that have an uptake capacity up to 112 *mg/g*, however metal loaded polymers require regeneration, furthermore metal ions can leach from the adsorbant, introducing chemicals to the effluent.

When amine modified polyketone is compared to other technologies, amine modified polyketone has advantageous properties; Amine modified adsorbant requires little pre- and post processing of influent water, such as pH adjustment or filtering. It is possible that amine modified polyketone has disadvantageous properties comparable to other technologies, such as loss of capacity by other ions present in the influent stream, this was not investigated.

Regeneration of amine modified polyketone was shown to be possible, however at regeneration temperatures above 30 °C, the resin showed swelling behavior witch resulted in loss of flowrate. In larger industrial scale adsorbant columns this is not necessarily problematic as back flushing is employed, whereby the adsorbant bed is fluidized, thus clogging should not occur.

Based on assumed equal regeneration characteristics, amine modified polyketone is competitive based on cost at a break even price range of 15-25 \$ per kg compared with activated alumina and activated carbon. Prices lower than this range is competitive at treatment volumes between 3785 *m*³ and 37854 *m*³. Polyketone produces less solid waste than both these adsorbants, and does not require chemical additions of strong base or acid, resulting in reduced waste and waste cost.

This research gives insight in the possible use of amine modified polyketone as an adsorbent for arsenates in water. However this insight is based on small scale testing and theoretical scale up by estimation, which by necessity does not include many variables that could be of importance. The result of the estimate is a model that captures a possible scenario of many possible real world scenarios.

To improve applicability of small scale testing, measurements should be done that represent conditions which occur in drinking water systems. This includes competing ions other than arsenate in influent water, such as phosphates and sulphates. Further measurements by conductometry could be done with lower arsenate concentrations, measurement was performed in a medium concentration range, however a low concentration range is possible with concentration as low as 1 *mg/L*. Even lower concentration could be measured if atomic-absorption or atomic-emission spectrophotometry is used for arsenate concentration measurement. Measurement of concentration as low as 10 μ *g/L* would give better insight if amine modified polyketone can function as an adsorbant the concentration that is

considered harmful. Lastly amine modified polyketone performance might be improved by pH adjustment as ionic arsenate species occur in different ratios dependent on pH. Different species of arsenate may have improved uptake capacity on amine modified polyketone.

Nomenclature

AA Activated Alumina

AC Activated Carbon

BAT Best Available Technology

EBCT Empty Bed Contact Time

GFH Granular Ferric Hydroxide

LOAEL lowest observable adverse effect level

MCL Maximum Contaminant Level

NOAEL no observable adverse effect level

ORP Oxidation Reduction Potential

TDS Total Dissolved Solid

US-EPA United States Environmental Protection Agency

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Part VI

Appendices

A Comparison of arsenic removal technologies

Process	Advantages	Disadvantages
Particle forming processes		
Precipitation	Solid obtained can be removed through sedimentation and filtration. Proven and reliable	Solids rather unstable and inadequate for direct disposal as they will produce As-containing sludge. Use of chemicals. Needs oxidizing agents
precipitation by lime softening	pH > 10.5 provides efficient As removal. Efficient to treat water with high hardness. Proven and reliable, reduces corrosion.	Low efficiency. High coagulant dose. High pH in the effluent. May require secondary treatment. Sulfate ions influence efficiency.
oxidation and precipitation	Relatively simple. Small installation costs. Easily applied to large water volumes. Arsenite can be directly oxidized by a number of chemicals and/or UV light. can be used in situ. Oxidizes other impurities and microbes	Some oxidants produce toxic and carcinogenic byproducts. Needs further removal treatment.
coagulation & filtration	Simple. Easily applied to large water volumes. Effective when As(V) is the only pollutant. Low capital and operative cost. Alumn is effective over a wide pH range and allows F removal.	Low removal efficiency. pH needs adjustment. Filtration needed. As(III) must be oxidized to As(V)

Table 10 – Technological comparison ([Litter et al., 2010](#); [Mondal et al., 2006](#); [Mohan and Pittman, 2007](#))

