Study of hybrid membrane processes for separation of heavy metals from water and wastewater

Dissertation

zur Erlangung des Grades
des Doktors der Ingenieurswissenschaften
der Naturwissenschaftlich- Technischen Fakultät III
Chemie, Pharmazie, Bio- und Werkstoffwissenschaften
der Universität des Saarlandes

von

Dipl.-Chem. Torsten Erwe

Saarbrücken
2010

Tag des Kolloquiums: 23. 07.2010

Dekan: Univ.-Prof. Dr.-Ing. Stefan Diebels

Berichterstatter: Prof. Dr.-Ing. Horst Chmiel
Prof. Dr.-Ing. Valko Mavrov

Vorsitz: Prof. Dr. Wilhelm F. Maier

Akad. Mitarbeiter: Dr. Bernd Morgenstern

Vorwort

Die vorliegende Arbeit entstand im Zeitraum von Januar 2001 bis April 2005 an der Gesellschaft für umweltkompatible Prozesstechnik mbH (upt) und am Lehrstuhl für Prozesstechnik der Universität des Saarlandes in Saarbrücken. Das Zusammenschreiben der Ergebnisse erfolgte in den Jahren 2009 und 2010.

Allen Freunden und Kollegen, die zum Gelingen dieser Arbeit beigetragen haben, möchte ich an dieser Stelle herzlich danken.

Mein besonderer Dank gilt Univ.-Prof. Dr.-Ing. habil. H. Chmiel, wissenschaftlicher Direktor der upt GmbH und Inhaber des Lehrstuhls für Prozesstechnik an der Universität des Saarlandes, für die vielen Anregungen und die konstruktive Kritik während meiner Arbeit. Bedanken möchte ich mich für die sehr guten Arbeitsmöglichkeiten und die weitgehende wissenschaftliche Freiheit, die mir von ihm gewährt wurden. Ebenso möchte ich mich ganz besonders bei Prof. Dr.-Ing. Valko Mavrov für die vielen Anregungen und die konstruktive Kritik während der Betreuung meiner Arbeit und natürlich für seine Geduld bis zum Zusammenschreiben der Ergebnisse bedanken. Auch gilt mein Dank Prof. Klaus Stöwe, der kurzfristig Prof. Mavrov im Kolloquium vertreten hat.

Allen Mitarbeitern der upt sowie des Lehrstuhls danke ich für die sehr gute Zusammenarbeit und Unterstützung. Insbesondere möchte ich mich bei Bernhard Schlichter, Christoph Blöcher und Martin Kaschek für die fachliche Unterstützung und den kontinuierlichen Meinungsaustausch.

Außerdem möchte ich mich bei meinen Diplomanten und wissenschaftlichen Hilfskräften Christian Weirich, Pepa Dimitrova und Claudia Brocker bedanken. Ihre tatkräftige Unterstützung beim Aufbau und der Betreuung der Versuchsanlagen ermöglichte erst das Gelingen dieser Arbeit.

Annette Speicher und Dr. Willems danke ich für die Durchführung der chemischen Analytik.

In gleicher Weise geht ein besonderes Danke an meine Zimmer-Kollegen Javier Dorda und Sylvie Verplancke, die immer ein offenes Ohr für mich hatten und mich bei Bedarf mit frischem Kaffee versorgt haben.

Besonderer Dank gilt nicht zuletzt meiner Ehefrau Jacqueline sowie meinen Eltern, die mir diesen beruflichen Werdegang ermöglicht haben.

„Soll es ein andrer Mensch sein? Oder eine andere Welt?
Vielleicht nur andere Götter? Oder keine?“
Bertold Brecht, “ Der gute Mensch von Sezuan”

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Abstract

The removal of heavy metals from industrial waste water or from groundwater is a big challenge for the industry. It’s not possible to discharge industrial wastewater contaminated with heavy metals directly into rivers, water reservoirs or into the sea, because the heavy metals present a considerable danger to the ecosystem. Indirect discharge of this wastewater into municipal sewage treatment plants may have a major effect on the activated sludge and hinder the efficiency of the plants. The state-of-the-art processes, such as chemical precipitation, ion-exchange bed filtration, adsorption bed filtration and membrane processes have numerous shortcomings for treating this type of contaminated water. Furthermore, problems are encountered in metal reuse procedures as well as in the disposal of concentrates or sludge. In the present work the new hybrid membrane processes for separation of heavy metals from water and wastewater with the objective of the re-use of water and metals were studied. The focus of the work was to characterise the used bonding agents and to study the new hybrid processes in bench scale under real industrial conditions for two different applications:

1. Removal of AsF_6^- from groundwater using the hybrid process consisting of sorption and micro membrane filtration.
2. Removal of heavy metals from wastewater of the copper foil production using the hybrid process consisting of sorption, flotation and submerged membranfiltration.

Zusammenfassung

Die Abtrennung von Schwermetallen aus Industrieabwasser oder Grundwasser stellt die Industrie vor eine große Herausforderung. Das belastete Abwasser kann nicht direkt in Flüsse oder das Meer eingeleitet werden, da die Schwermetalle ein großes Risiko für die Umwelt darstellen. Auch die Indirekteinleitung in städtische Klärwerke ist nicht ohne Weiteres möglich, da die Schwermetalle eine toxische Wirkung auf den Belebtschlamm haben können. Die bekannten Prozesse, wie z.B. chemische Fällung/Flockung, Ionenaustausch oder Membranprozesse weisen unzählige Probleme bei der Behandlung dieser Abwässer auf. Diese Probleme können u.a. dazu führen, dass die Metalle nicht wiederverwertet werden können und als schwermetallhaltiger Schlamm entsorgt werden müssen.

In dieser Arbeit wurden neue Hybrid-Prozesse zur Abtrennung von Schwermetallen aus Wasser und Abwasser mit dem Ziel das Wasser als auch die Schwermetalle der Wiederverwertung zuzuführen untersucht. Der Fokus der Arbeit lag dabei in der Charakterisierung der benutzen “bonding agents” und in der Untersuchung der neuen Hybridprozesse mit realen Wasser für zwei Anwendungen:

1. Entfernung von AsF_6^- aus belastetem Grundwasser mittels des Hybridprozesses bestehend aus Sorption und Mikrofiltration.
2. Entfernung von Schwermetallen aus Abwasser aus der Halbleiterindustrie mittels des Hybridprozesses bestehend aus Sorption, Flotation und getauchter Membranfiltration.

1 Introduction

Continuously evolving economic, social and cultural pressures on freshwater resources – including pollution and excessive uses – are causing threats which are increasing external costs and multiplying conflicts between users of this vital resource for domestic purposes, industrial, agricultural and food production. In this respect, e.g. a crucial issue is surface treatment in the metal-working and galvanic-technical industry with its numerous plants for electroplating, pickling etc. These require considerable quantities of water for the various process and rinsing stages. Water has to be used after each treatment stage to clean the parts as well as the carrier elements properly. The result of this water usage is that the water is highly contaminated with pollutants from the process baths and the solutions have to be continually renewed.

When discharged directly into rivers, this wastewater poses a great risk to the aquatic ecosystem, whilst discharge into the sewage system will negatively affect bio-sludge activity and lead to contamination of the excess sludge to be disposed of. As a result of the standards specified in the Water Resources Act, which was amended in 1986, industry takes precautions against these risks by treating dangerous components in a partial stream, i.e. before being mixed with other types of wastewater. Wastewater treatment with primary, physico-chemical and thermal processes results in the limits for dangerous materials being observed, as stipulated by the legislator.

Taking the circuit board industry as an example, in 1990 600 million square meters of circuit boards were processed. The production requires 15 to 18 treatment steps and annually about 120,000 m^3 of solutions and 10 million m^3 of rinse water are used. The result is that the circuit board industry produces each year 25,000 tons of toxic metal load in 200,000 m^3 of liquid effluent. These figures show the dimension of the economic potential that lies in the recovery of valuable materials from waste. Even the recovery of a few toxic or valuable metals would be economically interesting. On the one hand recovery means conservation of the scarce raw materials and reduction in the overall consumption of these materials; on the other hand recovery leads to a reduction in the disposal costs.

Yet these measures have the disadvantage of focussing mainly on the effluent quality and do not take into account the resulting impacts on other environmental areas. The components are transformed into hazardous metal ferrous waste, the treatment of which is very difficult owing to the complex composition. From one kilogram of metal, approximately 10-15 kg of dehydrated sludge is produced after precipitation. It may cause risks for soil and groundwater (if disposed of) or air (if incinerated). In life-cycle categories, valuable resources are wasted as metals, precipitating agents and other chemicals are not re-used. Thus an integrated approach towards the treatment of wastewater containing toxic metals is needed.

Advances in effluent-free technologies, made during the last 10 years, always make use of multi-stage current rinsing and still rinse together with evaporation techniques for concentration and/or purification purposes. Evaporators are regarded as very robust and there is a low to medium risk of breakdown - e.g. caused by foaming due to organic compounds, which often occurs when using processing chemicals in the form of adsorbable/non-adsorbable bonding agents (wetting and complexing agents, brighteners, etc).

The first two development levels are an extension of the end-of-the-pipe philosophy that has ruled for many years in purification technology. It is possible to bring about a further reduction in the content of metals, organic and toxic compounds. It may be possible to recycle the water to some extent, but the drawback of this method is that an increasing quantity of waste is produced which is too heterogeneous to be re-used in the process or even in an external process. Although present technologies used in effluent-free electroplating (third development level) operate well, their shortcomings are high energy consumption and high investment costs.

The polluter pays principle ensures nowadays that polluting companies do have to pay the costs associated with environmental damage, or at least in part. Therefore, from their point of view, an economic and effective solution to the problem is required by developing an improved treatment technique. On the other hand, many of the metal ions (cations or oxyanions), being target compounds and present in effluents, could be further concentrated for recycling, because incineration of toxic sludge has to be avoided, as this entails transferring pollution from one state to another. It was specified by the Environment Water Task Force that, for the action line of water and wastewater treatment, innovation should be promoted at the interface between leading technologies. Developments are needed for the technologies to be more easily retro-fitted into existing industrial processes or better adapted to the needs and contraints of the smaller operators. The industry's future will be shaped (in part) by advances in its enabling technologies that improve the application of its fundamental sciences.

Based on these facts the European Commission was funding the project “METASEP” within the 5th Framework Programme (2001-2004). The consortium consisted of 13 partners from all over Europe (Germany, Greece, Bulgaria, The Netherlands, Czech Republic, Belgium and Slovakia) and 7 industrial companies which formed an Industrial Advisory Board (IAB).

In the framework of the project, a highly innovative low-waste technology with the objective of the re-use of water and metals were developed.

The main results achieved in the project were as follows:

- development of selective, bonding agents (water-soluble, powdered and produced on-site) with very fast reaction kinetics for bonding the toxic metals and with very high capacities for these metals
- development/modification of MF hollow fibre polymer membranes with an active layer outside the fibres or of polymer and ceramic flat-sheet membranes
- development of membrane modules (pressure-driven and submerged) with hollow fibre or polymer and ceramic flat-sheet membranes
- development of hybrid separation processes combining sorption and microfiltration; sorption microfiltration and flotation as well as electrocoagulation / membrane filtration
- regeneration and recovery of the bonding agents by electrodialysis with bipolar membranes
- lab and bench-scale investigations into the selective separation of toxic metals from specially selected process water streams based on end-users' requirements involving recovery and recycling of bonding agents.

In the present work the new hybrid membrane processes for separation of heavy metals from water and wastewater with the objective of the re-use of water and metals was studied. The focus of the work was to characterise the selected bonding agents and to study the new hybrid processes in bench scale under real industrial conditions.

2 Problems to be solved and resolutions

2.1 *State of the art in the separation of heavy metals from water and wastewater*

The conventional processes [1] -[38] to treat water contaminated with heavy metals - namely precipitation; precipitation/reduction; ion exchange/sorption bed filtration and the membrane processes: electrodialysis (ED), nanofiltration (NF) and reverse osmosis (RO) as well as process combinations (e.g. chemical precipitation and ion exchange; NF/RO and ion exchange; chemical precipitation and NF/RO and ion exchange etc), have a lot of well-known disadvantages.

These processes and their disadvantages are presented in the following.

2.1.1 Precipitation

One of the most common processes to remove heavy metals from industrial wastewater is the precipitation process (Figure 2-1) [3]

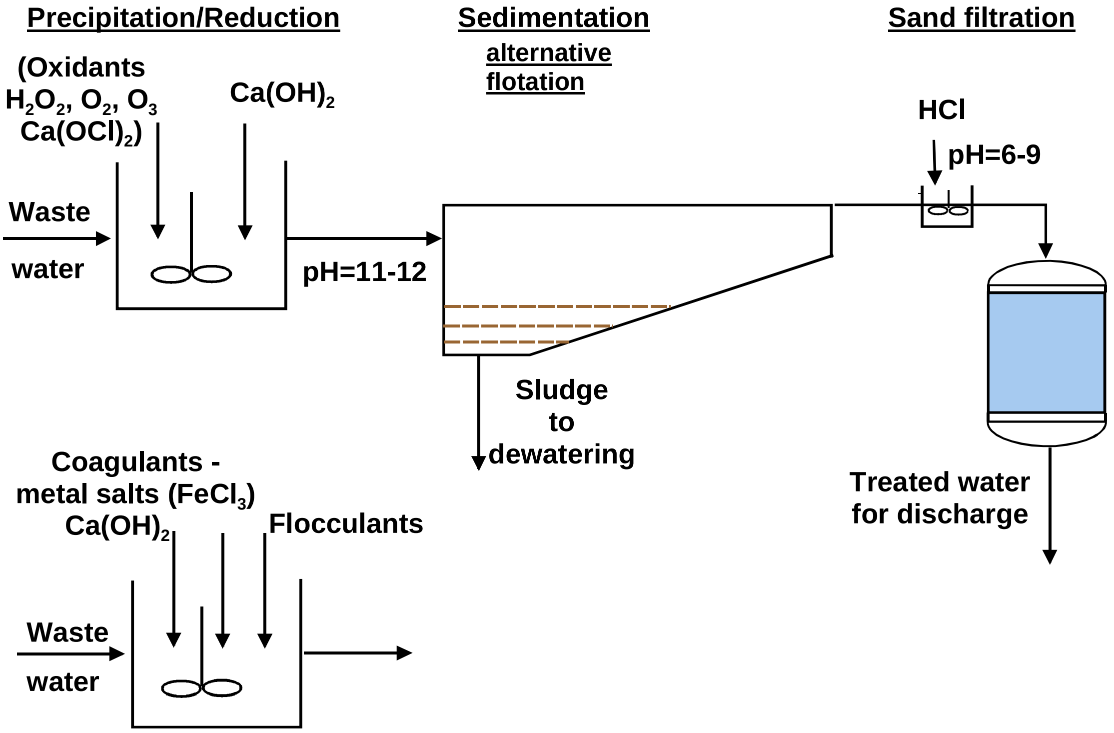


Figure 2-1: Precipitation/Reduction for the separation of toxic metals

A wide range of precipitation agents are used and only some of them are presented in the following pages:

Hydroxide Precipitation

Traditionally, dissolved metals have been removed from water by the process of hydroxide precipitation. Since most metal hydroxides are insoluble, it would appear easy to remove metals by this process. [4]

Ferric salts have been recognized as an effective scavenger of heavy metals for a long time and in the literature, extensive treatment has been given to the application and underlying removal mechanism. It has also been recognized that, metals, primarily ferric, hydroxide and oxide coating in the soil and sediments, play an important role in the transport, biotransformation and ultimate fate of trace constituents in natural systems [5].

At neutral to alkaline pH, ferric salts precipitate as amorphous hydrated oxide or oxy-hydroxide, which has relatively stable and reproducible surface properties. Upon aging, the precipitate transforms gradually into a crystalline iron oxide (goethite) form

In practical applications ferric hydroxide is precipitated in situ, which facilitates incorporation of heavy metal cations directly into the precipitate matrix in place of the similarly sized and charged ferric cations; mechanisms known as co-precipitation. This would account for only partial reversibility of the metal adsorption reaction upon reversal of pH [6], [7], [8].

It has been a common experience that pH-induced precipitation based on theoretical hydroxide (or hydrated oxide) solubility, frequently fails expectation. One of the likely reasons for higher than expected concentration of metals in soluble form, is the formation of chelates or complexes. The list of potential complexing agents is extensive and may include for various heavy metals, such diversified and ubiquitous substances as ammonia, chlorides, sulphates, cyanides, amines, thiourea, citric acid, and other organics. This includes agents specifically used in industrial applications for their chelating properties, such as EDTA [9]. Ferric salts appear to be capable of overcoming the masking effect of complexing agents or chelating ligands, perhaps by replacing trace heavy metal by the ferric cation.

An additional problem, which limits effectiveness of pH-induced precipitation of heavy metals, is the presence of emulsions and colloids stabilized by surfactants commonly found in industrial wastewater. Metals could be encapsulated into colloidal particles or emulsion globules (including in dissolved form), where they are relatively resistant to pH changes in the bulk liquid. Since ferric salts are also coagulants, their practical effectiveness in heavy metal removal extends into colloidal, emulsified and fine particulate forms of heavy metals.

The main problems associated with this process are that hydroxides of different metals have different pH levels for minimum solubility, and the reactions are of an equilibrium type, i.e., some of the metal hydroxide will disassociate with the resulting metal ions going back into solution.

For example, zinc has its lowest solubility at a pH of about 10, but chrome is at a minimum solubility at a pH of about 7.5 (Figure 2-2). Therefore, this method of metal removal can leave high levels of some metals still in solution or require an additional neutralization step.

The most common reagents used for hydroxide precipitation are caustic soda, lime, and magnesium hydroxide.

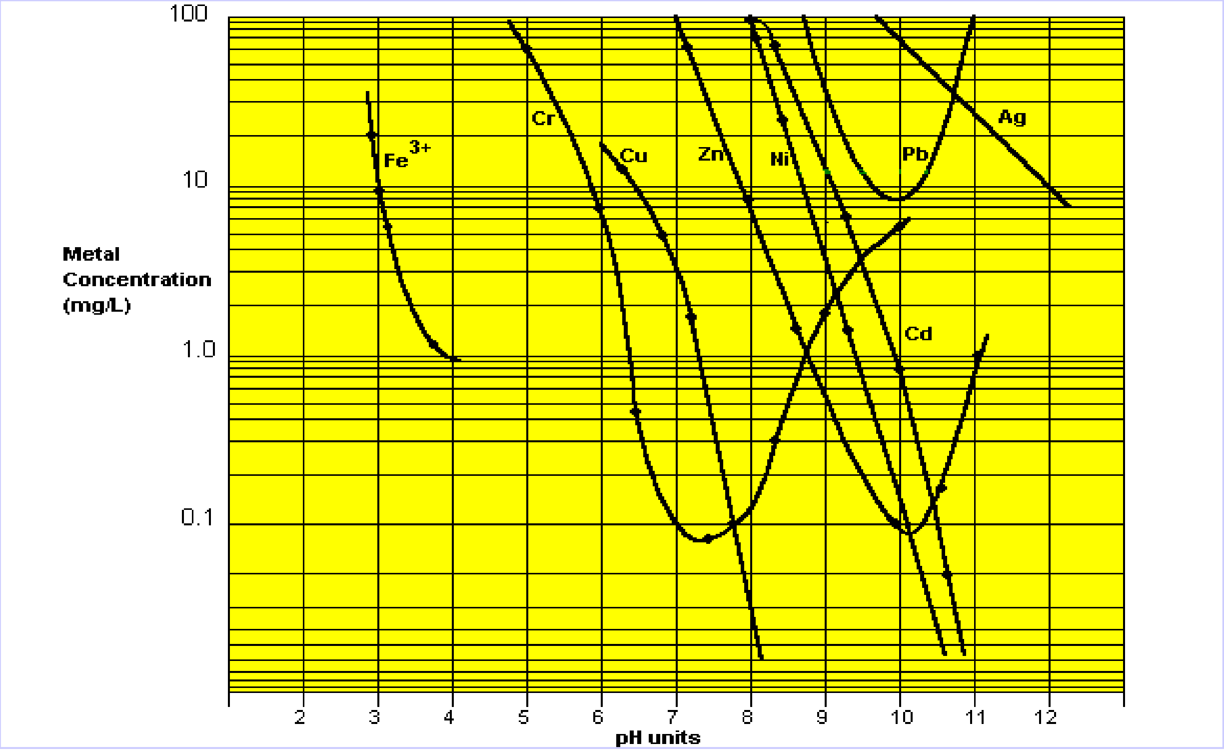


Figure 2-2: Influence of the pH to the dissolved metal concentration in the water [10]

Sulphide precipitation [10]

Recently, sulphur-based metals treatment technologies have been the focus of an increasing number of research studies and commercial applications for treating metals contamination in soil and groundwater. The solubility of these metals is highly pH dependent.

By the addition of sodium sulphide (Na_2S) to the solution the metal sulphides could be easily formed. This method yields more complete metal removal than hydroxide precipitation. But in the most cases this treatment is much more expensive than hydroxide precipitation since the excess sulphides are usually regulated and the resulting sludge may be difficult to landfill. Besides these facts it is very important to control the pH not to drop in the acid range. In acid pH range H_2S could be formed which is very toxic.

Another widely used agent besides Na_2S is e.g. calcium polysulfide (CaS4; brand name: Cascade®). It precipitates the highly soluble metals (arsenic, lead, copper, zinc, cadmium, molybdenum, uranium) as less soluble and non-toxic sulphides. In opposite to metal hydroxides the metal sulphides remain insoluble within a pH range of about 5 to 9.

Organometallic Precipitation [10]

The synthesis of organometallic and coordination compounds has attracted interest among chemists during the past few decades. Organometallic compounds are organic molecules containing at least one atom of a metal bonded to a carbon atom.

In 1991 Steve Holtzman [10] pioneered a new method of removing heavy metals. This process revolves around the formation of insoluble organometallic compounds formed by reacting metal bearing wastes with a proprietary organic agent.