Process	Advantages	Disadvantages
Sorption processes	Simple. No other chemicals required. Highly selective towards As(V). Effective with water with high Total Dissolved Solid (TDS). Useful at community or household levels.	Moderate efficiency. Regeneration needed. Interferences by Se, F ⁻ , Cl ⁻ and SO ₄ ²⁻ . Application of point of use treatment devices needs regeneration and replacement.
sorption on activated alumina	Well established suitable for home use, inexpensive, simple replacement requirements. Improves taste and odor. Commercially available	Needs monitoring. Effectiveness is based on contaminant type, concentration and flowrate. Bacteria may grow on alumina surface
sorption on activated carbon	Simple replacement requirements. Improves taste and odor.	Efficiency depends on the ash content and metal concentration. Not proven

Table 11 – Technological comparison (continued)

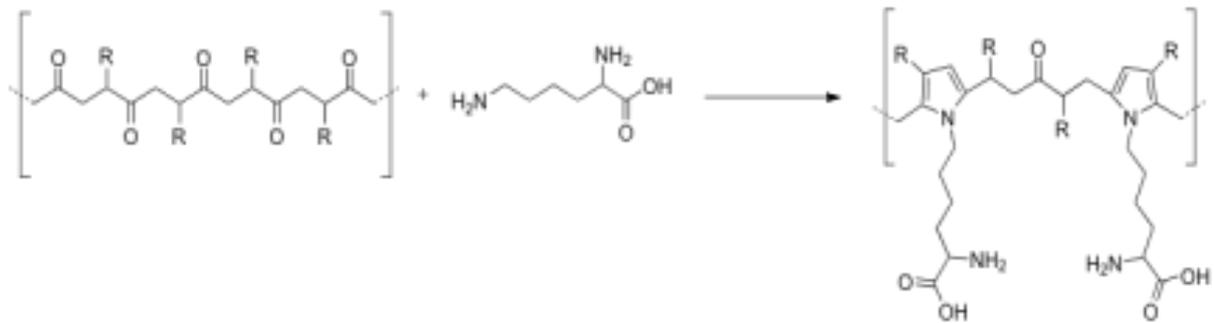
Process	Advantages	Disadvantages
membrane electrodialysis, electrodialysis reversal	Efficiency similar to reverse osmosis, effective in treating water with high TDS. Capable of removal of other contaminants.	Very high costs. Less proven. Needs oxidizing agents.
ion-exchange	Well-defined medium and capacity. pH independent. Exclusive ion specific resin to remove arsenic. Can produce water with [As] < 2 µg/L. Effective removal. Not pH and influent concentration dependent	As(III) is not removed. Sulfate, TDS, Se, F ⁻ and NO ₃ ⁻ , interfere. Precipitated irons causes clogging. May require pretreatment. Arsenic is exchanged for other ion(s). High cost medium. high-tech operation and maintenance. As(III) is difficult to remove. Life of resins can be too short
reverse osmosis and nanofiltration	Useful at community or household levels. Minimal membrane operation and maintenance. Highly effective towards As(V). Effective with water with high TDS. Highest water quality. Treats wide range of dissolved salts and minerals. Low turbidity. Well-defined and high-removal efficiency	Only low As levels can be treated. Poor As(III) removal. For high water volumes, multiple membrane units required. Low water recovery rates (10-20%). High energy consumption. High capital and operation costs. Membrane fouling. Many interferences. 20-25% water rejection. Other ions can be removed.

Table 12 – Technological comparison (continued)

B Experimental Piter

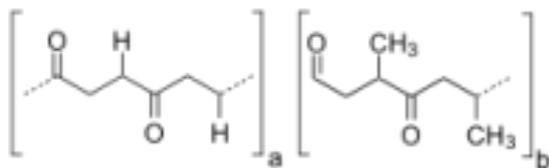
Experimental goal:

Synthesizing PK-Lys for the use as polymeric surfactant in Enhanced Oil Recovery.



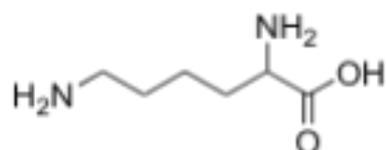
Materials:

Polyketone



PK-type	% ethylene (a)	% propylene (b)
PK-0	0	100
PK-30	30	70
PK-50	50	50

L-Lysine:



Procedure:

Synthesis:

For the syntheses of Lysine modified Polyketone, the following standard prescription is followed. The prescription which given below is used for the product with code PB3008. Table 2 shows the different compositions of the synthesized products.

First 13,20 g Polyketone30 (PK30) was dissolved in 132,3 g methanol with continuous stirring during 3 hours resulting in a white cloudy mixture of PK30 in methanol. Second 5,89 g of L-Lysine was added to the mixture. After heating to a temperature of 67,5°C 5,15 g of Triethylamine (TEA) was slowly dropped to the reaction mixture and further refluxed for 15,5 hours while the reaction occurred.

Code	PK-type	PK:Lys	Temp. °C	Time (hr.)	Lys (g)	PK (g)	Methanol (g)	Triethylamine (g)
PB2408	30%	0,204	66,2	16	3,41	15,07	151,0	3,30
PB3008	30%	0,402	67,5	15,5	5,89	13,20	132,3	5,15
PB0109	30%	0,613	60,0	16	9,78	14,38	143,1	8,20
PB0709	50%	0,201	60,0	10	3,31	14,22	170,0	2,98
PB0909	50%	0,401	60,0	10	6,50	13,98	170,0	5,48
PB1509	50%	0,601	60,0	10	7,03	10,10	152,3	5,85
PB2209	0%	0,20	60,0	10	3,18	15,13	151,03	3,10
PB2709	0%	0,40	60,0	10	5,89	14,11	149,5	4,89
PB2809	0%	0,60	60,0	10	10,01	16,10	167,5	8,50

Work up:

For the work up of the synthesized product, the following standard prescription is followed.

The final product was worked up in a rotor evaporator at 100 mbar and 45 °C to evaporate the methanol and the triethylamine. Further purification is done by dispersing the samples in water at a pH of 2,02, removing the unreacted monomer and the rest of the TEA. After separating the solids with a ultracentrifuge (200 hz.), the solids were put in a vacuum-oven at a temperature of 45°C for 15 hours.

Testing results:

Elemental analysis:

C, H and N analysis were performed using a Euro-EA elemental analyzer. The data were used to calculate the conversion of the carbonyl groups and the lysine according to the following equations:

	N%	C%	H%		N%	C%	H%	Xco% (N:C)	Xly% (N:C)	Xco% (N%)
PB2408	4,03%	68,47%	8,59%	measured	4,04%	68,61%	8,57%	21,99%	100%	23%
	4,04%	68,75%	8,54%	expected	3,62%	65,60%	8,46%	20,40%		
PB3008	6,37%	62,50%	7,98%	measured	6,36%	62,09%	7,95%	44,09%	100%	42%
	6,34%	61,67%	7,92%	expected	6,15%	64,30%	8,59%	40,22%		
PB0109	7,70%	60,93%	7,96%	measured	7,69%	60,63%	7,89%	59,68%	97%	56%
	7,67%	60,32%	7,82%	expected	8,16%	63,26%	8,70%	61,30%		
PB0709	5,05%	66,97%	8,00%	measured	5,13%	66,92%	8,03%	28,66%	100%	30%
	5,21%	66,87%	8,05%	expected	3,71%	64,88%	8,23%	20,10%		
PB0909	6,89%	63,77%	8,21%	measured	7,23%	63,06%	8,21%	48,76%	100%	49%
	7,56%	62,34%	8,20%	expected	6,33%	63,63%	8,41%	40,10%		
PB1509	8,19%	62,33%	8,27%	measured	7,98%	62,62%	8,28%	56,91%	95%	57%
	7,77%	62,90%	8,29%	expected	8,29%	62,70%	8,54%	60,10%		
PB2109	3,47%	68,21%	8,36%	measured	3,50%	68,13%	8,33%	18,75%	100%	20%
	3,52%	68,04%	8,30%	expected	3,40%	66,63%	8,75%	18,64%		
PB2709	5,47%	64,35%	8,19%	measured	5,47%	64,39%	8,16%	34,49%	93%	36%
	5,47%	64,43%	8,12%	expected	5,86%	65,24%	8,84%	37,03%		
PB2809	5,84%	53,70%	7,13%	measured	5,83%	53,35%	7,13%	48,24%	87%	40%
	5,82%	52,99%	7,13%	expected	7,71%	64,20%	8,91%	55,15%		