By forming specific types of insoluble organometallic compounds, all regulated metals can be reduced to non-detectable levels.

This process works over an extremely broad pH spectrum (1.5 to 12) and has the ability to break most chelates in extremely high concentrations. Since the metals are precipitated as an organometal complex at all pH values, there is no problem with different levels of solubility based on pH. The only reasons for pH control are to make certain that the waste effluent is in a range that is allowed by the discharge permit and to allow the polymer flocculants to be in a pH range where they are effective.

The sludge volume produced by this method and caustic soda is approximately 50% of the sludge that is produced by using caustic soda alone and precipitating the metals as hydroxides. If magnesium hydroxide is used as the caustic agent, sludge volumes can be as low as 25% of the sludge volume produced by hydroxide precipitation. Typical residuals of all regulated metals are 0.01 mg/l or less.

One important example for organic precipitants is DTC, (alkyl dithiocarbamates) which is used in the treatment of printed wiring boards, wastewater [11].

The process of precipitation/reduction (Figure 2-1) has the following disadvantages:

- a lot of treatment chemicals are used,
- a minimum of 2 - 3 treatment stages is needed,
- the high quantities of sludge produced have to be treated and disposed of,
- slow sedimentation (alternative flotation) step with very large treatment units and high investment costs are required,

- the residual metal concentration required in the treated water is not always achieved because of the structure of the precipitates,
- The presence of multiple metal species may lead to removal difficulties as a result of amphoteric natures of different compounds (i.e., optimization on one metal species may prevent removal of another).
- Dissolved salts are added to the treated water as a result of pH adjustment.
- Polymer may need to be added to the water to achieve adequate settling of solids.

2.1.2 Ion exchange/sorption bed filtration

Contaminant cations such as zinc, copper, nickel and lead and anions such as arsenate, selenate and chromate can be removed from water by using ion exchange with resins or by adsorption onto hydrous metal oxides such as activated alumina granules or coagulated Fe(II), Fe(III), Al(III), and Mn(IV) surfaces. [12]

Ion exchange with synthetic resins and adsorption onto activated alumina are water treatment processes in which a presaturant ion on the solid phase, the adsorbent, is exchanged for an unwanted ion in the water. In order to accomplish the exchange reaction, a packed bed of ion-exchange resin beads or alumina granules is used. Source water is continually passed through the bed in a downflow or upflow mode until the adsorbent is exhausted, as evidenced by the appearance (breakthrough) of the unwanted contaminant at an unacceptable concentration in the effluent.

The most useful ion-exchange reactions are reversible. In the simplest cases, the exhausted bed is regenerated using an excess of the presaturant ion. Ideally, no permanent structural change takes place during the exhaustion/regeneration cycle.

When the reactions are reversible, the medium can be reused many times before it must be replaced because of irreversible fouling or, in the case of alumina, excessive attrition. In a typical water supply application, from 300 to as many as 300,000 bed volumes (BV) of contaminated water may be treated before exhaustion.

Regeneration typically requires from 1 to 5 bed volumes of regenerant, followed by 2 to 20 bed volumes of rinse water. These wastewaters generally amount to less than 2 percent of the product water; nevertheless, their ultimate disposal is a major consideration in modern design practice. The disposal of the spent media also presents mostly a problem.

By far the largest application of ion exchange to drinking water treatment is in the area of softening, that is, the removal of calcium, magnesium, and other polyvalent cations in exchange for sodium. The ion-exchange softening process is applicable to both individual home use and municipal treatment. It can be applied for wholehouse (point-of-entry or POE) softening or for softening only the water that enters the hot water heater. Radium and barium are ions more preferred by the resin than calcium and magnesium; thus the former are also effectively removed during ion exchange softening.

Resins beds containing chloride-form anion exchange resins can be used for nitrate, arsenate, chromate, selenate, dissolved organic carbon (DOC), and uranium removal, and more applications of these processes will be seen in the future.

Activated alumina is being used to remove fluoride and arsenate from drinking water, particularly high total dissolved solids (TDS) waters, at point-of-use (POU), (POE), and municipal scales.

The choice between ion exchange or alumina adsorption (to remove arsenic from water, for example) is largely determined by (a) the wastewater quality -including TDS level, competing ions, alkalinity, and contaminant concentration- and (b) the resin or alumina affinity for the contaminant ion in comparison with the competing ions. The affinity sequence determines the run length, chromatographic peaking (if any), and process costs. As previously mentioned, process selection will be affected by spent regenerant and spent medium disposal requirements, and regenerant reuse possibilities, particularly if hazardous materials are involved.

Ion exchange/sorption bed filtration for the separation of toxic metals is a discontinuous process and implemented in two stages: working and regeneration stage (Figure 2-3).

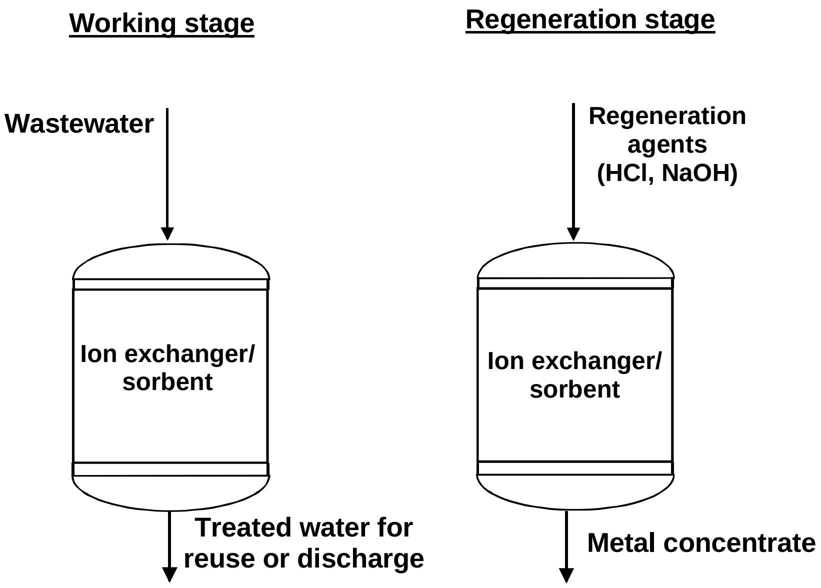


Figure 2-3: Ion exchange/sorption bed filtration for the separation of toxic metals [1]

The main disadvantages of ion exchange and sorption bed filtration for the separation of toxic metals are:

- slow bonding kinetics because of the size of ion exchangers (IX) and sorbents (0.5 to 1.2 mm), The size of the IX and sorbents is limited by the loose of pressure drop in a column. The smaller the particles the higher the pressure drop.
- low capacity of ion exchangers and sorbents,
- slow filtration velocity
- large filters are needed to obtain the low residual concentration of the metals in the treated water

2.1.3 Membrane processes

The most important membrane processes and separation mechanisms of these processes for the separation of toxic metals are shown in Figure 2-4 and Table 2-1.

The heavy metals in forms of particles e.g. as hydroxides or heavy metals sorbed at particles can be separated from the water by microfiltration. The heavy metals which are bonded on macromolecular substances as chalting agents can be removed by ultrafiltration. Dissolved heavy metals in molecular size can be removed by nanofiltration or reverse osmosis.

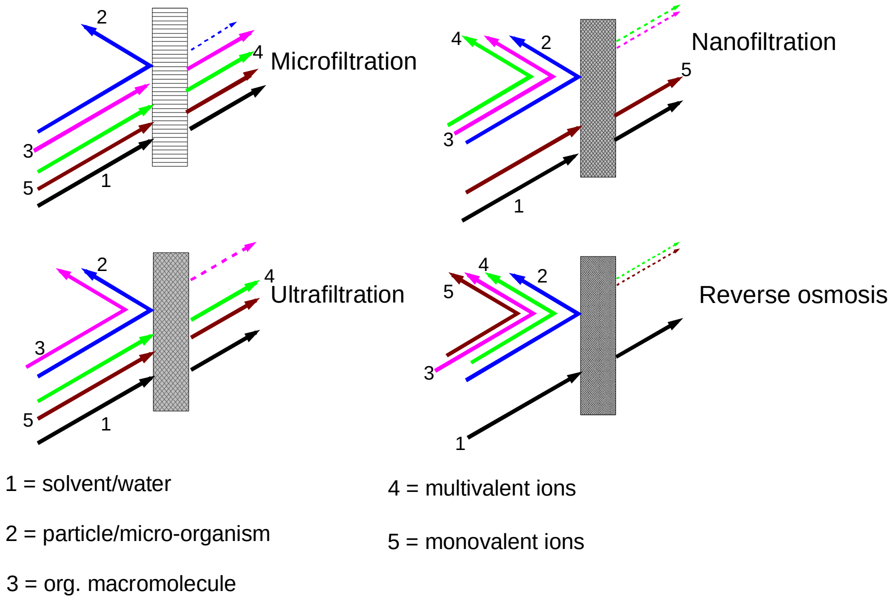


Figure 2-4: Pressure-driven membrane processes [1]

Table 2-1: The most important membrane processes (pressure-driven / electrically driven) for the separation of toxic metals

Membrane separation process	Driving force for mass transfer	Separation principle	Application
Microfiltration	Differential pressure	Sieving effect	Separation of suspended matter
Ultrafiltration	Differential pressure	Sieving effect	Separation of macromolecular substances
Nanofiltration	Differential pressure	Sieving effect Charge effect and solution /diffusion	Separation of low-molecular organic and multivalent inorganic components
Reverse osmosis	Differential pressure	Solution /diffusion	Separation of monovalent and multivalent inorganic components
Electrodialysis	Electric potential	Solution /diffusion	Separation of monovalent and multivalent inorganic components

The principle of the electro-driven membrane process, electrodialysis used for toxic metal separation is shown in Figure 2-5.

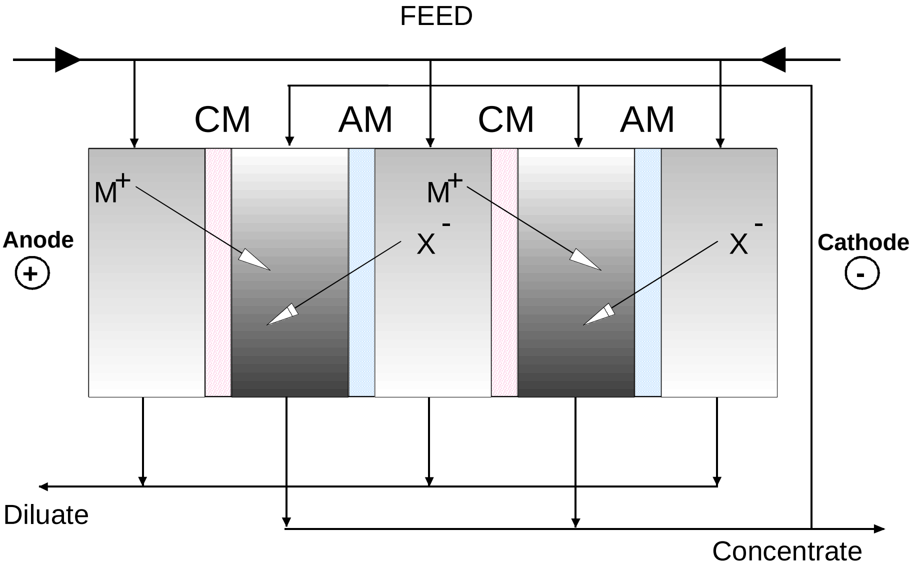


Figure 2-5: Conventional electrodialysis for toxic metal separation [1]

The main problems with the application of membrane processes are scaling and fouling. Scaling is caused by salt deposits (metals) on or in the membrane while fouling is caused by (ir)reversible deposits of retained particles, colloids, macromolecules, micromolecules etc. on or in the membrane. Blocking is a special form of fouling i.e. irreversible blocking of the pores inside the membrane which results in a reduction in flow through the membrane.

To prevent scaling and fouling, counter-measures have to be implemented. These can take the form of pre-treatment involving pre-filtration, precipitation, pH change or inhibitors. The choice of membrane such as the membrane material or the properties of the membrane surface (hydrophilic, electric charge, degree of roughness) as well as the choice of module i.e. module geometry and flow conditions also play an important role. Decreasing the water yield can also be effectual. To summarise: membrane separation of toxic metals from wastewater streams has the following disadvantages:

- low water yield (normally 75%) - 75% purified water and 25% concentrate
- low selectivity for metals (not only metals are contained in the concentrate but other monovalent and multivalent cations and anions)
- the metal concentrate cannot be re-used, because the concentrate is normaly a mixture of many different metals
- problems with the discharge of concentrates
- higher investment costs
- scaling and fouling of membranes

2.1.4 Summary of the state-of-the-art processes

As shown in chapter 2.1 the conventional processes namely precipitation, ion exchange/sorption bed filtration and the membrane processes as well as process combinations (e.g. chemical precipitation and ion exchange; NF/RO and ion exchange; chemical precipitation and NF/RO and ion exchange etc) have the following disadvantages:

- high use of treatment chemicals;
- the large quantities of sludge produced have to be treated and disposed of;
- inadequate selectivity. Metal re-use can be too complicated and the disposal of the concentrates or sludge may present problems;
- very slow bonding kinetics for the metals and their oxyanions and therefore very large water treatment units and high investment costs are required;
- low capacity of ion exchangers and sorbents;
- the residual metal concentration in the treated water streams can be high and water re-use or discharge could be problematic;
- fouling and scaling problems, very low membrane permeability and low water yield (up to 75%) are the main problems encountered with conventional membrane. This entails high investment costs and periodical membrane cleaning while high quantities of wastewater are generated;
- treatment processes are periodical and not continuous, followed by a regeneration step in which regeneration chemicals and rinsing water are employed, ultimately generating a new quantity of wastewater;
- treatment of wastewater streams with large volume flow and high concentrations is mostly not cost-effective.

2.2 *Methodology and scope of thesis*

The main scope of the thesis was to study the hybrid membrane processes for separation of heavy metals from water and wastewater leading to less disadvantages than the state-of-the-art processes.

The hybrid membrane processes comprised the following treatment stages:

First step: selective bonding of toxic metal cations or oxyanions to suitable, selective bonding agents (BAs) (water soluble and powdered BAs)

Second step:

Variant 1: separation of the formed BA-metal complexes by crossflow microfiltration / ultrafiltration (MF/UF) for wastewater with metal concentrations < 50 mg/l (Figure 2-6).

Variant 2: separation of the formed BA-metal complexes by a hybrid system of submerged MF membranes combined with flotation for wastewater with metal concentrations 50-500 mg/l (Figure 2-7) [39], [40], [41].

Third step: recovery, regeneration and recycling of the BAs with simultaneous production of metal concentrates for re-use (Figure 2-6 and Figure 2-7).

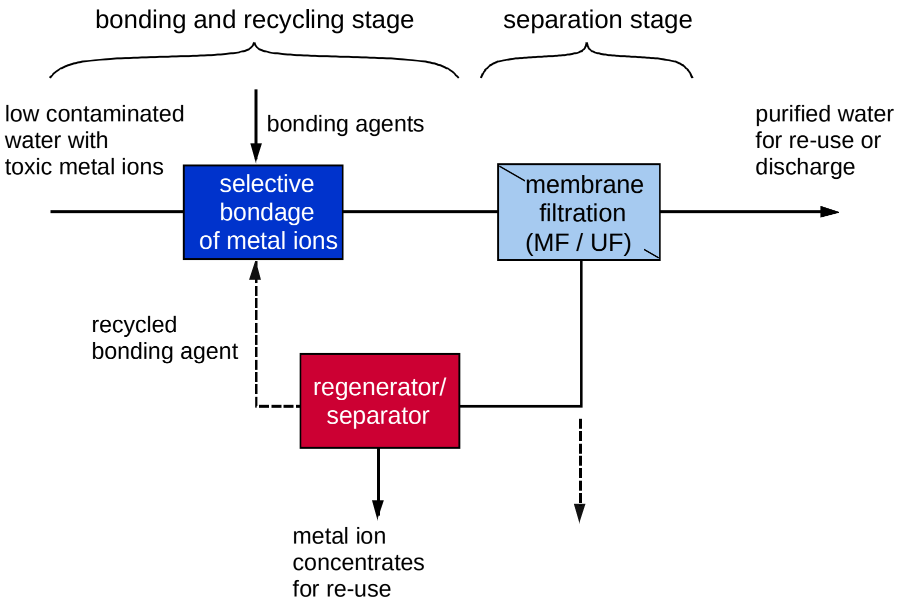


Figure 2-6: MF/UF membrane separation of BA/metal complexes for wastewater with metal concentration < 50 mg/l

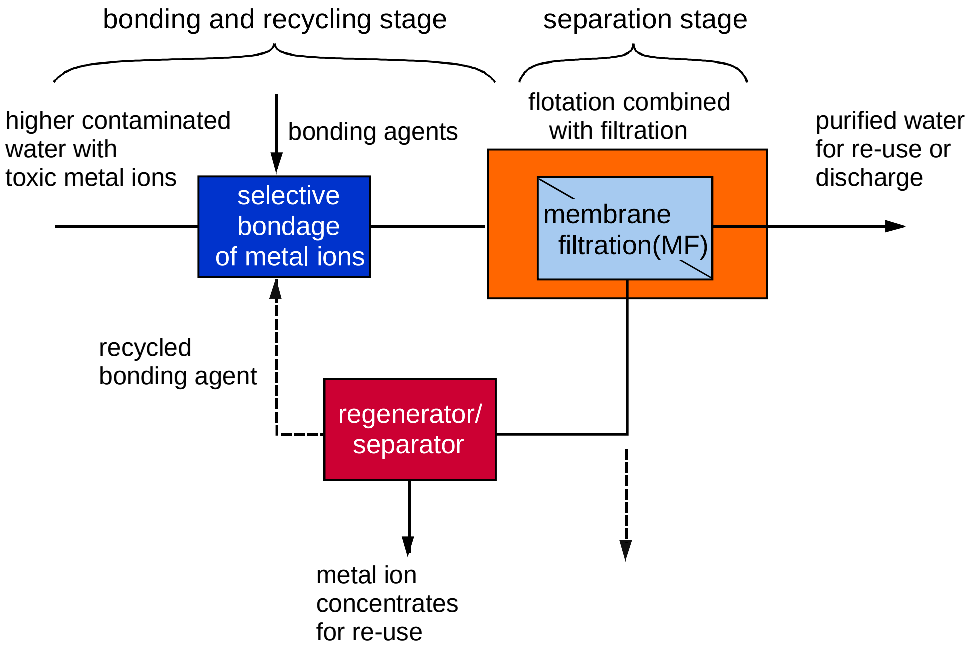


Figure 2-7: Hybrid system - Flotation combined with MF/UF membrane separation of the BA/metal complexes for wastewater with metal concentration > 50 mg/l

The present work which was part of the METASEP project is divided into two main parts:

1. Characterisation of suitable bonding agents and identifying of the observed sorption mechanisms

In this context two bonding agents – namely a synthetic zeolite P and a modified ionexchanger should be examinated for there sorption ability. Finally the sorption mechanism of the synthetic zeolite should be explained.

2. Study of the described hybrid process with real industrial wastewater in bench-scale

The first hybrid process containing sorption and crossflow microfiltration should bestudied for the treatment of a groundwater contaminated with hexafluoroarsenate using a modified powdered ion exchanger as bonding agent.

The second hybrid process containing sorption/submerged microfiltration and flotation should be studied with water from the semiconductor industry contaminated mainly with copper by using the new developed powdered synthetic zeolite P.

3 Theory

3.1 *Sorption of heavy metals*

The loss of a chemical species (e.g. heavy metal ions) from an aqueos solution phase to a contiguous solid phase may be termed as the sorption process. The sorption process can be divided among the mechanisms by which the sorption process occurs into three different categories:

1. adsorption: the accumulation of matter at the interface between an aqueous solution phase and a solid adsorbent without the development of a three-dimensional molecular arrangement
2. precipitation: the growth of a solid phase exhibiting a primitive molecular unit that repeats itself in three dimensional. If the precipitation is taking place on the surface of a solid is called as surface precipitation
3. ion exchange, the exchange of ions from a solid with ions from an aqueous solution

3.1.1 Adsorption

The adsorption which results from the influence of van der Waals forces is essentially physical in nature. The forces are not strong, so the adsorption can be easily reversed. In some systems, additional forces bind adsorbed molecules to the surface. These are chemical in nature involving the exchange or sharing of electrons, or possibly molecules breaking up into atoms or radicals. This phenomenon is called the chemisorption. It is restricted to just one layer of molecules on the surface, but may be followed by additional layers of physically adsorbed molecules.

The moving of molecules (e.g. heavy metal ions) from the bulk to the adsorbed phase is always connected with a loose of freedom and therefore the free energy of the molecules is reduced. So the process of adsorption is always accompanied by an increasing of the temperature.

In order to describe the adsorption process there are in particular two parameters of special interest:

- adsorption equilibrium
- adsorption dynamics

3.1.1.1 Adsorption equilibrium

Adsorption equilibrium is a dynamic concept achieved when the rate of the molecules which are adsorpted on a surface is equal to the rate of the molecules which are desorpted.
A lot of different mathematical models were developed to describe the adsorption equilibrium. But the most useful theories are still some of the earliest theories:

Freundlich Isotherm

Herbert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm for nonideal systems in 1906. The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as [50]:

$$q_{eq} = K_f * c_{eq}^{n^{-1}}$$ **Formula 3-1**

where:

q_{eq}: the adsorption density (mg of adsorbate per g of adsorbent) (mg/g)

c_{eq}: the equilibrium concentration of adsorbate in solution (mg/l)

K_f and n are the empirical constants dependent on several environmental factors, and n is greater than one.
This equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\ln q_{eq} = \ln K_f + \frac{1}{n} \ln c_{eq}$$ **Formula 3-2**

A plot of $\ln q_{eq}$ against $\ln c_{eq}$ yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption (see Figure 3-1). The constants can be determined from the slope and the intercept.

Linear Isotherm [50]

If in formula 3-2 n is set to 1, the Freundlich isotherm reduces to the linear isotherm. This linear isotherm is the simplest model to fit the data. In this model the available sorption sites are assumed to be unlimited.

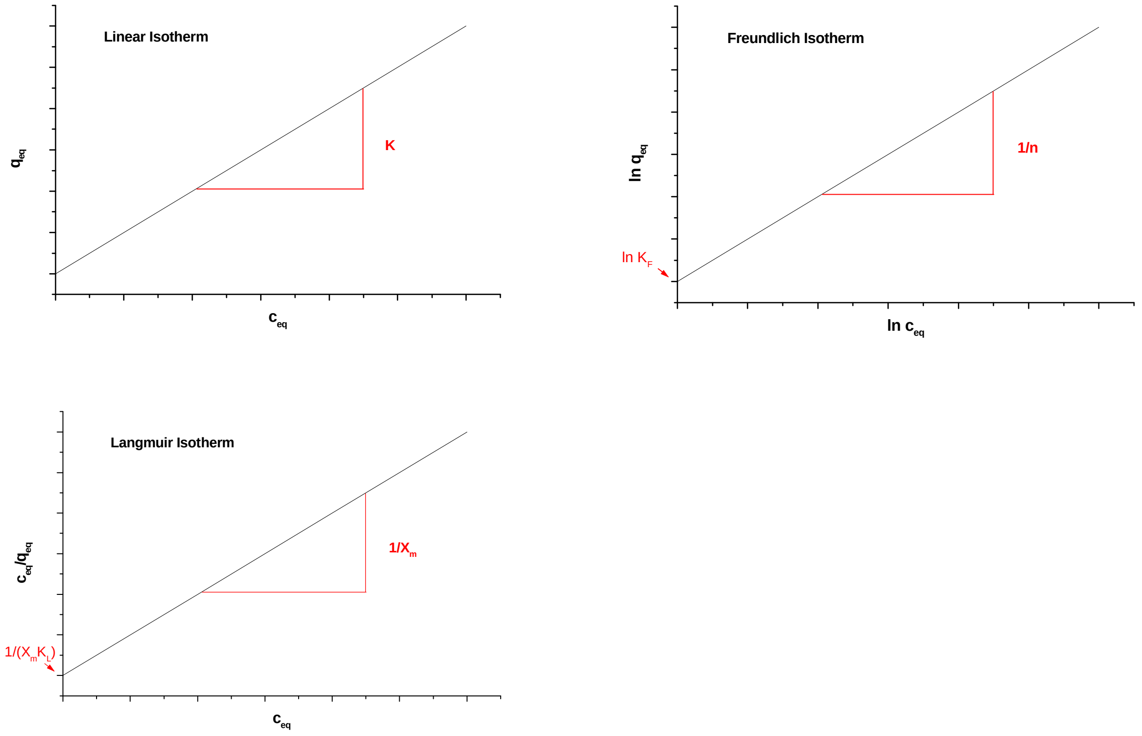


Figure 3-1: Linear fit of Freundlich isotherm , the linear isomtherm and the Languimir isotherm

The linear isotherm is defined by

$$q_{eq} = K_L * c_{eq}$$ **Formula 3-3**

where:

q_{eq}: the adsorption density (mg of adsorbate per g of adsorbent) (mg/g)

c_{eq}: is the equilibrium concentration of adsorbate in solution (mg/l)

K_L: empirical constants dependent on several environmental factor (l/g)

Langmuir Isotherm [50]

The Langmuir adsorption isotherm is often used for adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as [50]:

$$q_{eq} = \frac{X_m * K_{La} * c_{eq}}{1 + K_{La} * c_{eq}}$$ **Formula 3-4**

where:

q_{eq}: the adsorption density at the equilibrium solute concentration c_{eq} (mg of adsorbate per g of adsorbent) (mg/g)

c_{eq}: the equilibrium concentration of adsorbate in solution (mg/l)

X_m: the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent) (mg/g)

K_{La}: the Langmuir constant related to energy of adsorption (l of adsorbent per mg of adsorbate).

A number of assumptions are implicit in this equitation:

- limited to monolayer adsorption
- no interaction of the adsorbed molecules on the surface
- the energy of adsorption is all over the surface the same
- the adsorbed molecules are fixed on the surface and do not move over the surface

The above equation can be rearranged to the following linear form:

$$\frac{c_{eq}}{q_{eq}} = \frac{1}{X_m * K_{La}} + \frac{c_{eq}}{X_m}$$

Formula 3-5

The linear form can be used for linearisation of experimental data by plotting c_{eq}/q_{eq} against c_{eq} (Figure 3-1). The Langmuir constants X_m and K_{La} can be evaluated from the slope and intercept of linear equation.

3.1.1.2 Adsorption dynamics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. To show the adsorption dynamics in a diagram in the literature [51] is often used the graph which shows the fractional approach to equilibrium U versus time t (Figure 3-2).

$$U = \frac{c_0 - c_t}{c_0}$$

Formula 3-6

With

U: Fractional approach to equilibrium (-)

c_0: the beginning concentration of adsorbate in the solution (mg/l)

c_t: the concentration of adsorbate at time t in the solution (mg/l)

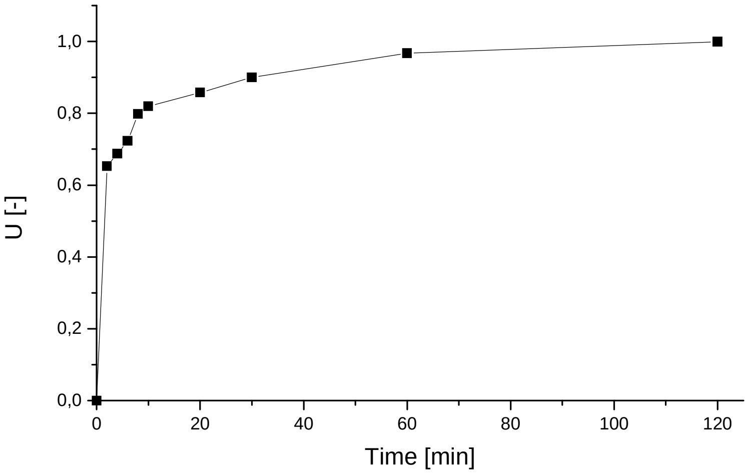


Figure 3-2: typical changing of the approach to equilibrium with contact time

A lot of different mathematical models to describe the kinetics of the adsorption process can be found in the literature, e.g.

- pseudo first-order kinetic model [52],
- pseudo second-order kinetic model [53]
- Elovich kinetic model [54], [55]

The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2, values close or equal to 1).

It is apparent from studies of chemical kinetics that different chemical reactions belong to different orders of reaction. A zero-order reaction is one in which the reaction rate does not depend on the concentrations or activities of the reactants. Reaction rate is dependent on one reactant only in the case of a first-order reaction. A second-order reaction rate depends on the concentrations of two reactants, while a pseudo first-order process is one in which the crucial reaction involves two reactants, but only one of these is seen to change during the period of observation. Each of these types of reaction may be described mathematically in differential form as follows:

The pseudo first-order equation

The pseudo first-order equation is generally expressed as follows [52], [56]:

$$\frac{dq_t}{dt} = k_1 * (q_{eq} - q_t)$$

Formula 3-7

where:

q_{eq}: the adsorption density at equilibrium (g/g),

q_t: the adsorption density at time t (g/g)

k_1: the rate constant of pseudo first-order adsorption (l /min).

After integration and applying boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, the integrated form of Formula 3-7 becomes:

$$\log(q_{eq} - q_t) = \log(q_{eq}) - \frac{k_1}{2{,}303} * t$$

Formula 3-8

The values of log (q_{eq} - q_t) were linearly correlated with t. The plot of log (q_{eq} - q_t) vs. t should give a linear relationship from which k_1 and q_{eq} can be determined from the slope and intercept of the plot, respectively.

The pseudo second-order equation

The pseudo second-order adsorption kinetic rate equation is expressed as [53][52]:

$$\frac{dq_t}{dt} = k_2 * (q_{eq} - q_t)^2$$

Formula 3-9

where:

k_2: the rate constant of pseudo second-order adsorption (mg/(g*min)

With the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, the integrated form of Formula 3-9 becomes:

$$\frac{1}{q_{eq} - q_t} = \frac{1}{q_{eq}} + k_2 * t$$

Formula 3-10

which is the integrated rate law for a pseudo second-order reaction.

Formula 3-10 an be rearranged to obtain Formula 3-11 which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 * q_{eq}^2} + \frac{1}{q_{eq}} * t$$

Formula 3-11

if the initial adsorption rate, α (mg/(g min)) is:

$$a = k_2 * q_{eq}^2$$ **Formula 3-12**

then Formula 3-11 and Formula 3-12 become:

$$\frac{t}{q_t} = \frac{1}{a} + \frac{1}{q_{eq}} * t$$ **Formula 3-13**

The plot of (t/q_t) and t of Formula 3-13 should give a linear relationship from which q_{eq} and k_2 can be determined from the slope and intercept of the plot, respectively.

The Elovich equation

The Elovich model equation is generally expressed as [54], [55]:

$$\frac{dq_t}{dt} = a * e^{(-b * q_t)}$$ **Formula 3-14**

where:

α: the initial adsorption rate (mg/ (g·min))

β: the desorption constant (g/mg)

To simplify the Elovich equation, Chien and Clayton [54] assumed α β t >> t and by applying the boundary conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t Formula 3-14 becomes:

$$q_t = \frac{1}{b} * \ln(a * b) + \frac{1}{b} * \ln(t)$$ **Formula 3-15**

If the adsorption fits the Elovich model, a plot of q_t vs. ln(t) should yield a linear relationship with a slope of (1/ β) and an intercept of (1/ β * ln (α β)).

3.1.2 Precipitation

Precipitation of metals has long been the primary method of treating metal-laden industrial wastewaters. As a result of the success of metals precipitation in such applications, the technology is being considered and selected for use in remediating ground water containing heavy metals, including their radioactive isotopes. In ground water treatment applications, the metal precipitation process is often used as a pretreatment for other treatment technologies (such as chemical oxidation or air stripping) where the presence of metals would interfere with the other treatment processes.

Metals precipitation from contaminated water involves the conversion of soluble heavy metal salts to insoluble salts that will precipitate. The precipitate can then be removed from the treated water by physical methods such as clarification (settling) and/or filtration. The process usually uses pH adjustment, addition of a chemical precipitant, and flocculation. Typically, metals precipitate from the solution as hydroxides, sulfides, or carbonates. The solubilities of the specific metal contaminants and the required cleanup standards will dictate the process used (see Figure 2-2: Influence of the pH to the dissolved metal concentration in the water [10]). In some cases, process design will allow for the generation of sludges that can be sent to recyclers for metal recovery.

In the precipitation process, chemical precipitants, coagulants, and flocculantation are used to increase particle size through aggregation. The precipitation process can generate very fine particles that are held in suspension by electrostatic surface charges. These charges cause clouds of counter-ions to form around the particles, giving rise to repulsive forces that prevent aggregation and reduce the effectiveness of subsequent solid-liquid separation processes. Therefore, chemical coagulants are often added to overcome the repulsive forces of the particles. The three main types of coagulants are inorganic electrolytes (such as alum, lime, ferric chloride, and ferrous sulfate), organic polymers, and synthetic polyelectrolytes with anionic or cationic functional groups. The addition of coagulants is followed by low-sheer mixing in a flocculator to promote contact between the particles, allowing particle growth through the sedimentation phenomenon called flocculant settling.

Flocculant settling refers to a rather dilute suspension of particles that coalesce, or flocculate, during the sedimentation operation. As coalescence or flocculation occurs, the particles increase in mass and settle at a faster rate. The amount of flocculation that occurs depends on the opportunity for contact, which varies with the overflow rate, the depth of the basin, the velocity gradients in the system, the concentration of particles, and the range of particles sizes. The effects of these variables can only be accomplished by sedimentation tests.

3.1.3 Ion exchange

Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications. [57]

An organic ion exchange resin is composed of high-molecular-weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin.

Resins currently available exhibit a range of selectivity's and thus have broad application. As an example for a strong acid resin the relative preference for divalent calcium ions (Ca^{2+}) over divalent copper ions (Cu^{2+}) is approximately 1.5 to 1. For a heavy-metal-selective resin this preference is reversed. It prefers copper by a ratio of 2.300 to 1.

Ion exchange reactions are stoichiometric and reversible:

A resin with protons available for exchange will exchange those ions for metal ions from solution. The reaction can be written as follows:

$$2\,(R\text{-}SO_3^-\,H^+) + Me^{2+} \leftrightarrow (R\text{-}SO_3)_2Me + 2\,H^+$$

R indicates the organic portion of the resin and SO_3 is the immobile portion of the ion active group. Two resin sites are needed for one metal with a plus 2 valence.

As shown, the ion exchange reaction is reversible. The degree the reaction proceeds to the right will depend on the resins preference. or selectivity, for a each single metal ion compared with its preference for hydrogen ions. The selectivity of a resin for a given ion is measured by the selectivity coefficient K_{sel}. which in its simplest form for the reaction

$$R\text{-}A^+ + B^+ \leftrightarrow R\text{-}B^+ + A^+$$

is expressed as:

$$K_{sel} = \frac{c(R-B^+)*c(A^+)}{c(R-A^+)*c(B^+)}$$ **Formula 3-16**

The selectivity coefficient expresses the relative distribution of the ions when a resin in the A^+ form is placed in a solution containing B^+ ions. It should be pointed out that the selectivity coefficient is not constant but varies with changes in solution conditions. It does provide a means of determining what to expect when various ions are involved. [57]

Regeneration

The resin can be converted back to the hydrogen form by contact with a concentrated solution of an acid , e.g. sulphuric acid (H_2SO4):

$$(R\text{-}SO_3)_2Me + H_2SO_4 \rightarrow 2(R\text{-}SO_3H) + MeSO_4$$

There are a number of different ion exchange regeneration technologies that can be used, from the basic co-current regenerated systems to counter-flow block systems and through to packed bed technology.

Counter-Current Regeneration Systems [57]

In these systems, the regenerant is applied in the opposite direction to the service flow, resulting in reduced chemical consumption, improved water quality and less waste volumes compared to traditional co-current regenerated systems.

There are two main types of counter-current systems:

- Blocked Systems, including air hold down, water hold down and inert mass blocked. The service flow is downwards and regeneration upflow. To avoid disturbance of the resin polishing zone at the bottom of the vessel, the resin bed is held down (blocked) during regeneration by air pressure, water flow or an inert mass in the top part of the vessel. The regenerant passes up through the resin and out of a collector system in the middle part of the vessel. Such systems have similar high cylindrical height as co-current systems to allow resin backwash within the vessel.
- Packed Bed Systems, these may be up-flow service with down-flow regeneration or down-flow service with up-flow regeneration.

Co-Current Regeneration Systems

These are the simplest systems, where the resin is regenerated in the same direction as the service flow (downwards). The vessel has a large freeboard to allow expansion of the resin bed when backwashing is carried out to remove suspended solids and resin fines. Co-current regeneration single bed systems will generally produce water of much lower quality than counter-current systems, with typical leakage values ~10 times higher. Such quality will also be even more affected by the water composition, the type of regenerant chemical and dosage being used.

3.2 *Microfiltration*

3.2.1 Definitions

The most common terms that are used in microfiltration processes are shortly described in this section. An important property of a membrane is its flux, which is defined as the permeate volume (or mass) through the membrane per unit of membrane area. The permeate flux or simply the flux J_F through the membrane is given by the general Formula 3-17 [58] in $m^3/(m^2 * s)$. In practice the flux J_F is represented as litre filtered volume per m^2 membrane area per hour as $L/(m^2 * h)$.

$$J_F = \frac{dV}{dt} * \frac{1}{A}$$ **Formula 3-17**

Where

J_F: Flux $[L/(m^2 \cdot h)]$

V: filtered volume (L)

t: time (h)

A: membrane area (m^2)

The pressure difference over a membrane is called the Trans Membrane Pressure (TMP) and is the difference between the pressures at the feedwater side and the pressures at the permeate side. The relationship between flux J and TMP is defined by a modified form of Darcy's law [59] and is introduced in Formula 3-18.

$$L_P = \frac{J_F}{TMP} = \frac{1}{R_M \cdot \eta}$$ **Formula 3-18**

Where

L_P: Permeability $[L/(m^2 \cdot h \cdot bar)]$

J_F: Flux $[L/(m^2 \cdot h)]$

R_M: Membranresistance [1/m]

TMP: Trans membrane pressure [bar]

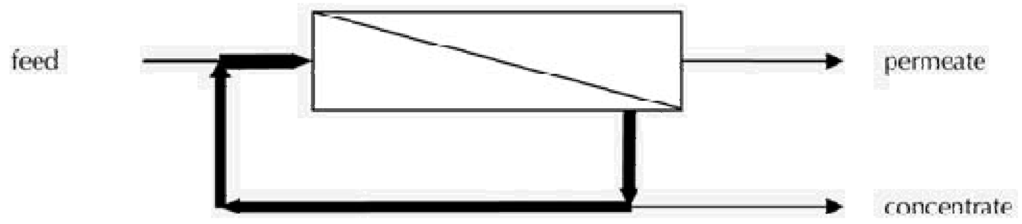
In general two different the process configurations for membrane filtrations are possible:

- cross-flow filtration method

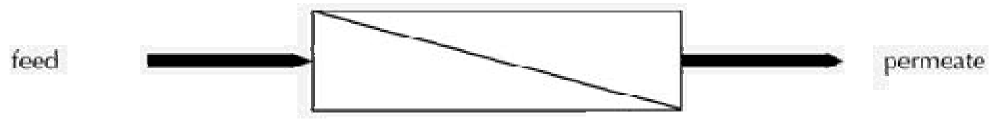
  In cross-flow systems the concentrate is constantly transported with a recirculation loop, as is shown in Figure 3-3a. Cross-flow systems are widely used [60] but these systems use more energy than dead-end configured systems [61]

- dead end filtration method

  In dead-end systems the total volume of the feedwater passes the membrane, leaving all components that are larger than the membrane pores in or on the membrane material (see Figure 3-3b)



(a) cross-flow



(b) dead-end

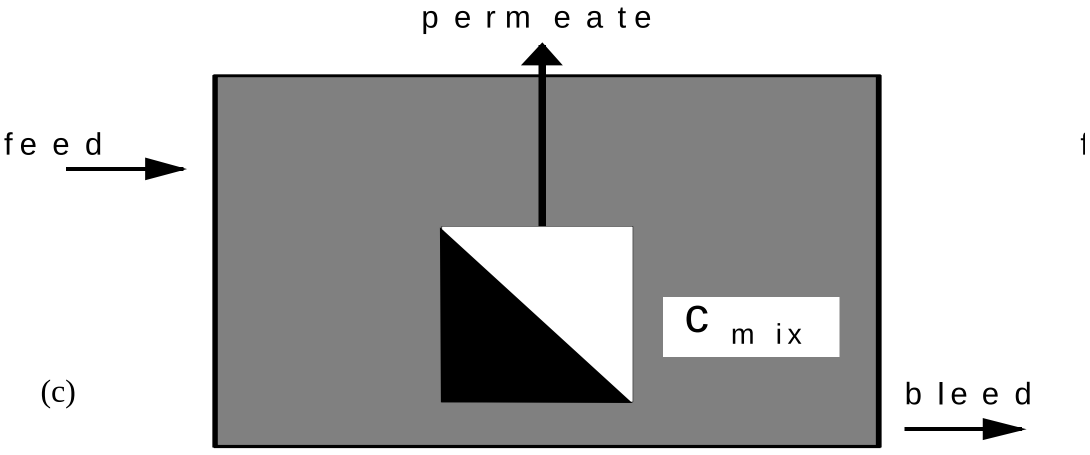


Figure 3-3: Typical operational modes for microfiltration membrane processes: (a) cross-flow configuration, and (b) dead-end configuration (c) submerged configuration

3.2.2 Fouling

The International Union of Pure and Applied Chemistry defines fouling as follows: “The process that results in a decrease in performance of a membrane, caused by the deposition of suspended or dissolved solids on the external membrane surface, on the membrane pores, or within the membrane pores” [62]. A typical dereasing of the permeability during the filtration caused by fouling is shown in Figure 3-4.

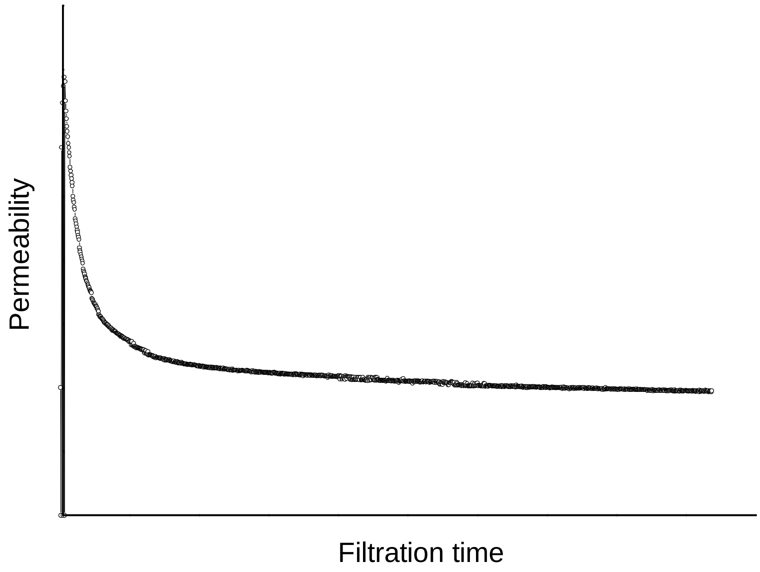


Figure 3-4: Characteristic decreasing of permeability with time caused by fouling

3.2.2.1 Fouling model – resistance-in-series-model

When clean water is filtered, the membrane material is the only resistance caused (R_m). The flux is than called the clean water-flux. As a result of the accumulation of particles on the membrane through the filtration of water with a certain level of suspended solids, a cake will form on the membrane (R_c). When particles block the membrane pores, this is called pore plugging (R_p). In addition one resistance as a consequence of adsorption in or on the membrane can occur (R_a) (see Figure 3-5).