C Experimental Results

flowrate (ml/min)	resin mass (g)	[As] (mg/L)	Thomas model		Yoon-Nelson model			R^2
			k_{Th} (ml/min/mg)	q_0 (mg/g)	k_{YN} (min ⁻¹)	τ (min)	q_0 (mg/g)	
2,5	0,53	10,2122	0,1332	178,1	1,360	3,697	94,4	0,987
2,5	0,51	20,1641	0,0713	376,5	1,437	3,809	192,0	0,983
2,4	0,50	29,9832	0,0505	548,7	1,515	3,813	274,4	0,986
2,5	0,55	39,9639	0,0374	697,7	1,494	3,841	383,8	0,984
2,5	0,53	49,9566	0,0311	900,7	1,552	3,822	479,7	0,986

Table 13 – Measurement results nonlinear fitting method

flowrate (ml/min)	resin mass (g)	[As] (mg/L)	Thomas model			Yoon-Nelson model			
			k_{Th} (ml/min/mg)	q_0 (mg/g)	R^2	k_{YN} (min ⁻¹)	τ (min)	q_0 (mg/g)	R^2
2,5	0,53	10,2122	0,0569	178,7	0,847	6,095	3,812	97,3	0,955
2,5	0,51	20,1641	0,0360	400,6	0,876	6,069	3,992	201,3	0,912
2,4	0,50	29,9832	0,0273	598,4	0,844	7,408	4,093	294,5	0,876
2,5	0,55	39,9639	0,0217	763,9	0,863	6,668	4,068	406,4	0,882
2,5	0,53	49,9566	0,0184	984,7	0,852	7,261	4,046	505,3	0,875

Table 14 – Measurement results linear fitting method

D R programming code

R script to generate results and plots

Adjust parameters and file location for all other measurements

J.Sikkema

September , 2018

```
# coefficients y=ax+b from calibration regression
b=1.60275
a=8.07258

#Set experimental parameters
Mass_AS=10.2122 #mg

# MM = 312.0136 #molecular mass of sodium orthoarsenate (Na2HAs)4*7H2O
# CO= Mass_AS/MM ##mmol
CO=Mass_AS # in mg
flowrate=2.5 #ml/min
Mass_adsorbent = 0.53 # gram
u=flowrate/(pi*0.25^2) # linear flowrate
h = 1.0 # bed height

# load data from file
adsorptioncurve <-
  read.csv(
    "/run/media/johan-mark/0624289961/experimental_data/measurements/cleaned_up/10ugl_2pun
    header = TRUE,
    sep = ",",
    na.strings = "NA",
    dec = ".",
    strip.white = TRUE,
    as.is = TRUE
  )

# ad time in minutes
adsorptioncurve$tijd_min <- adsorptioncurve$tijd * 60
# create columns Ct, CO*t, ln(CO/Ct)-1, with calculated values
adsorptioncurve$Ct <- ((adsorptioncurve$C - b) / a)
adsorptioncurve$COt <- adsorptioncurve$tijd_min * CO
adsorptioncurve$CtCO <- adsorptioncurve$Ct / CO
# in R log is the natural logarithm
adsorptioncurve$lntrans <- log(CO / adsorptioncurve$Ct) - 1

#find 90% breakthrough Ct with interpolation function and use as Ct
y <- approxfun(adsorptioncurve$C, adsorptioncurve$tijd_min)
Ct <- y(0.9 * max(adsorptioncurve$C))
```

```

# show original measurement in plot
ggplot(data = adsorptioncurve, aes(tijd_min, C)) +
  geom_point(alpha = 0.5, shape = 1) +
  #scale_x_continuous(limits=c(0,10))+
  geom_hline(yintercept = max(adsorptioncurve$C * 0.9),
             linetype = 3) +
  geom_vline(xintercept = Ct, linetype = 3) +
  #scale_y_continuous(breaks=seq(0,250,10))
  # scale_x_continuous(breaks=seq(0,20,1))
  #geom_rug()+
  #geom_smooth(method="loess",span=0.05)+
  labs(
    title = "adsorptioncurve",
    subtitle = expression(paste("[AS] = 10", mu, "g/l")),
    x = "time (minutes)",
    y = expression(paste("conductivity (", mu, "Siemens)"))
  )