Using the resistance-in-series-model [63] which describes filtration resistance as the fraction of TMP to flux, the resistance of the cake layer can be evaluated according to Formula 3-19:

$$\mathbf{J_F} = \frac{TMP}{h\,(R_m + R_c)}\ \mathbf{3.6 \cdot 10^8} \qquad \textbf{Formula 3-19}$$

Where,

J: permeate flux [l m^{-2} h^{-1}],

R_m: membrane resistance [m^{-1}],

R_c: the resistance of the cake layer (or in general fouling resistance) [m^{-1}],

TMP: transmembrane pressure [mbar]

η: viscosity of water to be filtered.

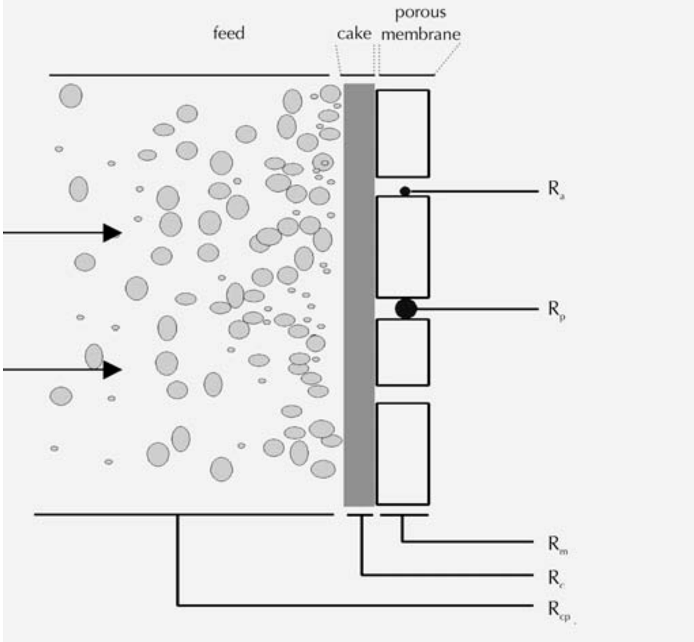


Figure 3-5: Various resistances hindering mass transfer through a UF/MF [63]

Ra = adsorption, Rp = pore blocking, Rm = initial membrane resistance, Rc = cake filtration, Rcp = concentration polarisation

3.2.2.2 Mechanisms of fouling

In general the mechanism of fouling is divided into three different types (see Figure 3-6).

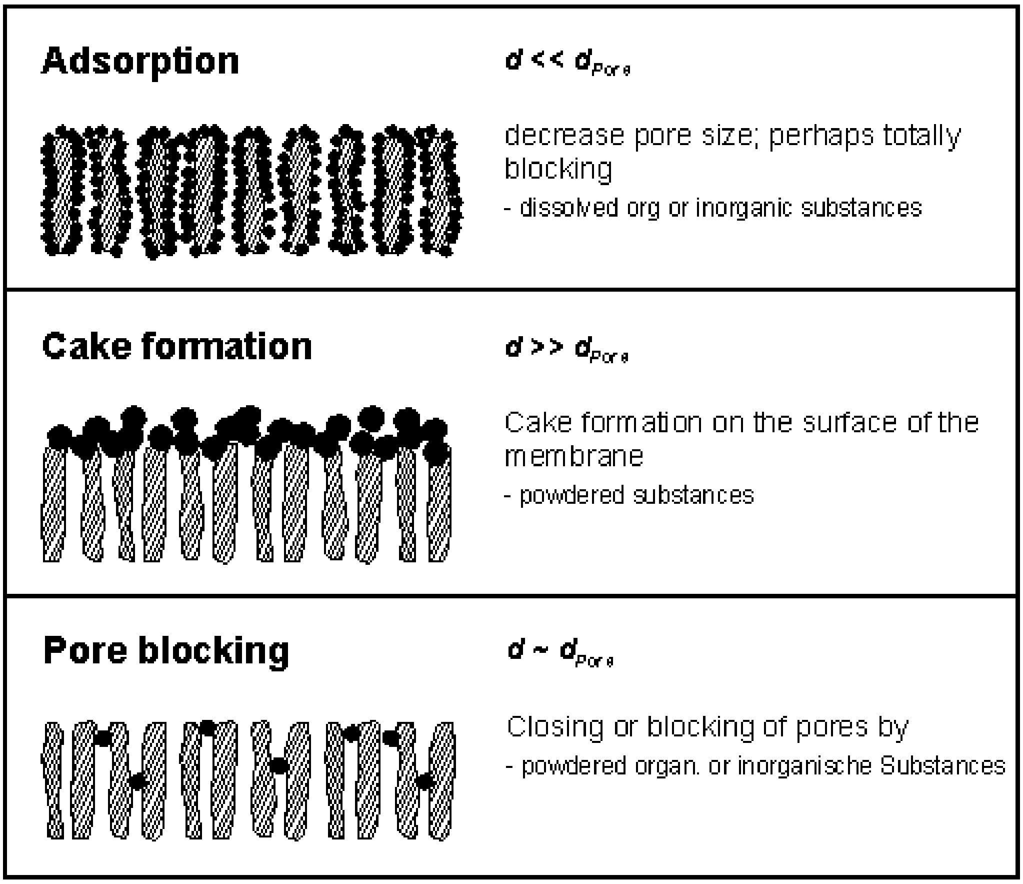


Figure 3-6: Different types of fouling [64]

Adsorption

Generally the adsorption is caused by small particles or dissolved substances, which have diameters much smaller than this one of the pores. Therefore they are adsorbed not only on the outer surface of the membrane, but also inside the pores.

Cake formation

During the filtration time on the surface of the membrane a filtration cake is formed by particles with sizes much bigger than these one of the pores. This cake layer builds up continuously during operation and because of the additional hydraulic resistance the flow correspondingly increases. This cake layer is also called “secondary membrane”, because particles can be rejected by this secondary membrane.

Pore blocking

The pore blocking is caused by particles with similar sizes as the pores. These particles fit very easy in the space inside the pores and block them totally.

3.2.2.3 Control of fouling

Although fouling cannot generally be avoided in membrane separations there are several methods, which can be used to control the amount of fouling or to correct the fouling, by cleaning. The methods can be summarised as, feed pre-treatment, adjustment of membrane properties, membrane cleaning and modification of operating conditions.

The methods for cleaning membranes after fouling has occurred are based on hydraulic, mechanical, chemical and electrical methods. The method(s) used depend upon the separation process and the configuration of the module. The hydraulic cleaning of the membrane is typically achieved with back flushing of the permeate through the membrane. The process is carried out by reversing the direction of flow of the permeate, usually for a short time, at a pressure which can be 1,5 times higher as the filtration pressure. The permeate is forced in the reverse direction through the membrane, therefore lifting off the cake layer and cleaning the membrane surface. The cake lifted would normally be resuspended by the tangential flow. As a result, the average permeate flux obtained per cycle is much higher (see Figure 3-7) than the long term flux when no reverse filtration is used.

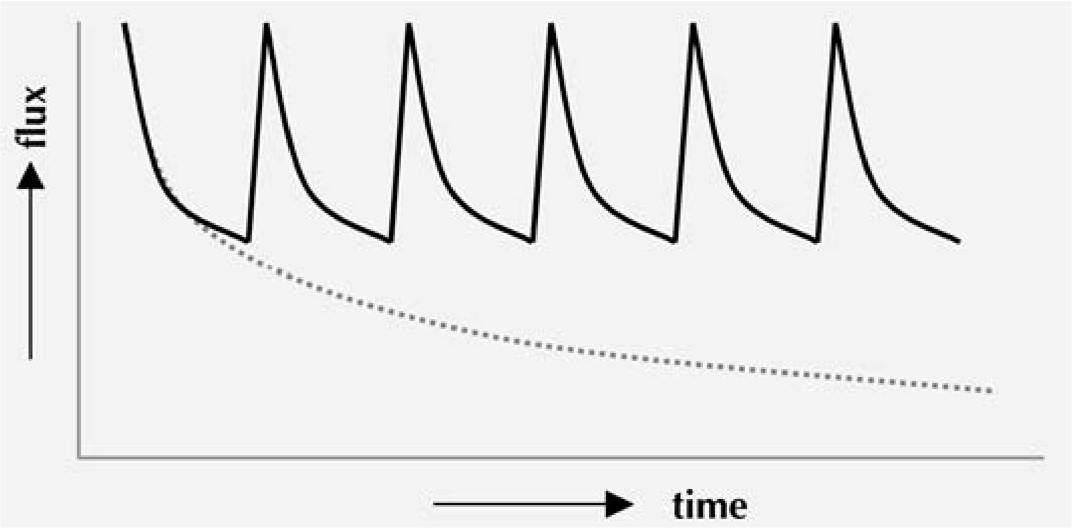


Figure 3-7: Typical change of the permeability using back flush in dependence of time [64]

Other methods to reduce fouling are reported in the literature. Some of them include: change in the surface interaction between particles; change in the hydrophobicity of the membrane; change in the hydrodynamics in the membrane module in order to increase the turbulence close to the membrane.

Controlling and preferably reducing the rate of fouling of micro- and ultrafiltration membranes is a major challenge.

3.3 *Flotation*

Flotation can be described as a gravity separation process in which gas bubbles attach to solid particles to cause the apparent density of the bubble-solid agglomerates to be less than that of the water, thereby allowing the agglomerate to float to the surface. Different methods of producing gas bubbles give rise to different types of flotation processes. These are electrolytic flotation, dispersed-air flotation, and dissolved-air flotation [65]-[72].

Electrolytic Flotation

The basis of electrolytic flotation, or electroflotation, is the generation of bubbles of hydrogen and oxygen in a dilute aqueous solution by passing a DC current between two electrodes [73]. The bubble size generated in electroflotation is very small, and the surface loading is therefore restricted to less than 4 m/h (13.3 ft/h). The application of electrolytic flotation has been restricted mainly to sludge thickening and small wastewater treatment plants in the range 10 to 20 m3/h (50,000 to 100,000 gpd).

Dispersed-Air Flotation

Two different dispersed-air flotation systems are used: foam flotation and froth flotation [74]. Dispersed-air flotation is generally unsuitable for water treatment as the bubble size tends to be large and either high turbulence or undesirable chemicals are used to produce the air bubbles required for flotation. However, the French Ozoflot system applies ozone-rich air for treating waters high in algae using diffusers to achieve dispersion.

Dissolved-Air Flotation.

In dissolved-air flotation, bubbles are produced by the reduction in pressure of a water stream saturated with air. The three main types of DAF are vacuum flotation [72], microflotation [75] and pressure flotation [73]. Of these three, pressure flotation is currently the most widely used. In pressure flotation, air is dissolved in water under pressure. Three basic pressure DAF processes can be used: full-flow, split-flow, and recycle-flow pressure flotation [72]. For water treatment applications requiring the removal of fragile floc, recycleflow pressure flotation is the most appropriate system. In this process, the whole influent flows either initially through the flocculation tank or directly to the flotation tank if separate flocculation is not required. Part of the clarified effluent is recycled, pressurized, and saturated with air. The pressurized recycle water is introduced to the flotation tank through a pressure-release device and is mixed with the flocculated water. In the pressure-release device, the pressure is reduced to atmospheric pressure, releasing the air in the form of fine bubbles (10 to 100 µm in diameter).The air bubbles attach themselves to the flocs, and the aggregates float to the surface. The floated material (the float) is removed from the surface, and the clarified water is taken from the bottom of the flotation tank.

To achieve efficient clarification by DAF, particles and natural color present in the water must be coagulated and flocculated effectively prior to the introduction of the microbubbles to form the bubble-floc aggregates.

Floatable bubble-floc agglomerates might form by any of three distinct mechanisms:

- entrapment of bubbles within a condensing network of floc particles,
- growth of bubbles from nuclei within the floc, and
- attachment of bubbles to floc during collision.

Work by Kitchener and Gochin (1981) [80] has shown that all three mechanisms can occur but that the principal mechanism in DAF for potable water treatment is the attachment mechanism.Their work also indicates that the organic content of surface waters is usually high enough to render the floc surface sufficiently hydrophobic for bubble attachment. Only in waters very low in dissolved organic matter will flotation efficiency be reduced.

3.4 *Hybrid processes*

3.4.1 Sorption/crossflow microfiltration [76]

The sorption/crossflow process, which is a membrane assisted affinity separation, is schematically depicted in Figure 3-8.

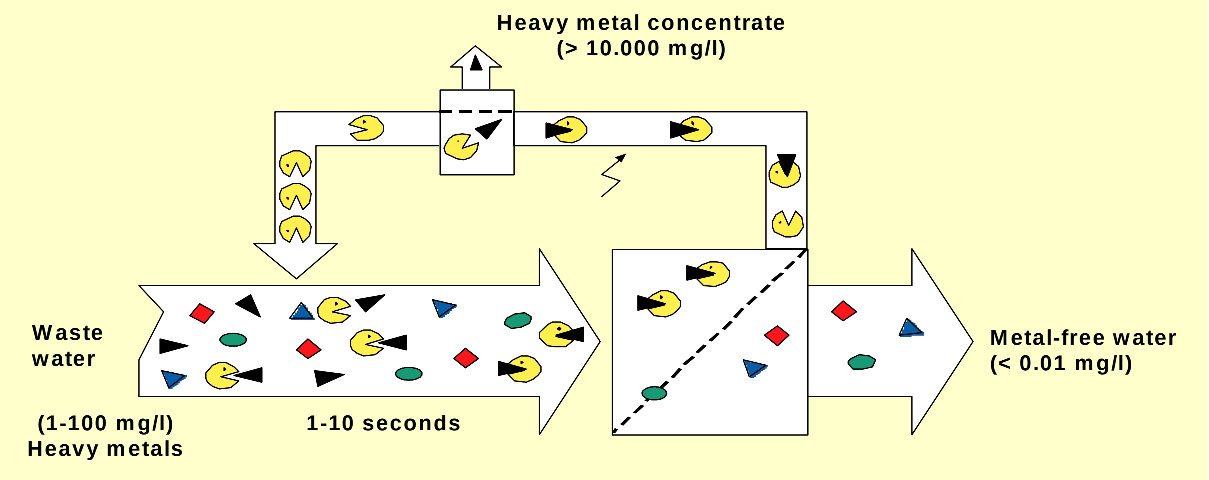


Figure 3-8: The basic idea of the sorption/crossflow microfiltration process [76]

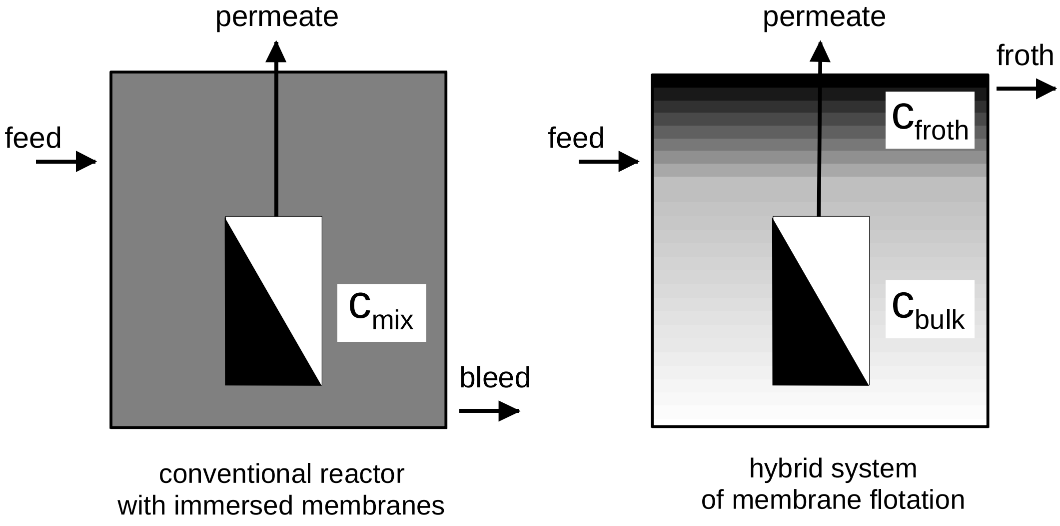
A bulky water effluent enters the process and the metals are bonded to selective bonding agents within seconds or a few minutes, while the bulky water leaves the process immediately through membrane filtration, clean of bonding agents and metals. At recovery rates of over 100 there is time to regenerate the bonding agents and harvest the metals. Moreover, a single bonding agents particle is used several times per hour in sharp contrast with for instance ion exchange columns resulting in much lower ion exchange-inventory for the process.

As a result of the added bonding agent and the high recovery rates aimed at, a high solid content is obtained and should be managed as a retentate. In that case state-of-the-art capillary membranes are unsuitable. These membranes have the active layer on the inside of the membrane. Filtration from inside to the outside is impossible since the solids would block the entrance of the capillary membranes soon. Filtration could be carried out from the outside to the inside, but then the pores of standard membranes would be blocked soon. State-of-the-membranes for the filtration of solids are tubular membranes. There disadvantages are that their specific membrane area is much lower than that of capillary membranes resulting in a large set-up and high energy consumption is necessary to provide high enough shear at the membrane surface. So for the sorption/crossflow process transversal flow membrane modules with capillary membranes with outside to inside filtration are used, resulting in relative low energy use and compact equipment (see Figure 4-2).

The advantages of this configuration is that capillary membranes can be used for a high specific area, outside-to-inside filtration leaves enough space at the retentate side for the high solid stream to flow without plugging or channelling, while the permeate can be collected readily. Furthermore, relatively little energy is used because turbulence only occurs at the membrane wall while the bulk of the fluid is at laminar flow [77], [78], [79]. Turbulence at the membrane wall is exactly where it should be, resulting in high shear, a thinner cake layer and a higher flux.

3.4.2 Sorption/ flotation and submerged microfiltration

In the hybrid process developed, specially designed submerged microfiltration modules (with multi-channel flat-sheet membranes) are integrated directly into the flotation reactor. Since most of the bonding agents have already been removed by flotation from the bulk solution and passed to the froth layer, the membranes are subjected to only a part of the initial concentration of the bonding agents. As a consequence the flux can be established at a high level even at a very low level of turbulence created in the hybrid flotation module. Thus energy requirements for membrane operation are minimised. Furthermore, the bonding agents to be regenerated or discharged are concentrated in the froth, whereas in a conventional process with immersed membranes, the concentration in the bleed is the same as in the reactor and thus limited. This is due to the fact that these conventional systems (e. g. with immersed hollow fibre membranes) consist of fully mixed reactors with a uniform concentration in the whole reactor volume [81]. The basic idea of the new hybrid process is illustrated in Figure 3-9.



$$c_{bulk} \ll [c_{mix} = c_{bleed}] \ll c_{froth}$$

Figure 3-9: The basic idea of the new hybrid process [82]

4 Methodology

4.1 *Characterisation of the bonding agents*

In this work two different bonding agents which were suitable for the of hybrid membrane processes for separation of heavy metals from water and wastewater were characterised and used for study of these processes in bench scale under real industrial conditions:

- the synthetic zeolithe P of INEOS Silicas Ltd.

The zeolite P (with max. Al^{3+}) has a pore diameter of 0.2 nm. The pore volume tends to be low (cca 0.3 cm^3 g^{-1}) and only small molecules will be able to enter the pore structure. Because of this totally uniform small pore size the zeolites are also used in molecular "sieving" (Figure 4-1).

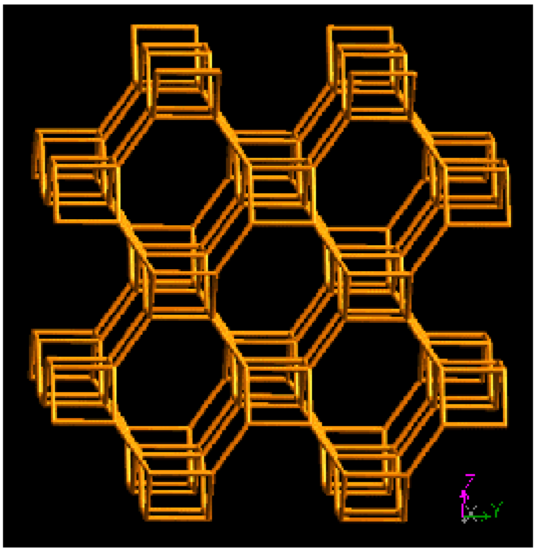


Figure 4-1: Structure of a zeolite P [48]

- the modified cation exchanger - named Lewatit TP 208 and the modified anion exchanger Lewatit MP 62

The commercial synthetic Lewatit TP 208 cation-exchange resin in sodium form and the commercial Lewatit MP62 were kindly obtained from LANXESS. The charcteristics of this commercial resins are given in Table 4-1 resp. Table 4-2.

Table 4-1: Characteristic of the commercial Lewatit TP 208

Characteristics	**Value**
Physical characteristics	
Appearance	beige−grey, opaque
Ionic forms as shipped	Na+
Mean particle size (mm) (>90%)	0.55±0.05
Chemical characteristics	
Structure	Macroporous
Matrix	crosslinked−polystyrene
Functional group	iminodiacetic acid
pH range	0−14
Total exchange capacity (eq/L)	2,9
Bulk density (g/L)	740

Table 4-2: Characteristic of the commercial Lewatit MP 62

Characteristics	**Value**
Physical characteristics	
Appearance	beige−grey, opaque
Ionic forms as shipped	free base
Mean particle size (mm) (>90%)	0.47±0.06
Chemical characteristics	
Structure	Macroporous
Matrix	crosslinked−polystyrene
Functional group	tert. Amin
pH range	0−14
Total exchange capacity (eq/L)	1,7
Bulk density (g/L)	670

The commercial resin was crashed and siewed. Finally a fraction was obtained with a diameter of 40–70 µm. These modified resins were used for the experiments.

The treatment and characterisation of the BAs were conducted as follows: A certain amount of the powdered bonding agent was dried in a vacuum – drying cabinet at 50°C for 24h under vacuum conditions and then stored in an exicator.