```

```

# show original measurement with concentration on y
ggplot(data = adsorptioncurve, aes(tijd_min, Ct)) +
  geom_point(alpha = 0.5, shape = 1) +
  #scale_x_continuous(limits=c(0,10))+
  geom_hline(yintercept = max(adsorptioncurve$Ct * 0.9),
             linetype = 3) +
  geom_vline(xintercept = Ct, linetype = 3) +
  #scale_y_continuous(breaks=seq(0,250,10))
  # scale_x_continuous(breaks=seq(0,20,1))
  #geom_rug()+
  #geom_smooth(method="loess",span=0.05)+
  labs(
    title = "adsorptioncurve",
    subtitle = expression(paste("[AS] = 10", mu, "g/l")),
    x = "time (minutes)",
    y = expression(paste("concentration (", "mg/l)"))
  )

```

```

# breakthrough curve
ggplot(data = adsorptioncurve, aes(tijd_min, adsorptioncurve$CtC0)) +
  geom_point(shape = 1) +
  scale_y_continuous(breaks = seq(0, 1, 0.1)) +
  #scale_x_continuous(limits=c(0,10))+
  geom_hline(yintercept = 0.9, linetype = 3) +
  geom_vline(xintercept = Ct, linetype = 3) +
  geom_rug(size = 0.05,
           alpha = 0.5,
           colour = "grey10") +
  #geom_smooth(method="loess",span=0.05)+

```

```

labs(
  title = "adsorptioncurve",
  subtitle = expression(paste("[AS] = 10", mu, "g/l")),
  x = "time (minutes)",
  y = expression(paste(C[t] / C[0]))
)

# cutoff data at breakthrough for linear regression
# = 90% of maximum concentration
# find index of Ct
index<-max(which(adsorptioncurve$tijd_min<=Ct))
# use relevant data for linear regression leave the original data
adsorptioncurveLR<-adsorptioncurve[0:index,]

# plot linear model fitting Thomas model
ggplot(data = adsorptioncurveLR, aes(tijd_min, lntrans)) +
  geom_point(alpha = 0.5, shape = 1) +
  #scale_x_continuous(limits=c(0.0,0.5))+
  geom_rug() +
  geom_smooth(method = "lm") +
  labs(
    title = "Thomas Model fitting",
    subtitle = expression(paste("[AS] = 10", mu, "g/l")),
    x = "time (minutes)",
    y = expression(paste(ln (C[0] / C[t] - 1)))
  )

# we should do this until breakthrough

lm <- lm(formula = lntrans ~ tijd_min, data = adsorptioncurveLR)
# show linear regression result
summary(lm(formula = lntrans ~ tijd_min, data = adsorptioncurveLR))

##
## Call:
## lm(formula = lntrans ~ tijd_min, data = adsorptioncurveLR)
##
## Residuals:
##      Min       1Q   Median       3Q      Max
## -0.6915 -0.3164 -0.1249  0.2091  1.0149
##
## Coefficients:
##              Estimate Std. Error t value Pr(>|t|)
## (Intercept)  2.15466    0.14176   15.2 < 2e-16 ***
## tijd_min    -0.58083    0.04302  -13.5 5.4e-15 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##