500 mg/l of Mg^{2+} in the form of $Mg(NO_3)_2$ and 500 mg/l of Na^+ in the form of $NaNO_3$ added to 250 ml of the model solution which was used in the experiments to determine the kinetics of heavy metal bonding on BA. If necessary the pH value of the solution was adjusted by NaOH or HNO_3 and a certain amount of bonding agent was added. Subsequently the slurry was placed in a shaker (frequency approximately 400 min^{-1}). Samples of $1cm^3$ were taken for analysis at given time intervals. Each sample was diluted with a proper amount of fully desalinated water and then routed through a membrane filter (milipore with 0.45µm pore diameter). Immediately after filtration all the samples were subjected to heavy metal photometric analysis using cuvette tests (Dr. Lange – Photometer LASA 100).

During the bonding capacity measurements, the metal concentration in the solution was fixed. Different amounts of bonding agent was added to the solution and left for 24h until a steady state was established.

The pH stability of the zeolite was determined via contact with solutions of different initial pH values. Since the structure of the bonding agent comprises Al^{3+} ions, these ions are released into the solution when the zeolite structure is altered. The content of Al^{3+} in the corresponding slurry was used for indirect BA stability measurement.

4.2 *Study of the hybrid process consisting of sorption and crossflow microfiltration in bench-scale experiments-*

4.2.1 Materials

The bonding agent used in the investigations is a weak-base anion exchange resin MP 62 with a particle diameter of 40-60 µm .

Heavy metal concentrations were analysed using ICP – Optical Emission Spectroscopy.

The membrane module (Figure 4-2), which is used with the test unit, consists of a cylindrical part in the shape of a transparent tube, in which the membrane is put. It is made of PVC and has the following sizes: diameter 20mm and L=75cm. The tube is provided with two especially detached side hose connections and by means of them the feed and retentate solutions are transported from the module. The feed solution comes into the module through one of these two connections.

The characteristics of the polymeric hollowfibre membranes are given in Table 4-3. The filtration direction of the hollow fibre membranes is from outside to inside the fibres. So a mechanically blocking of the fibres could be prevented.

Table 4-3: Characteristics of the polymeric hollow fibre membranes used in the experiments

Type	hollow fibre membrane
Material	Polypropylen
Mean pore size	0.1 µm
Permeability (pure water)	300 l m^{-2} h^{-1} bar^{-1}
Membrane area	0,75 m^2
Transmembrane pressure	0,15 bar

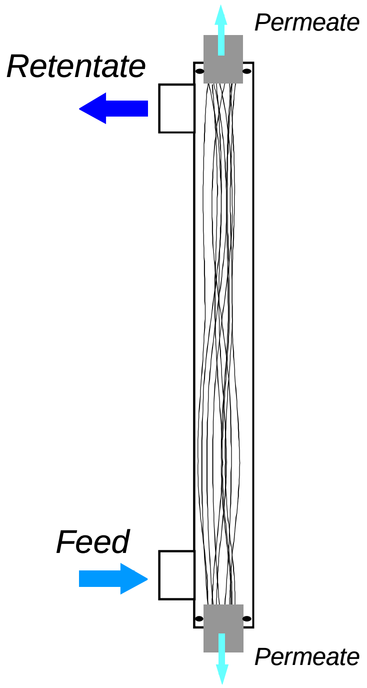


Figure 4-2: Schematic representation of a hollow fibre membrane module

4.2.2 Bench-scale plant and procedure

A simplified flow scheme of the plant used for the investigations is presented in Figure 4-3. The unit consists of: feed tank with volume 50l, which contains the feed solution to be filtrated ; permeate tank - capacity 20l, in this tank the purified solution after filtration, called permeate is gathered; tank for solution for disinfection..

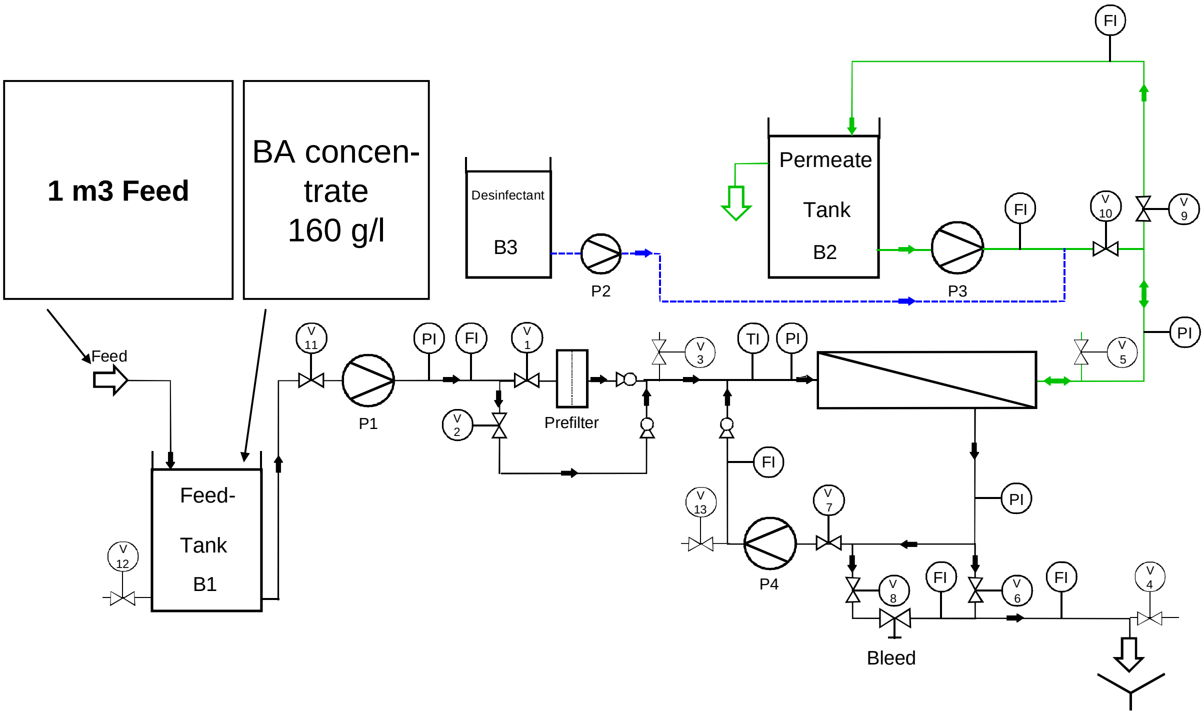


Figure 4-3: **Simplified flow scheme of the bench-scale plant used for the investigations**

Pump P1 transports the feed solution from the feed tank to the module, where the filtration is carried out. The cross-flow is carried out through pump P4. By means of pump P3 the backflush is implemented - the permeate solution is transported from the permeate tank to the module. The cross-flow is carried out through pump P4. The yield was

For the bench-scale tests with the groundwater two additional tanks were used - one with volume 1 m3 for the groundwater and the second one with 30l for preparation of the suspension of the IX (IX concentration - 160g/l). Each of the tanks is provided with a pump to regulate the quantity of the respective solution. Subsequently the both solutions are mixed in the feed tank B1 (final BA concentration 0,3 g/l). In this way the filtration is continuous and this allows running of the unit for a longer period of time.

4.3 *Study of the hybrid process consisting of sorption, submerged microfiltration and flotation in bench scale experiments*

4.3.1 Materials

The concentrations of the bonding agent were measured gravimetrically in the high concentration range (froth) and via turbidity measurement in the low concentration range (bulk solution). In the latter case, the correlation between zeolite concentration and turbidity followed a linear function up to 1.0 g l-1 solid concentration. Heavy metal concentrations were analysed using atomic adsorption spectroscopy.

The cationic surfactant hexadecyl-trimethyl-ammonium bromide (CTABr, Merck, analytical grade) was used as a collector during flotation experiments. At a pH of 8-10, which was used in the experiments (see chapter “results and discussion”) the used bonding agents (synthetic zeolite P, modified Lewatit TP208) has a negative surface charge, therefore the collector binds with its cationic ammonia group to the bonding agents, whereas the hydrophobic end of the molecule is able to be trapped by the bubbles, making the bonding agent rise to the surface. CTABr was fed as an ethanolic solution with a final ethanol concentration in the hybrid cell of 0.17 vol-%. In most runs, 20 mg CTABr per 1 g bonding agent (c(CTABr) = 10 mg g-1) were used.

Ceramic multi-channel flat-sheet membranes were used in the process, supplied by the Hermsdorfer Institut für Technische Keramik, HITK (Thuringia, Germany). The characteristics of the membrane type used in the investigations are presented in Table 4-4.

Table 4-4: Characteristics of the ceramic membranes used in the experiments

Type	Multi-channel flat-sheet
Geometry	100 mm x 100 mm x 6 mm
Mean pore size	0.28 µm
Area per membrane	0.018 m²
No. of membranes operated in hybrid reactor	1 - 3
Permeability (pure water)	3.000 $l\ m^{-2}\ h^{-1}\ bar^{-1}$
Membrane resistance R_M	$1.2 \cdot 10^{11}\ m^{-1}$

Modules were prepared by sealing these at one end and providing a permeate collector at the other end. A schematic representation of this module type and of the hybrid reactor is shown in Figure 4-4.

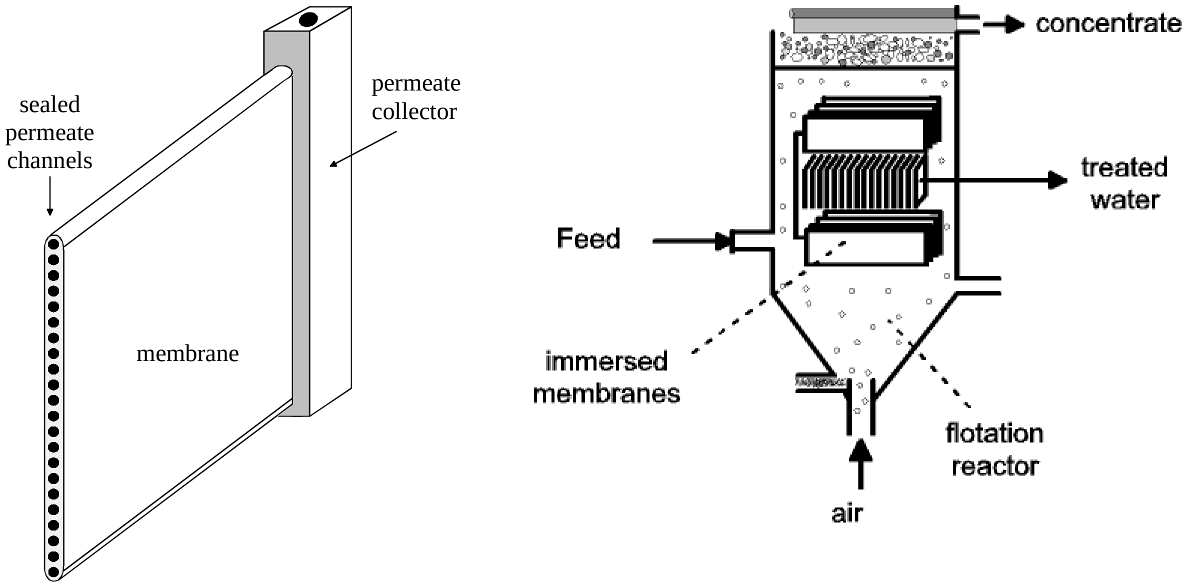


Figure 4-4: left: Schematic representation of a module of the ceramic multi-chanel flat-sheet membrane used in the tests; right: the hybrid flotation reactor with submerged ceramic membranes

4.3.2 Bench-scale plant and procedure

A simplified flow scheme of the plant used for the investigations is presented in Figure 4-5. The main part of the plant is the hybrid reactor (net volume 2.2 l) where flotation takes place and in which the membrane modules are installed. The whole bottom of the reactor is made of a porous ceramic plate (mean pore size 1 µm), through which the air was introduced. This gave a uniform bubble distribution across the whole cross-section. Resulting from preliminary investigations [40] the air superficial velocity (ug) was kept at 0.33 cm s-1.

The solution to be treated was prepared in a feed tank (150 l) at least 3 hours before starting the experiments to give sufficient wetting time. The resulting pH ranged from 9 to 10 and in cases in which other values were needed, the pH was adjusted by hydrochloric acid to the required value. From the feed tank the solution entered the hybrid reactor via a small feed regulator chamber.

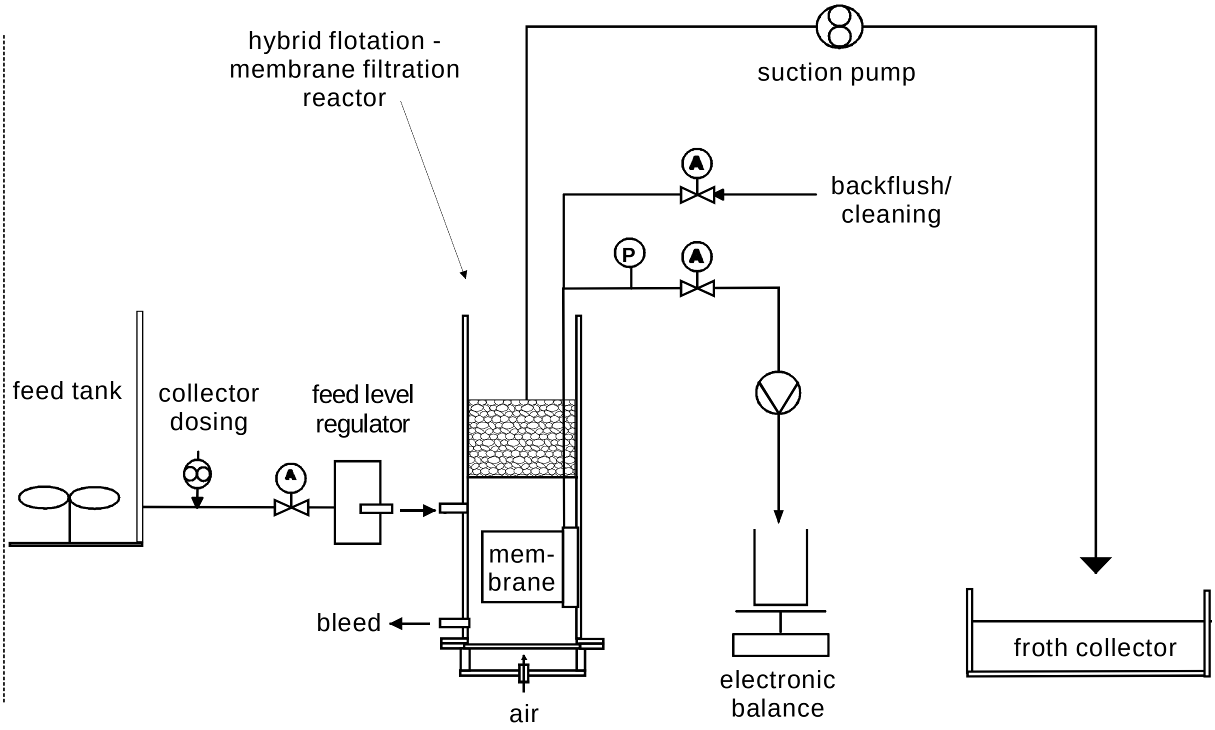


Figure 4-5: Schematic representation of a module of the ceramic multi-chanel flat-sheet membrane used in the tests

Collector was dosed in-line into the feed pipe and mixed with the zeolite solution, guaranteeing a conditioning time greater than 30 minutes. Permeate was withdrawn from the membranes via a suction pump, the respective suction pressure was read via electronic pressure transducer. The permeate flow rate was calculated from permeate weight that was measured via electronic balance. When backflushing of the membranes was applied for fouling control, time intervals were controlled via automated valves. Froth was withdrawn from the top via overflow or suction pump. All relevant process data were read continuously by PC. As in industrial applications, the wastewater flow to be treated is a pre-set value, the plant was operated at constant flux.

5 Results and discussion

5.1 *Study of suitable bonding agents*

5.1.1 Introduction

In order to realise the new hybrid processes presented in chapter 2, one of the most important tasks is to find a suitable bonding agent. A adequate bonding agent has to have the following characteristics:

- Fast sorption dynamics

The sorption dynamic descripes the relation between the residual metal concentration and the contact time. A fast removal of the heavy metals from the water will lead to smaller mixing reactors and so to smaller units at all.

- High sorption equilibrium

The quantity of the heavy metals sorbed by the bonding agent should be as high as possible. The higher the capacity the smaller is the needed amount of bonding agent to remove a several quantity of heavy metals. The use of less amount of bonding agent will lead to a decrease of the stress to the following separation step

- High selectivity

The selectivity does not mean only the selectivity of one heavy metal against another, but also the selectivity of heavy metals against accompanying ions as Mg^{2+}, Ca^{2+}, SO_4^{2-}, etc.

- High stability

The stability of the bonding agent (mechanical stability, pH-stability) will allow to use the bonding agent in a wider application area.

- Possibility of regeneration

The option of regeneration will be an outstanding contribution to the protection of the environment, because the re-use of the bonding agent will decrease the consumption of resources. But the regeneration could also be an important factor from the economic point of view.

In order to obtain information on commercially available bonding agents (e.g. commercial ion exchanger), the binding kinetics of these agents were investigated in preliminary experiments. The findings showed that none of these agents had sufficiently fast kinetics (Figure 5-1). One requirement of the new process is that approximately 90% of the metal ions must be removed within roughly ten minutes.

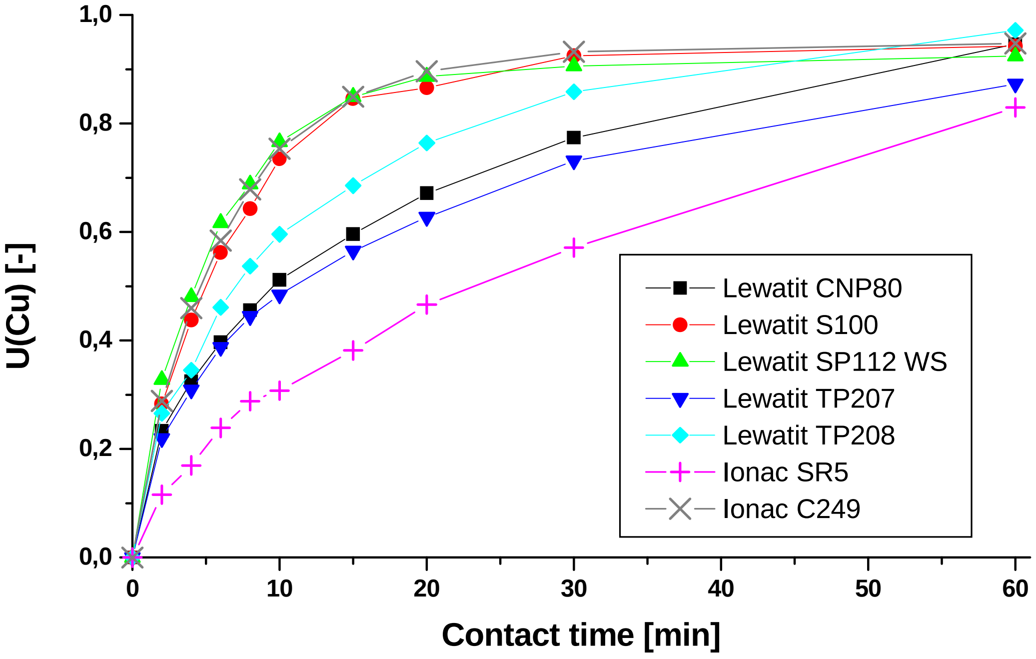


Figure 5-1: U(Cu) versus contact time ; Initial Cu-concentration ~ 560mg/l ; 8 g Ion-exchanger (dry mass)/l solution

The conventional ion exchanger removed only 20% to 75% of the initial copper concentration within 15 min.

This velocity of heavy metal removal was not sufficient for the suggested processes. In cooperation with the ion exchange resin producer new bonding agent were developed and existing resins modificated.

The discussion of these bonding agents can be found in the following chapters.

5.1.2 Synthetic zeolite P ($Na^+_{48}(AlO_2^-)_{48}(SiO_2)_{48}\cdot xH_2O$) (INEOS Silicas Ltd., 2001)

5.1.2.1 Properties of the synthetic zeolite P

In order to observe the surface charge of the synthetic zeolite at different pH values the zeta potential was measured (Figure 5-2). At pH values higher than 6 the zeta potential is negative. For pH values lower than 6 the zeta potential is positive. Than the oxides on the surface start to be protonated. These results are important to select collectors for the flotation of the zeolite.

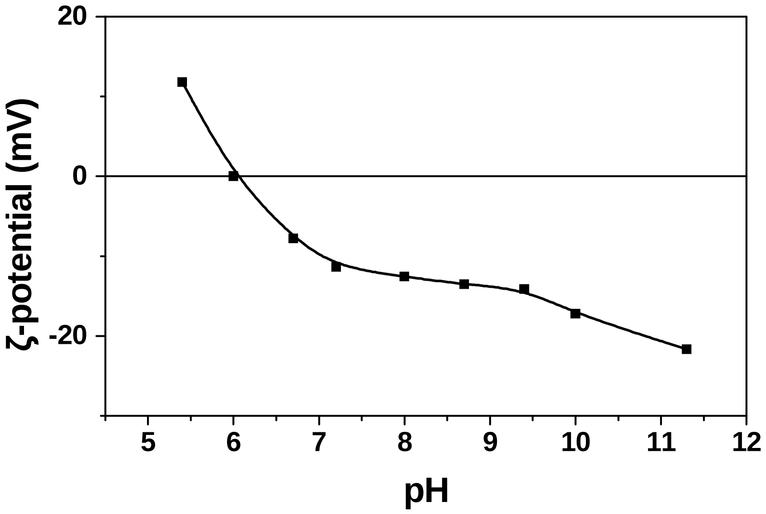


Figure 5-2: Zeta potential of the synthetic zeolite in dependence of the pH

According the information of the producer the particle size of this synthitic zeolite P is around 2 µm.

In the following REM pictures (Figure 5-3) the real size of the particles can be estimated between 10 micrometers to some hundred micrometers. This seeming difference is easy to explain:

- The information of the producer is valid for dry phase
- The REM measurements were performed in wet phase. Some particles are agglomerated.

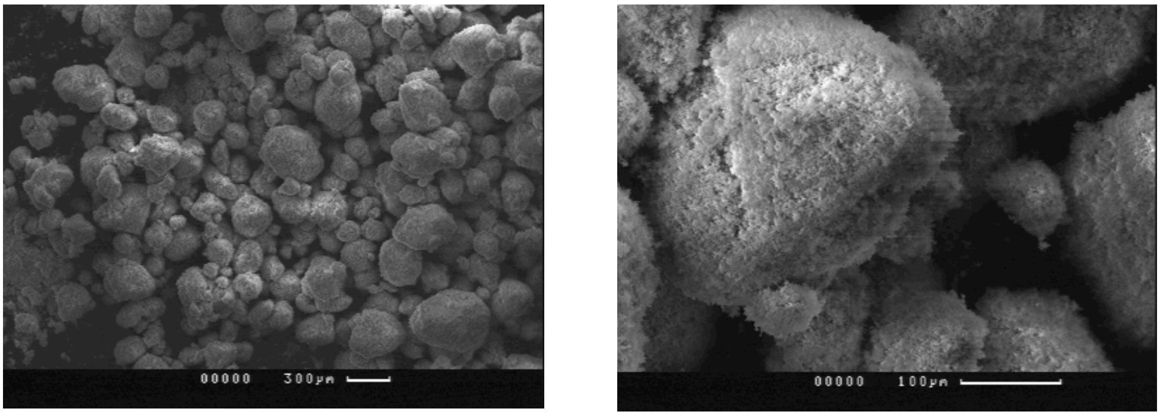


Figure 5-3: Raster electron microscopy (REM) of the synthetic zeolite

Stability of the synthetic zeolite P

pH-stability

The pH stability of the bonding agent was determined via contact with solutions of different initial pH value. Since the structure of the bonding agent comprises Al^{3+} ions, these ions are released into the solution when the zeolite structure is altered. The content of Al^{3+} in the corresponding slurry was used for indirect BA stability measurement (Table 5-1).

Table 5-1: **pH Stability of the synthetic zeolite P**

pH of the BA slurry	Al concentration/(mg dm^{-3}) in the BA slurry	dissolved BA /%
2	830	100
3	830	100
4.3	771	93
5.2	2.1	< 0.5
6.2	2.2	< 0.5
7.1	1.7	< 0.5

The synthetic zeolite is stable at pH values higher than 5. Below a pH of 5 this bonding agent will be dissolved.

In addition it can be said that the lower the pH the faster the dissolving took place. At a pH<3 the dissolving only took some minutes.

Mechanically stability

Because of the strong hydrodynamic conditions for the bonding agents while a e.g. cross-flow microfiltration they have to be also mechanically stable.

In Figure 5-4 is shown a particle size distribution of the synthetic zeolite before and after a 48h cross flow filtration.

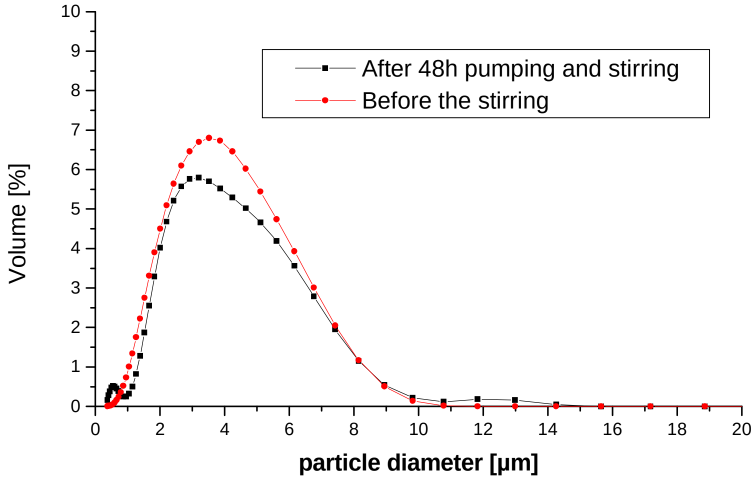


Figure 5-4: Particle size distribution before and after filtration

As the figure shows there is no significant change in the particle size distribution. The average particle size is for both cases between 3-4 µm.

5.1.2.2 Investigation of the sorption mechanisms of the synthetic zeolite P

The synthetic zeolite put into dematerialized water proved to release significant amounts of Sodium, Aluminium and Siliciumdioxide as well as to raise solution pH, as shown on Figure 5-5.

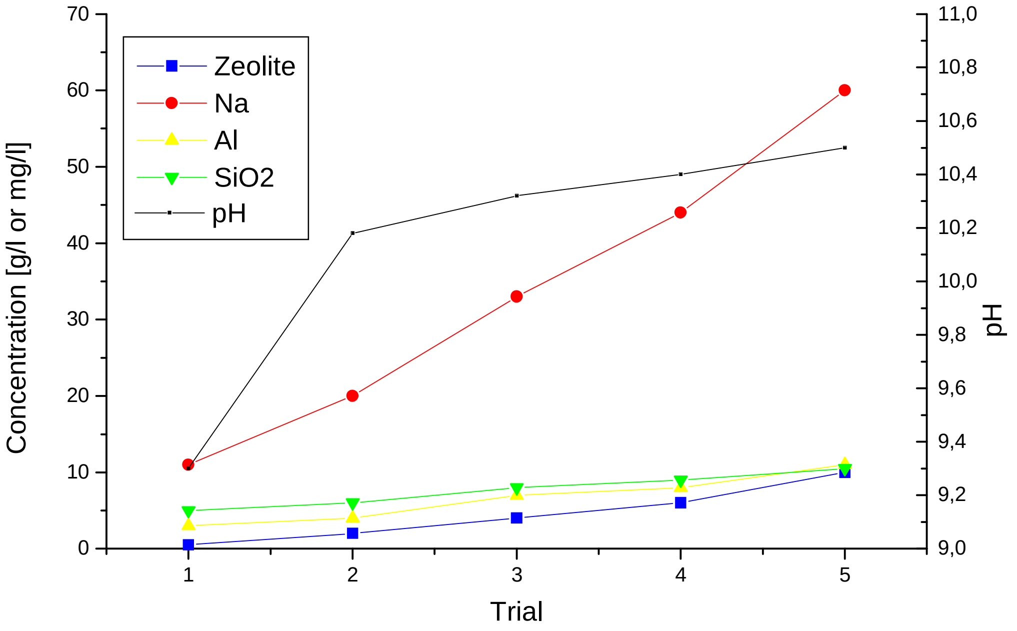


Figure 5-5: Released ions from the zeolite

A comparison of the balance of the cations and identified anions shows a lack of anions (Figure 5-6). This comparison is based on the following hypothesis:

- Na^+ and H^+ are the only cationic species;
- SiO_2 is presumed to be in the SiO_3^{2-} form
- Al in the AlO_2^- form;
- OH^- is also taken into account, according to pH.

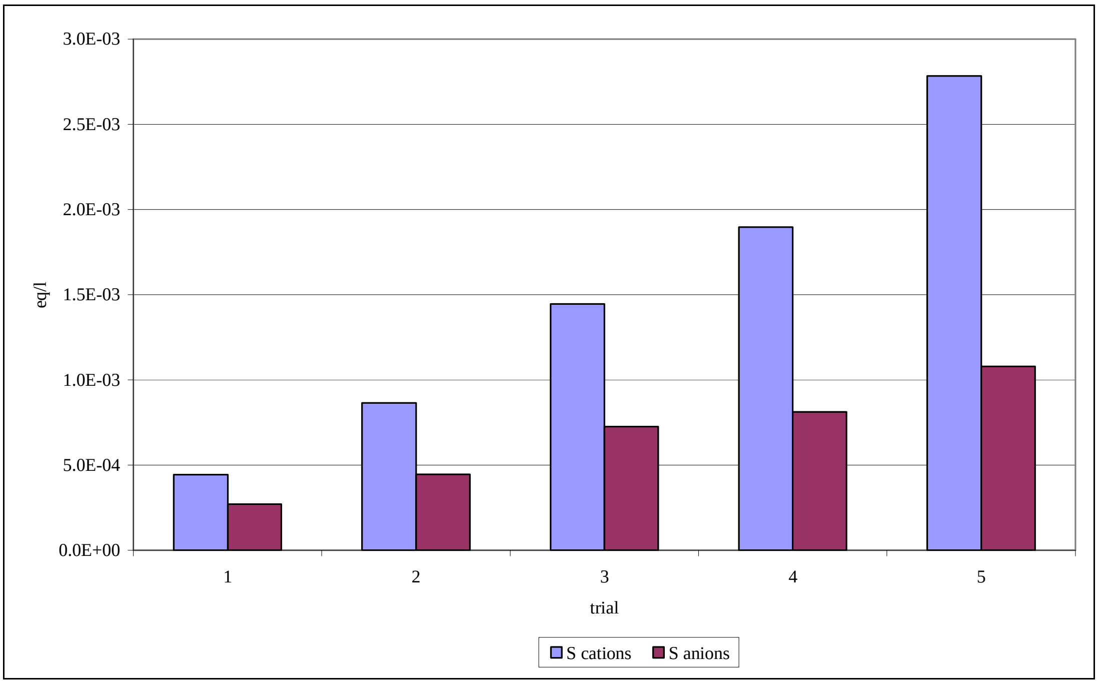


Figure 5-6: Balance of identified cations and anions released of the synthetic zeolite

From these results it is obviously that another anionic species must be present.

According to the way of production of most synthetic zeolite this species seems to be carbonate. Carbonate can be also responsible for the raise of pH which is not proportional to the amount of zeolite, and thus of dissolved NaOH, as shown on Figure 5-7.

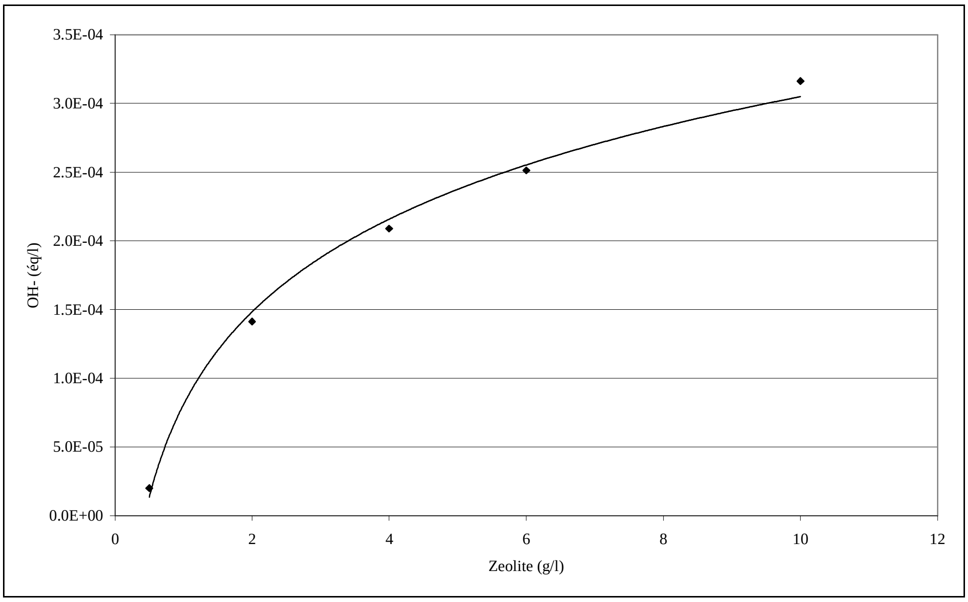


Figure 5-7: Concentration of hydroxide versus concentration of zeolite

Total concentration of the carbonic acid and its repartition (carbonate and hydrogencarbonat) can be estimated from pH value (neglecting in rough approach other parameters such as ionic strength) [83]. (Bi)carbonates can then balance some of the excess cations (Na^+) previously identified, as shown in Table 5-2 and Figure 5-8.

Table 5-2: Sodium concentrations in dependence of the zeolite concentration

Zeolite	g/l	2	4	6	10
Total Na (measured)	eq/l	$8.66\ 10^{-4}$	$1.44\ 10^{-3}$	$1.90\ 10^{-3}$	$2.78\ 10^{-3}$
Na associated to OH^-	eq/l	$1.41\ 10^{-4}$	$2.09\ 10^{-4}$	$2.51\ 10^{-4}$	$3.16\ 10^{-4}$
Na associated to AlO_2^-	eq/l	$1.29\ 10^{-4}$	$2.38\ 10^{-4}$	$2.51\ 10^{-4}$	$4.10\ 10^{-4}$
Na associated to $SiO_3^=$	eq/l	$1.75\ 10^{-4}$	$2.79\ 10^{-4}$	$3.10\ 10^{-4}$	$3.53\ 10^{-4}$
Na associated to $CO_3^=$	eq/l	$2.26\ 10^{-4}$	$4.95\ 10^{-4}$	$7.15\ 10^{-4}$	$1.19\ 10^{-3}$
Na associated to HCO_3^-	eq/l	$1.43\ 10^{-4}$	$2.11\ 10^{-4}$	$2.54\ 10^{-4}$	$3.27\ 10^{-4}$
Total Na (calculated)	eq/l	$8.14\ 10^{-4}$	$1.43\ 10^{-3}$	$1.78\ 10^{-3}$	$2.59\ 10^{-3}$
% of “explained” Na	%	94.1	99.1	93.9	93.1

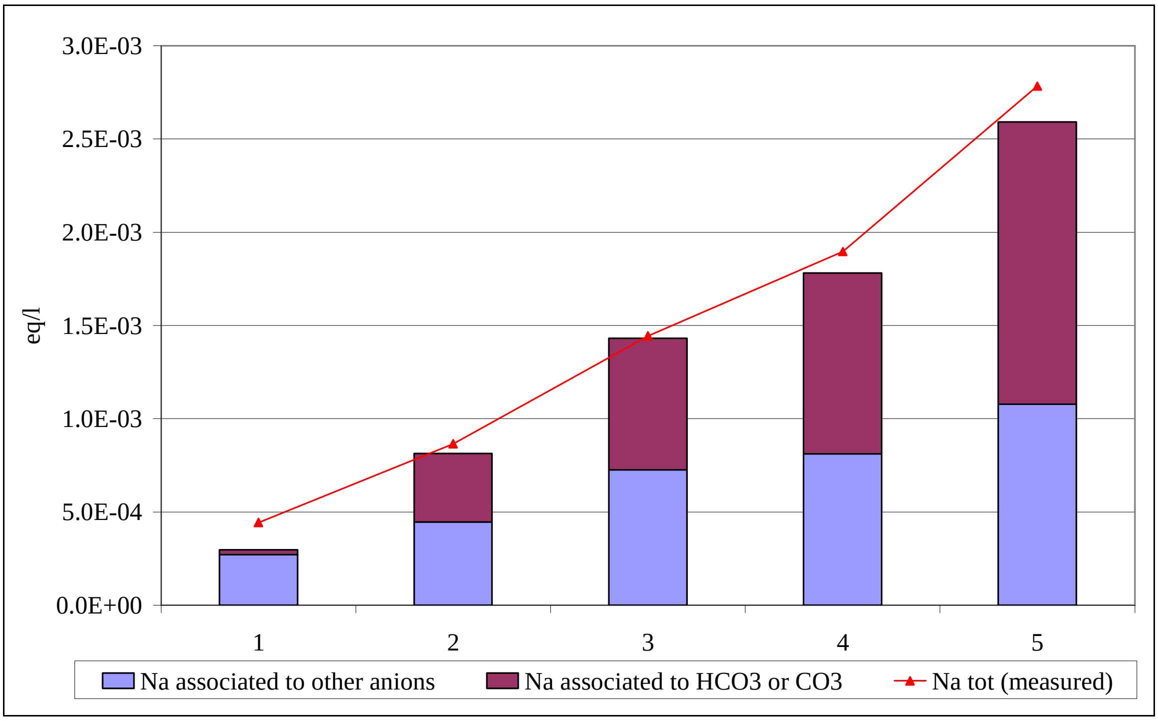


Figure 5-8: Measured and “explained” sodium

Obviously the zeolite is not a pure product. It must contain a lot of additional sodium-carbonate.

Cationic exchange capacity (CEC)

CEC of this zeolite was told by supplier to be of 6 meq/g.

The CEC was measured by ion exchange out of a Ca^{2+} solution with two “kinds” of this zeolite. (One raw zeolite and one treated zeolite). The treatment consists in rinsing with sodiumchlorid solution and then thoroughly with deionized water; it ensures that zeolite’s active sites are saturated with sodium. By this treatment the carbonate impurity was removed and so a precipitation of $CaCO_3$ could be hindered. So the calcium could be removed by ion exchange, which can be calculated than indirectly by the amount of the released sodium. One calcium-ion is replaced by two sodium ions in the liquid phase.

In these conditions, treated zeolite shows an average CEC of 5.39 meq/g, which is a bit lower then announced.

Table 5-3 shows the results of the experiments conducted with treated zeolite (NaZ 1 and 2) and raw zeolite (Z1 and 2).

Table 5-3: Determination of CEC with $CaCl_2$ solution $[Ca^{++}]$ = 7108 mg/l;

Trial	Ca_{eq} (mg/l)	Na_{eq} (mg/l)	Δ Ca meq/l	Δ Na meq/l	CEC meq/gzeolite
Z1 (raw)	5664	1489	72.06	65.02	6.005
Z1Na (treated)	5846	1330	62.98	57.85	5.248
Z2 (raw)	5698	1449	70.36	63.28	5.864
Z2Na (treated)	5780	1325	66.27	57.63	5.523

Δ Ca [meq/l] is a little bit higher than the release Δ Na [meq/l]. This can be explained by additional adsorption of Ca on the surface of the zeolite.

Copper-sodium balance

On basis of ionic exchange equation, apparition of Na^+ in solution should be balanced by equivalent disappearance of Cu^{2+}. Tests have been conducted with raw and treated zeolite. In the first case, blank experiment is conducted to take into account the amount of sodium that might be present as impurity in the zeolite sample. The results are shown in Table 5-4.

Table 5-4: Raw Zeolite

Zeolite	c_0(Cu)	c_{eq}(Cu)	c_{eq}(Na)[1]	Δc(Cu)	Δc(Na)	Δc(Na)/Δc(Cu)	q_{eq}(Cu)
g/l	mg/l	mg/l	mg/l	meq/l	meq/l	%	meq/g
0.25	100	42	39.9	1.825	1.736	95.1	7.2
0.5	100	0.6	61.2	3.128	2.662	85.1	6.3
0.25	200	110	48.2	2.833	2.097	74.0	11.3
0.5	200	55.6	92.1	4.545	4.006	88.1	9.1
0.25	400	280	47.4	3.777	2.062	54.6	15.1
0.5	400	180	109	6.924	4.741	68.5	13.8

In all these experiments with the raw zeolite the sorption density is significant higher than the cation exchange capacity which is told from the producer (6 meq/g). Δc(Cu) is almost always significant higher than Δc(Na). The sorption of copper obviously follow another elimination path in addition to ion exchange, carbonate precipitation or and adsorption of Cu on the surface of the zeolite.

By washing of the zeolite the removing of copper by carbonate precipitation should be avoided. The results are shown in Table 5-5.

Table 5-5 Treated zeolite

Zeolite	c_0(Cu)	c_{eq}(Cu)	c_{eq}(Na)	Δc(Cu)	Δc(Na)	Δc(Na)/Δc(Cu)	q_{eq}(Cu)
g/l	mg/l	mg/l	mg/l	meq/l	meq/l	%	meq/g
0.25	100	80.9	15.3	0.601	0.666	110.7	2.4
0.5	100	53.8	41.6	1.454	1.809	124.4	2.9
0.25	200	176	13.5	0.755	0.587	77.7	3.0
0.5	200	112	57.5	2.770	2.501	90.3	5.5
0.25	400	350	20.4	1.574	0.887	56.4	6.3
0.5	400	247	80.9	4.815	3.519	73.1	9.6

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[1] Na in blank (6.5 or 9.9 mg/l respectively) has been subtracted

The sorption density of copper using the washed zeolite is much lower than in case of the raw zeolite. By washing with sodiumchlorid solution the carbonate were removed from the zeolite and a coppercarbonate precipitation could be hindered.

As shown on Figure 5-9 raw and treated zeolite give appreciably different results. It looks like previous treatment lowers sorption capacity. In fact, thorough rinsing after treatment might eliminate carbonates present as impurity in zeolite and thus decrease precipitation phenomenon.

In most of the cases, Δ Cu and Δ Na are well above Cationic Exchange Capacity of the zeolite of 5,2 to 6 meq/g (see Table 5-3).