```

```

## Residual standard error: 0.4284 on 33 degrees of freedom
## Multiple R-squared: 0.8467, Adjusted R-squared: 0.8421
## F-statistic: 182.3 on 1 and 33 DF, p-value: 5.404e-15
# calculate r-squared value
rsquared(lm)

## [1] 0.8467434
# show model coefficients
coef(lm)

## (Intercept)    tijd_min
## 2.1546597    -0.5808291
# put coefficients in dataframe for later use
x <- as.data.frame(coef(lm))
A = x$"coef(lm)"[1]
A

## [1] 2.15466
B = x$"coef(lm)"[2]
B

## [1] -0.5808291
linfit_kth=-B/C0
linfit_kth

## [1] 0.056876
linfit_q0=(A*flowrate)/(linfit_kth*Mass_adsorbent)
linfit_q0

## [1] 178.6956
# direct calculation of parameters by nonlinear regression
y=adsorptioncurve$CtC0
x=adsorptioncurve$tijd_min

fitnlsLM<-nlsLM(y~1/(1+exp(kth/flowrate*(q0*Mass_adsorbent-C0*flowrate*x))),
               start = list(kth=0,q0=0)) # this works nicely
# show results
fitnlsLM

## Nonlinear regression model
## model: y ~ 1/(1 + exp(kth/flowrate * (q0 * Mass_adsorbent - C0 * flowrate * x)))
## data: parent.frame()
## kth q0
## 0.1332 178.1090
## residual sum-of-squares: 0.1587
##

```

```

## Number of iterations to convergence: 17
## Achieved convergence tolerance: 1.49e-08
# fit BDST model via nonlinear fitting
BDSTfit<-nlsLM(y~1/(1+exp((Ka*NO*h/u)-Ka*CO*x)),start = list(Ka=0,NO=0))

# Yoon Nelson model
adsorptioncurveLR$YNtransform <-
  log(adsorptioncurveLR$Ct / (CO - adsorptioncurveLR$Ct))

YNlinfit <-
  lm(adsorptioncurveLR[15:34, ]$tjld_min ~ adsorptioncurveLR[15:34, ]$YNtransform)
rsquared(YNlinfit)

## [1] 0.9551612

ggplot(data = adsorptioncurveLR[15:34,],aes(YNtransform,tjld_min))+
  geom_point(shape=1)+
  geom_smooth(method = "lm")+
  labs(title="Yoon Nelson fitting",
       subtitle = expression(paste("[AS] = 10",mu,"g/l")),
       x=expression(paste(ln (C[t]/(C[0]-C[t])))),
       y="time (minutes)")

# lonlinear fit Yoon Nelson model and calculate capacity
YNfit<-nlsLM(data=adsorptioncurve,CtCO~1/(1+exp(k*(tau-tjld_min))),start = list(k=0,tau=0)
# q0 = CO*flowrate*tau
YNq0=CO*flowrate*3.697

# x is different for this fitting
x = adsorptioncurve$tjld_min * CO
model_linear_fit = (1 / (1 + exp((linfit_kth * linfit_q0 * Mass_adsorbent /
                                flowrate) - linfit_kth * x
)))

modellINFIT_YN = 1 / (1 + exp(6.0948 * (3.8117 - adsorptioncurve$tjld_min)))
z <-
  as.data.frame(
    cbind(
      time = adsorptioncurve$tjld_min,
      measurement = adsorptioncurve$CtCO,
      model = predict(fitnlsLM),
      Thomas_linear_fit = model_linear_fit,
      YoonNelson_linear_fit = modellINFIT_YN
    )
  )
z <- melt(z, id.vars = "time")
# plot curve from parameters obtained from linear regression
ggplot(data = z, aes(time, value, color = variable)) +