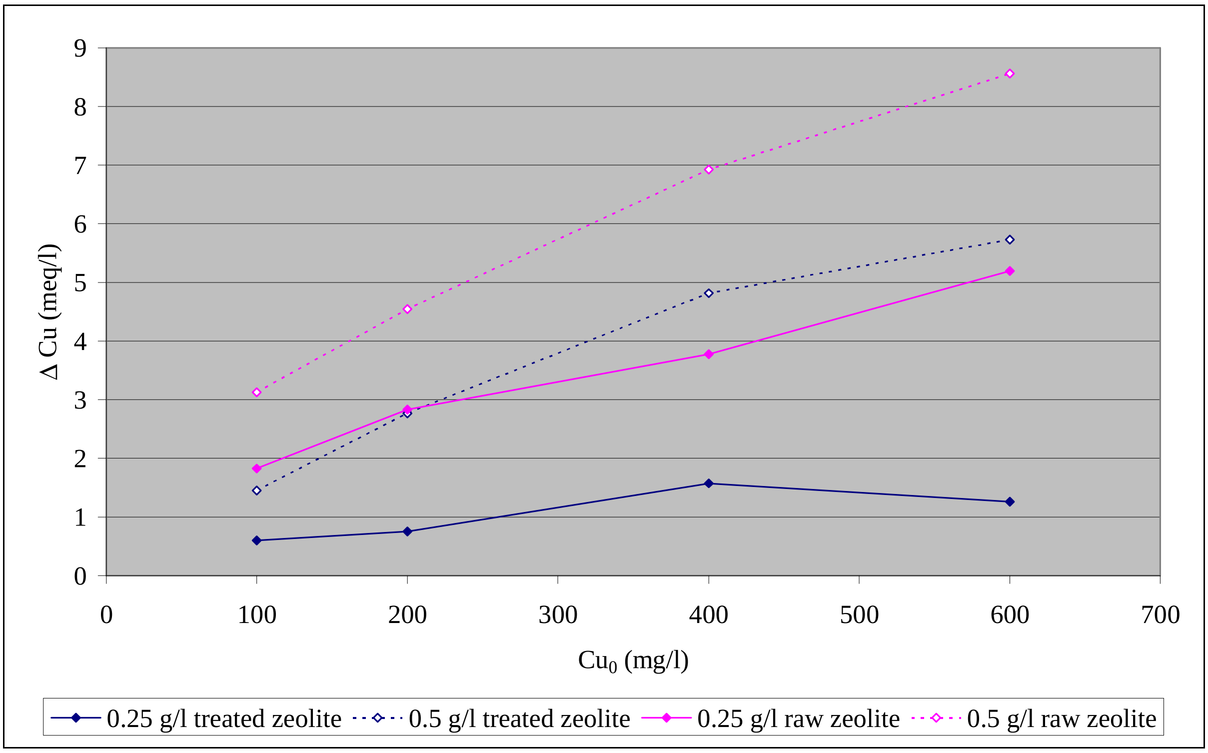

Figure 5-9: Comparision between washed zeolite and raw zeolite

Precipitation (Surface precipitation)

According to anionic species present in zeolite and pH, Cu precipitation might be possible either as $CuCO_3$ (pK = 9.6) and/or $Cu(OH)_2$ (pK = 19.7). Figure 5-10 shows [Cu] in equilibrium with OH- or with $[CO_3^{2-}]$tot = 0.1 mmol/l as function of pH of the solution.

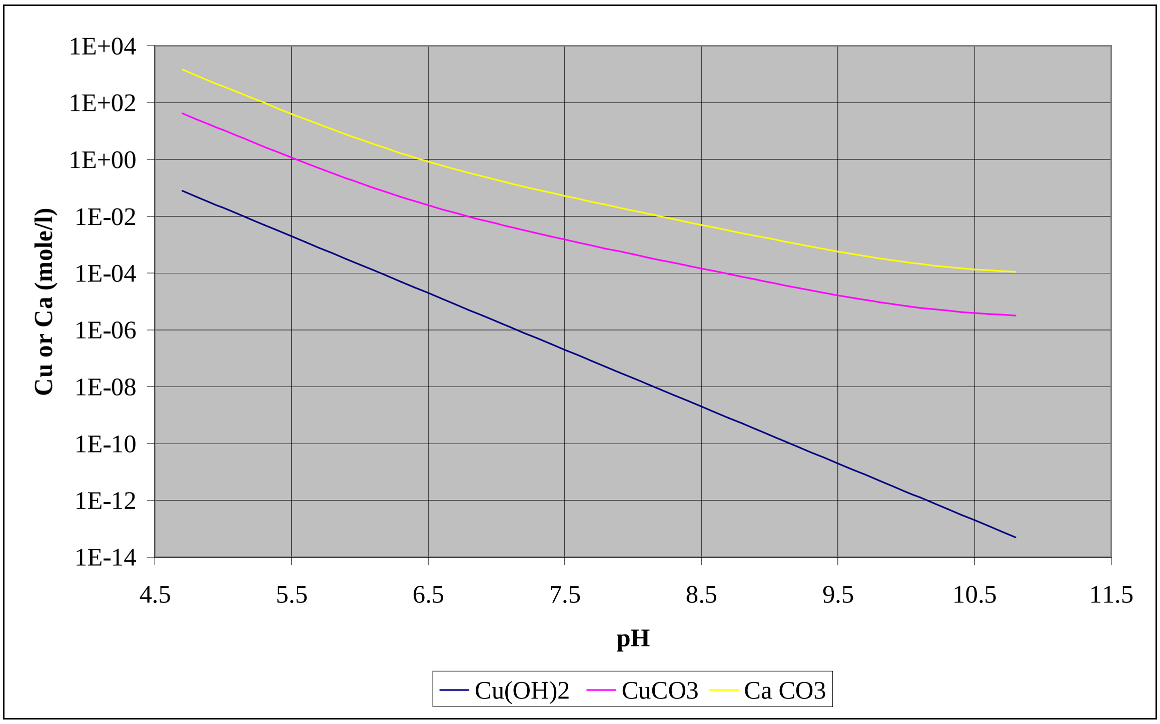

Figure 5-10: Effect of pH on $Cu(OH)_2$, $CuCO_3$ and $CaCO_3$ precipitation

Conclusions to the sorption mechanisms of the synthetic zeolite P

The zeolite is not a pure, and probably not homogeneous, product: main impurity is carbonate (as CO_3^{2-} or HCO_3^- associated with Na^+);

Me^{++}/Na^+ ionic exchange is not the only phenomenon in addition to adsorption standing for heavy metal elimination.

Because of the alkaline tendancy of zeolite, several precipitation reaction are to be taken into account at observed high pH (namely $Me(OH)_2$ and $MeCO_3$). This seems in agreement with Alvarez-Ayuso [49].

By accepting that the sorption mechanism consists only of

- ion exchange
- adsorption
- precipitation

and by taking into account the results showing in Table 5-4 and Table 5-5 the amount of copper eliminated by the different processes can be estimated as shown in Figure 5-11.

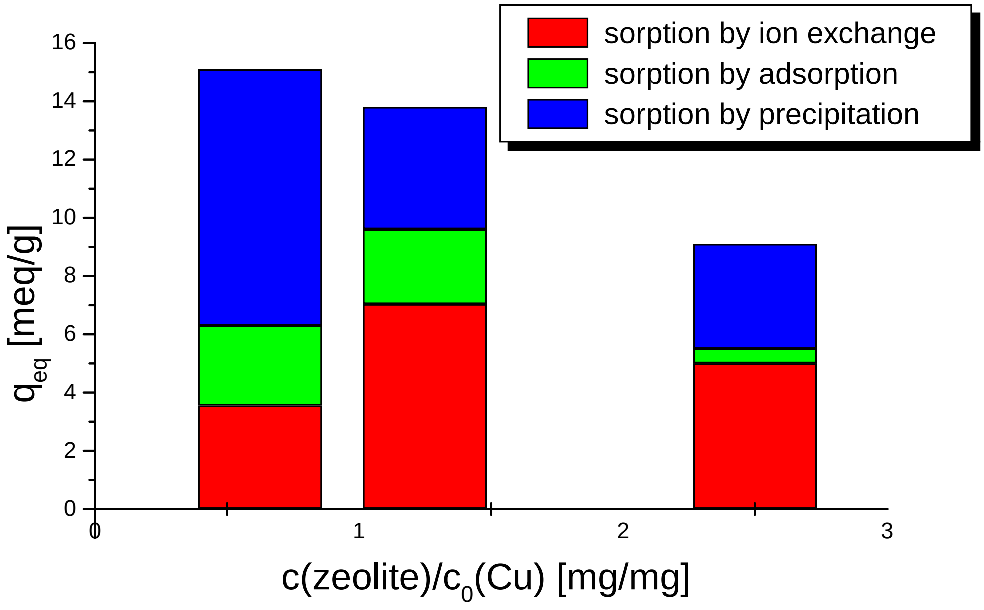

Figure 5-11: Estimation of the different sorption mechanisms

The ion exchange is determinated by the amount of sodium which is released in the experiments with the washed zeolite. Two sodium ions were replaced by one copper ion. In the same experiments the total amount of removed copper is higher than this amount of released sodium. The additional amount of copper can not be removed by precipitation but only by adsorption.

The overall removed copper in the experiments with the raw zeolite occurs by a combination of all the different mechanisms. So also the amount of copper removed by precipitation can be estimated. This means in detail:

1. the ion exchange capacity of the zeolite can be estimated by removing calcium from a calciumchloridesolution with the washed zeolite and by the amount of sodium which was release during these experiments (see Table 5-3)
2. the adsorption capacitity can be estimated by the amount of Cu removed by washed zeolite. The difference between the removed copper and the copper which is removed by ion exchange (point 1) shows the adsorpted copper.
3. the precipitation can be estimated by removing copper with the raw zeolite from the solution. The difference between the total removed copper, the copper removed by ion exchange (point 1) and adsorption (point 2) must be removed by precipitation.

5.1.2.3 Sorption dynamics of the synthetic zeolite P

In this chapter the sorption dynamics of the zeolite is investigated. For these experiments the used model solutions contained only one heavy metal cation (Cu^{2+}, Ni^{2+}, Zn^{2+}) and in some cases additional ionic strength caused by $MgCl_2$ and NaCl. (see Figure 5-12)

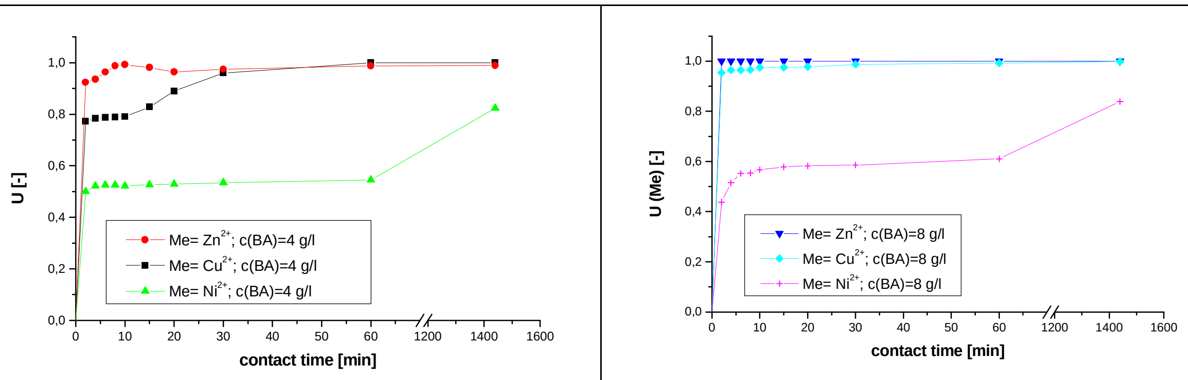

Figure 5-12: Changing of the approach to equilibrium with contact time for different metals and different amount of BA (initial metal concentration ~ 560 mg/l) without competition ions

Zinc and copper are removed up to 80 to 90% within 10 min contact time with 4g/l bonding agent. By adding 8g/l bonding agent nearly 100% of copper and zinc were removed within a few minutes contact time. The removal of nickel is in both case limited to 50 to 60%.

In the following Table 5-6 is shown the conformity between experimental data and the mathematical models. The correlation coefficients (R^2) show the correspondence between the mathematical model (Pseudo first order model, second-order model and Elovich model) and the experimental data. The closer the correlation coefficient is to 1 the better fits the mathematical model. It is obviously that the experimental data fit the second-order model. The correlation coefficient is in this case always higher than 0,999.

The coefficient also shows that the other models don’t fit the problem. For the Elovich model the coefficient is between 0,3 and 0,8 and for the pseudo first order the coefficient is between 0,14 and 0,77.

Table 5-6: Results of the mathematical modelling of the sorption dynamics

	c(zeolite) (g/l)	Pseudo first-order model		Pseudo second-order model			Elovich model		
		k_1	R^2	α	q_{eq}	R^2	α	β	R^2
c_0(Cu)= 250 mg/l	4	0,07	0,777	142,90	71,94	0,999	65,48	0,945	0,683
	8	0,07	0,6884	107,5	33,33	0,999	31,521	3,025	0,6777
c_0(Ni)= 250 mg/l	4	0,01	0,1443	147,06	39,84	0,9998	32,616	0,372	0,7335
	8	0,02	0,3712	46,3	28,99	0,9998	25,086	1,168	0,8009
c_0(Zn)= 550 mg/l	4	0,08	0,917	909,1	144	0,9976	100,16	0,158	0,6902
	8	-	-	-	70,42	-	-	-	-
c_0(Cu)= 550 mg/l	4	0,08	0,5382	65,8	138,9	0,9973	139,12	0,820	0,3967
	8	0,05	0,5264	357	71,94	0,9999	138,08	0,925	0,7533
c_0(Ni)= 550 mg/l	4	0,04	0,3481	200	75,8	0,9998	57,389	0,116	0,5084
	8	0,04	0,3481	44	41,2	0,9997	57,389	0,116	0,5084

Influence of ionic strength to the sorption kinetic

In the Figure 5-13 is shown the influence of a high amount of to the magnesium and sodium salts to the sorption dynamics of different heavy metals.

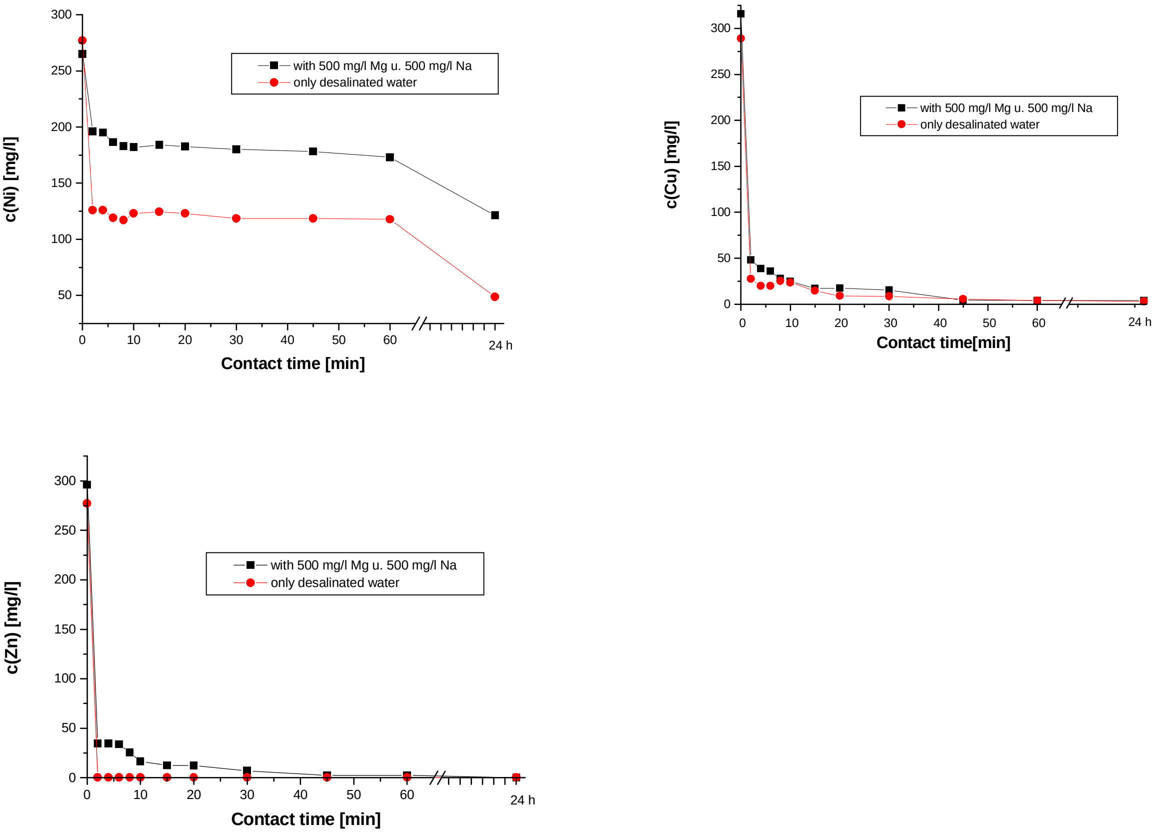

Figure 5-13: Influence of ionic strength to the sorption kinetic

Obviously there exists only a slightly influence to the sorption of copper, a higher influence to zinc and the highest influence to the sorption dynamics of nickel.

Influence of the initial pH to the sorption kinetic

A very important parameter for the sorption of heavy metals on the synthetic zeolite is the initial pH of the solution (see Figure 5-14).

The higher the starting pH the faster is the removal of the heavy metals from the solution due to additional precipitation of the heavy metals. At low pH < 5 the sorption is very poor, because the zeolite starts to dissolve and in addition the impurities as carbonates will be lost in form of CO_2 and is not available only more for additional carbonate precipitation.

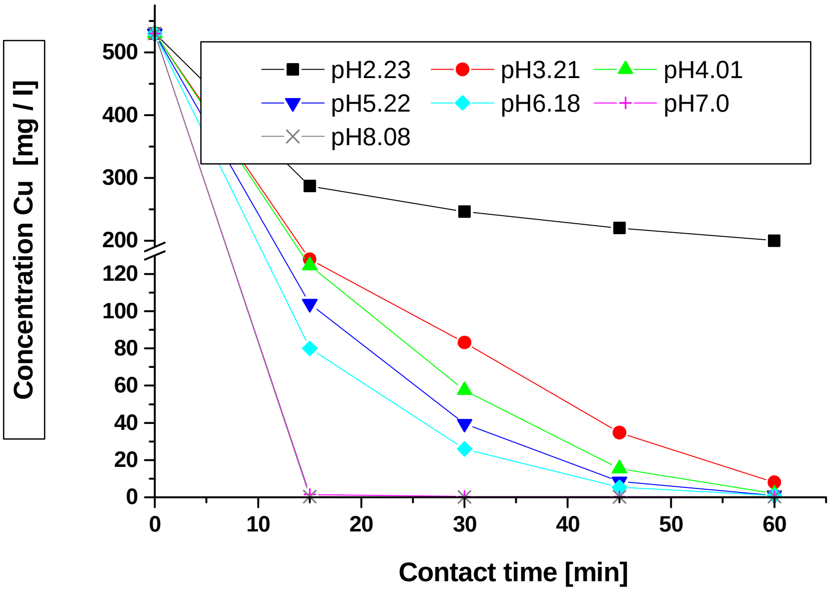

Figure 5-14: Change in heavy metal concentration in the solution as a function of contact time (4g BA/l, ~500mg Cu/l, 500mg Mg/l, 500mg Na/l)

5.1.2.4 Sorption equilibrium of the synthetic zeolite P

In this chapter the sorption equilibrium of the zeolite is investigated. For these experiments the used model solutions contained only one heavy metal cation (Cu^{2+}, Ni^{2+}, Zn^{2+}) and in some cases additional ionic strength caused by $MgCl_2$ and NaCl.

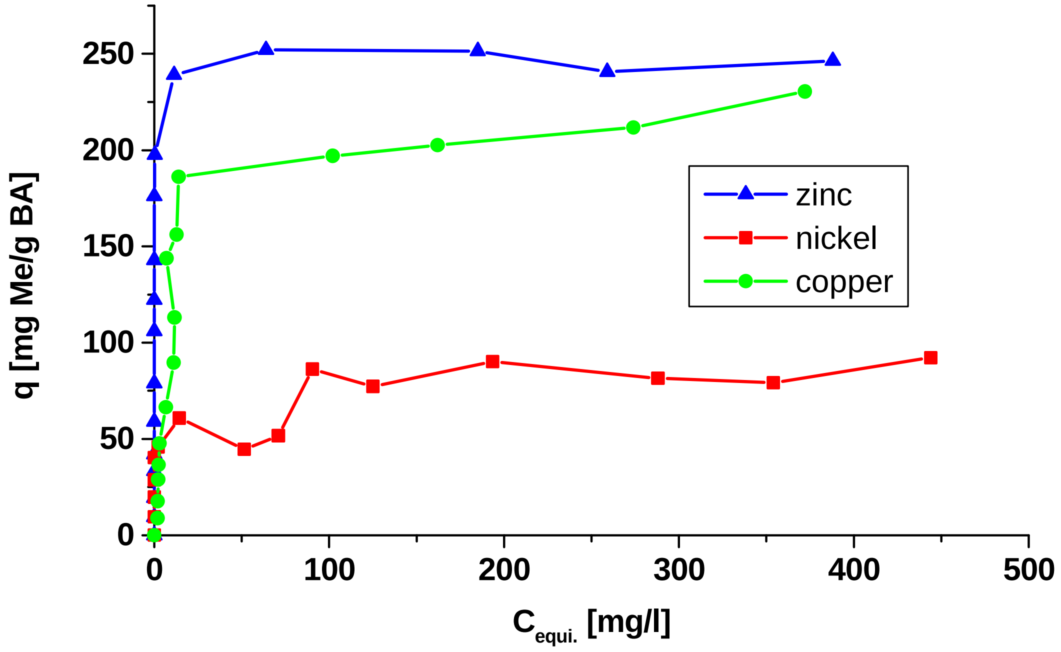

Figure 5-15: Sorption equilibrium without competition ions

The maximum sorption density in desalinated water is for nickel about 90 mg/g BA, for copper about 200 mg/ g BA and for zinc about 240 mg/g BA.

Calculated as meq/g the values 3,2 meq Ni/g , 6,3 meq Cu/g and 7,3 meq Zn/g fit the information of the producer.

In the next figure the sorption density of the heavy metals in combination with competition ions is shown Figure 5-16.

Obvioulsly the maximum sorption density for nickel and copper are nearly the same. Only the maximum sorption density of nickel is significant lower – only 40 mg/g.