```

```

geom_point(data = filter(z, variable == "measurement"),
           aes(time, value),
           shape = 1) +
scale_x_continuous(breaks = seq(0, 20, 1)) +
scale_y_continuous(breaks = seq(0, 1, 0.1)) +
geom_line(data = filter(z, variable == "model"),
          aes(time, value),
          linetype = "solid") +
geom_line(
  data = filter(z, variable == "Thomas_linear_fit"),
  aes(time, value),
  linetype = "dashed"
) +
geom_line(
  data = filter(z, variable == "YoonNelson_linear_fit"),
  aes(time, value),
  linetype = "twodash"
) +
theme(legend.position = "bottom") +
scale_colour_manual(
  values = c("black", "black", "red", "blue"),
  guide = guide_legend(override.aes = list(
    linetype = c("blank", "solid", "dashed", "twodash"),
    shape = c(1, NA, NA, NA)
  ))
) +
labs(
  title = "Thomas & Yoon-Nelson Model fitting",
  subtitle = expression(paste("[AS] = 10", mu, "g/l")),
  x = "time (minutes)",
  y = expression(paste(C[0] / C[t]))
)

```

Documenting file creation

- File creation date: 2018-09-18
- R version 3.5.1 (2018-07-02)
- R version (short form): 3.5.1
- mosaic package version: 1.4.0.9000
- Additional session information

```

## R version 3.5.1 (2018-07-02)
## Platform: x86_64-pc-linux-gnu (64-bit)
## Running under: Antergos Linux
##
## Matrix products: default
## BLAS: /usr/lib/R/lib/libRblas.so

```

```

## LAPACK: /usr/lib/R/lib/libRlapack.so
##
## locale:
## [1] LC_CTYPE=en_US.UTF-8      LC_NUMERIC=C
## [3] LC_TIME=nl_NL.UTF-8      LC_COLLATE=en_US.UTF-8
## [5] LC_MONETARY=nl_NL.UTF-8  LC_MESSAGES=en_US.UTF-8
## [7] LC_PAPER=nl_NL.UTF-8     LC_NAME=C
## [9] LC_ADDRESS=C             LC_TELEPHONE=C
## [11] LC_MEASUREMENT=nl_NL.UTF-8 LC_IDENTIFICATION=C
##
## attached base packages:
## [1] stats      graphics  grDevices  utils      datasets  methods    base
##
## other attached packages:
## [1] bindrcpp_0.2.2      broom_0.5.0          minpack.lm_1.2-1
## [4] easynls_5.0         scales_0.5.0         MASS_7.3-50
## [7] reshape2_1.4.3     mosaic_1.4.0.9000   Matrix_1.2-14
## [10] mosaicData_0.17.0  ggformula_0.8.0     lattice_0.20-35
## [13] forcats_0.3.0      stringr_1.3.1       dplyr_0.7.6
## [16] purrr_0.2.5        readr_1.1.1         tidyr_0.8.1
## [19] tibble_1.4.2       ggplot2_3.0.0.9000  tidyverse_1.2.1
## [22] RevoUtils_11.0.1   RevoUtilsMath_11.0.0
##
## loaded via a namespace (and not attached):
## [1] tidysselect_0.2.4  splines_3.5.1      haven_1.1.2        colorspace_1.3-2
## [5] htmltools_0.3.6   yaml_2.2.0         rlang_0.2.1        pillar_1.3.0
## [9] glue_1.3.0        withr_2.1.2        modelr_0.1.2       readxl_1.1.0
## [13] bindr_0.1.1       plyr_1.8.4         mosaicCore_0.6.0   munsell_0.5.0
## [17] gtable_0.2.0     cellranger_1.1.0  rvest_0.3.2        evaluate_0.11
## [21] labeling_0.3     knitr_1.20         Rcpp_0.12.18       backports_1.1.2
## [25] jsonlite_1.5     gridExtra_2.3      hms_0.4.2          digest_0.6.15
## [29] stringi_1.2.4    ggrepel_0.8.0     grid_3.5.1         rprojroot_1.3-2
## [33] cli_1.0.0        tools_3.5.1        magrittr_1.5       lazyeval_0.2.1
## [37] gg dendro_0.1-20  crayon_1.3.4       pkgconfig_2.0.1    xml2_1.2.0
## [41] lubridate_1.7.4  assertthat_0.2.0  rmarkdown_1.10     httr_1.3.1
## [45] rstudioapi_0.7   R6_2.2.2           nlme_3.1-137       compiler_3.5.1

```