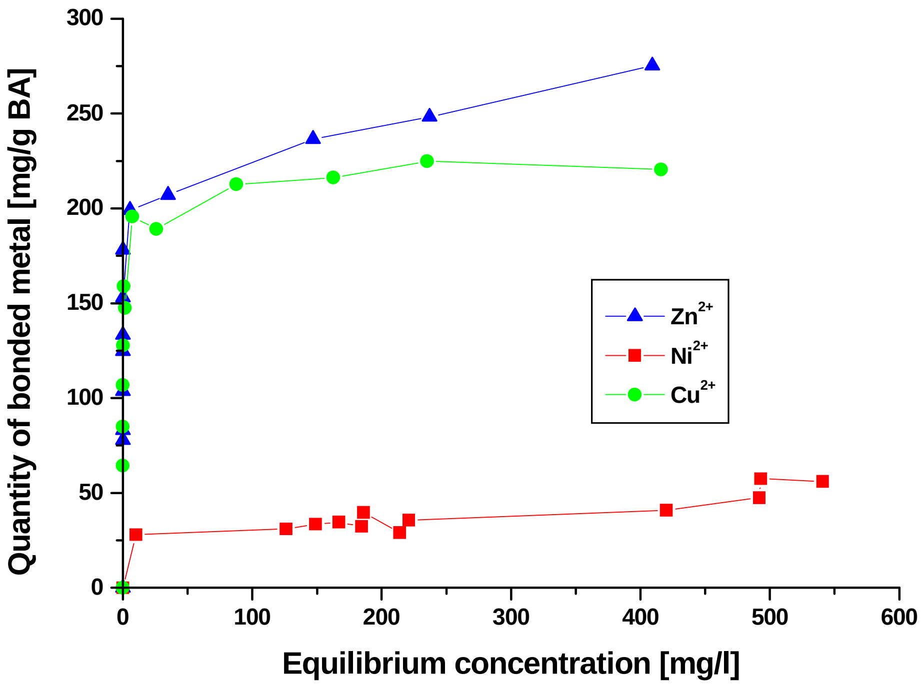

Figure 5-16: Sorption equilibrium with high amount of competition ions (500 mg/l Mg^{2+} and Na^{+})

In the following tables (Table 5-7 and Table 5-8) are shown the conformity between experimental data and the mathematical models. The correlation coefficients (R) show the correspondence between the mathematical model (Linear Isotherm, Freundlich Isotherm and Langmuir Isotherm) and the experimental data. The closer the correlation coefficient is to 1 the better fits the mathematical model. It is obviously that the experimental data fit in both cases (with competition ion and without competition ions) the Langmuir model.

Table 5-7: Results of the mathematical modelling of the sorption equilibrium with competition ions

	Linear Isotherm		**Freundlich Isotherm**			**Langmuir Isotherm**		
	R	K_L	R	K_f	n	R	X_m	K_{La}
Copper	0,6	0,33	0,9	6,59E-16	0,14	0,99986	221	0,92
Zinc	0,71	0,44	0,94	4,60E-28	0,08	0,99782	267	0,03
Nickel	0,86	0,07	0,73	1,59E-03	0,31	0,93023	62	0,01

Table 5-8: Results of the mathematical modelling of the sorption equilibrium without competition ions

	Linear Isotherm		**Freundlich Isotherm**			**Langmuir Isotherm**		
	R	K_L	R	K_f	n	R	X_m	K_{La}
Copper	0,61	0,51	0,90	207,85	33,33	0,99988	246	-10,18
Zinc	0,72	0,52	0,82	24,78	2,21	0,99516	234	0,06
Nickel	0,75	0,16	0,76	38,47	7,69	0,98978	88	0,08

5.1.2.5 Regeneration of the synthetic zeolite P

As shown in chapter 5.1.2.2 differnet sorption mechanism take place to remove the havy metals from the water.By regeneration only heavy metals removed by ion exchange can be released from the bonding agent by regeneration.

Based on the fact that the synthetic zeolite P is not pH stable (see chapter 5.1.2.1) it is not possible to regenerate the bondiong agent by a pH shift to an acid pH value. So the standard regeneration procedure for an ion exchange material is not possible.

So a new regeneration procedure was developed.

The regeneration was performed by using a 20% NaCl solution and by adjusting the pH to 5 by using HCl. The contact time for the regeneration was about 1h.

The regeneratuion experiments were performed 4 times. The zeolite was loaded with Cu (4 g zeolite/l with 260mg Cu/l). The residual concentration in the regenerate was finally messured.

The regenerated BA was than again loaded by Cu and again regenerated in the descripted way.

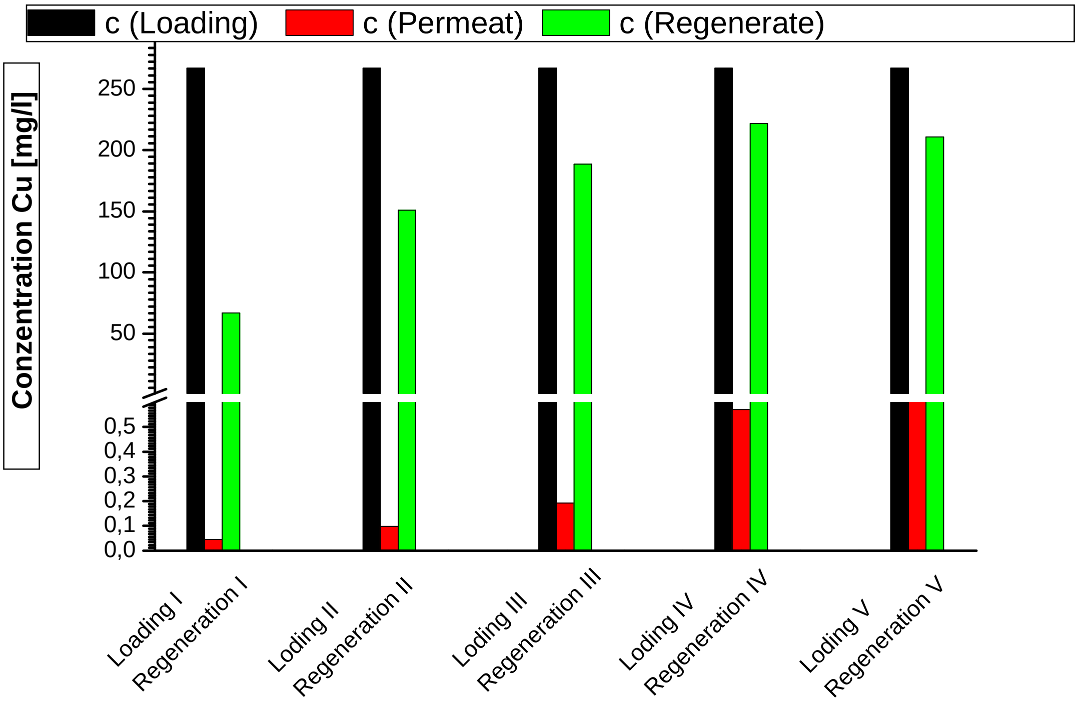

Figure 5-17: Regeneration of the synthetic zeolite P

As shown in the figure above after the first loading only about 25% could be regenerated. The reson is as discussed before: in the first sorption step only a part of the cupper ions were removed by ion exchange (see Figure 5-11). Only this amount can be again released during the regeneration procedure. The about 25% fit relatively good to the results in chapter 5.1.2.2. For the next loading steps the ion exchange mechanism becomes more and more the most important one. The precipitation "capacity" and the adsorption capacity start to be exhausted. Finally the expected about 6meq could be regenerated.

Based on the fact that during the last loading asteps only the ion exchange mechanism is available also the residual concentration in the permeat solution increases from 0,05 mg/l to about 0,6 mg/l. This behaviour is well known from the loading of ion exchange material.

5.1.3 Modified cation exchanger (TP 208)

Lewatit TP 208 is a premium grade weakly acidic, macroporous-type ion exchange resin with chelating iminodiacetate groups for the selective removal of alkaline earth and heavy metal cations.

Because this commercial resin is well known and chracterised in Literature only the important properties are discussed in this chapter.

5.1.3.1 Properties of the modified cation exchanger

Influence of the particle size to the sorption dynamics

In order to increase the sorption dynamics and the sorption capacity of the resin the particle size was decreased (see Figure 5-18).

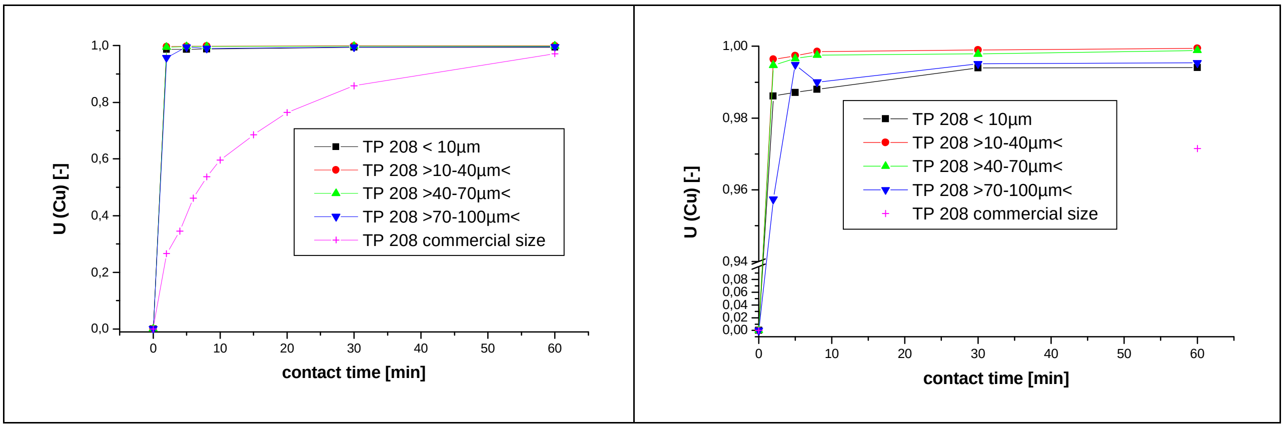

Figure 5-18: Influence of the particle size to the sorption dynamics

As expected the lower the particle size the better are the sorption dynamics. The best size in terms of sorption dynamics is between 40-70 µm. By lowering the size below that diameter no significant improvement can be observed. On the contrary at very small sizes below 10µm the sorption dynamics start to become worse. It seems that than some active groups from the resin are destroyed.

For all following results the resin with a diameter of 40-70 µm were used (see Figure 5-19).

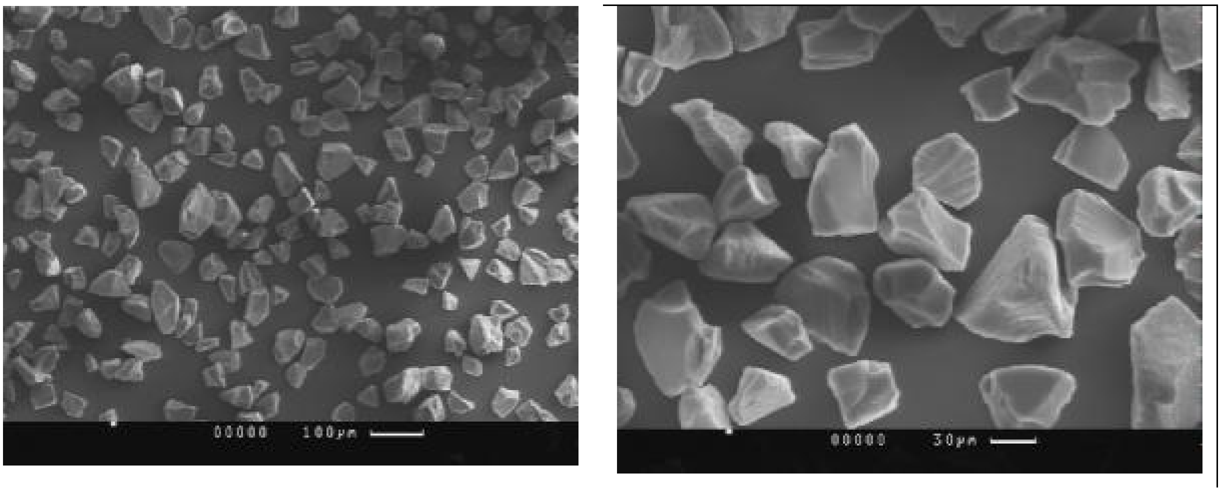

Figure 5-19: REM of the modified Lewatit TP 208 (particle size 40-70 µm)

In order to observe the surface charge of the synthetic zeolite at different pH values the zeta potential was measured (see Figure 5-20) At pH values higher than 2 the zeta potential is negative. For pH values lower than 2 positive. These results are very important to select collectors for a possibility of flotation of the ion exchanger.

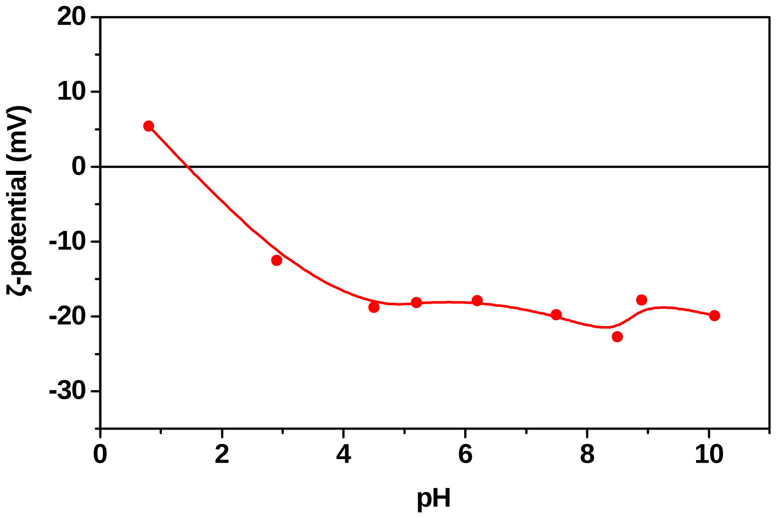

Figure 5-20: Zeta potential of the modified Lewatit

5.2 *Study of of the new hybrid processes in bench scale under real industrial conditions*

5.2.1 Study of the hybrid process consisting of sorption and micro membrane filtration for the removal of AsF_6^- from groundwater

5.2.1.1 Definition of the problems to be solved

A groundwater from Czech Republic contaminated with hexafluoroarsenate should be treated with the hybrid process I (Figure 2-6). The hexafluoroarsenate was formed during the decorative treatment of glass products surfaces by the contact with hydrofluoric acid.

As it is shown in Table 5-9 the groundwater contains beside the hexafluoroarsenate also a very high amount of sulphate (> 1000 mg/l). The problem was the selective uptake of monovalent anion AsF_6^- from solution containing a high excess of bivalent anion sulphate.

Table 5-9: The composition of the contaminated groundwater

Parameter	Values
DOC	2.6 mg/l
TOC	4.1 mg/l
pH	7.2
SO_4^{2-}	1100 mg/l
As	0.96 mg/l
Fe	<0.1 mg/l
Mg	64 mg/l
Ca	471 mg/l
Mn	<0.05 mg/l

Both this special species of arsenic and the high amount of the sulphate were the reasons why the commercial processes were inefficient for this groundwater.

The conventional methods as using of ironhydroxid or activated alumina as sorbents for the removing of arsenic were inefficient for this special type of arsenic. Also membrane processes as e.g. reverse osmosis were not suitable for this water because with these processes not only the arsenic but also the other compounds in the water were removed.

5.2.1.2 Methodology

In order to solve this kind of problem the hybrid process consisting of sorption and cross-flow microfiltration was studied (Figure 5-21).

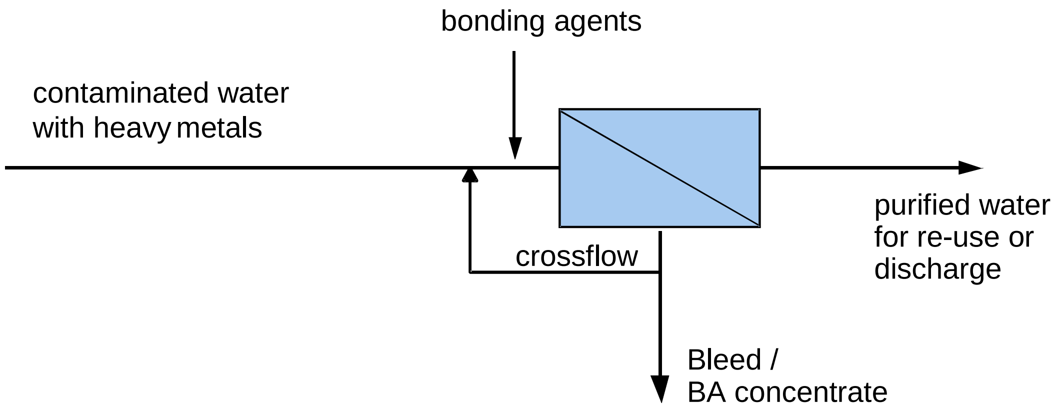

Figure 5-21: Flow sheet of the integrated processes combining metal bonding and separation of the loaded BA by crossflow membrane filtration for low contaminated wastewater

5.2.1.3 Results and discussion

Analog to the Lewatit TP 208 the particle size of the resin was decreased to 40 – 60 µm in order to increase the sorption capacity and the sortion dynamic.

In Figure 5-22 the sorption kinetics of the modified ion exchanger MP62 is shown for this species of arsenic. The horizontal line shows the requested As-concentration of 0,1 mg/l.

These experiments were performed with the real groundwater. To have a better overview the points are connected with a straight line.

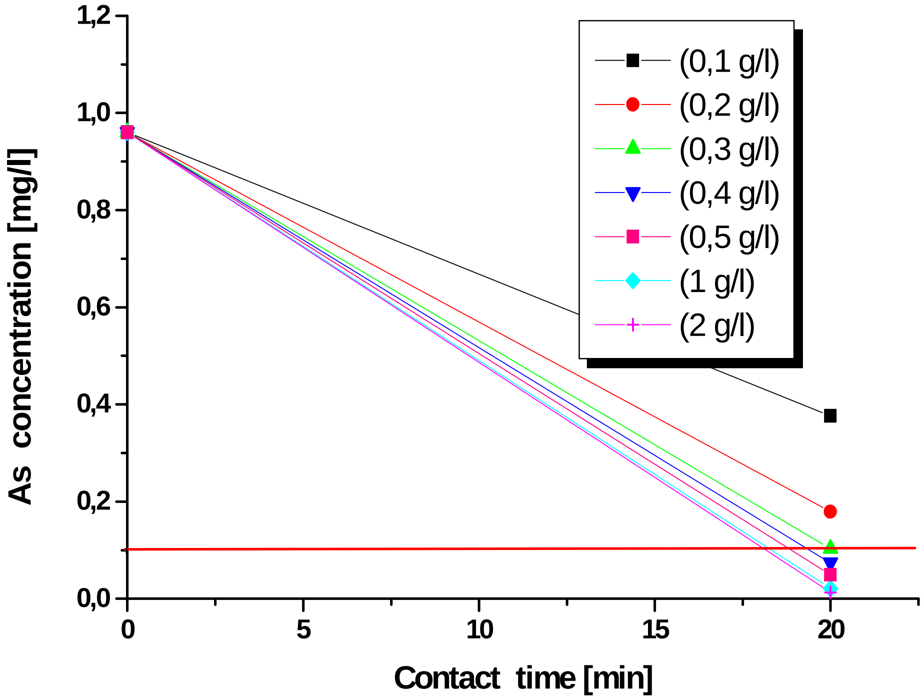

Figure 5-22: Sorption kinetics of the modified weak base anion exchange resin (particle size 40-60 µm) MP 62

Depending on the concentration of the ion exchange resin a very low concentration of As after 20 min. contact time was reached, e.g. with 0,3 g/l IX a final concentration of As of 0,07 mg/l was reached. With a higher concentration of the IX also an arsenic concentration of lower than 0,02 mg/l could be reached.

Bench-scale results

By using a periodically backflush each 20 min. for 20 sec at 0,4 bar. with permeate a stable permeability (**Figure 5-23**) was reached. This permeation rate was about 30% of the pure water flux. Also by running the plant for one week there was found no significant change in the permeation rate.

By using these parameters in the feed and bleed mode 1 l concentrate out of 300 l feed was produced (yield > 97%). The concentration of the sorbent in this bleed was about 90g/l.

The permeate was analysed during the filtration periodically each 60 min. The arsenic concentration in the permeate was always lower than 0,07 mg/l.

The concentration of the sorbent in the cross-flow was stable at about 90g/l.

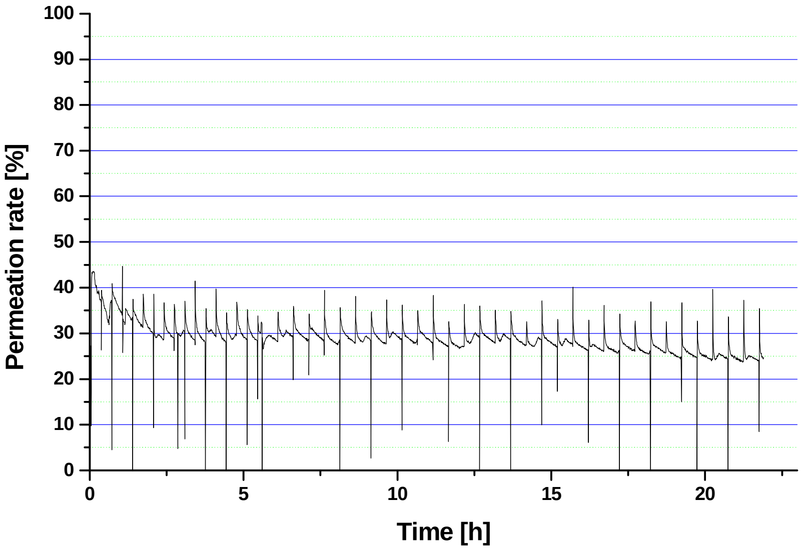

Figure 5-23: Membrane performance in the feed and bleed operation mode. (100% is pure water flux)

Regeneration of the ion exchange resin

The regeneration was performed by using 2M sodium hydroxide according the following formula.

$$-NH_3^+ AsF_6^- + OH^- \rightleftharpoons -NH_2 + AsF_6^- + H_2O$$

To one liter concentrate with 90g loaded sorbent 1 liter 2M-NaOH solution was added, which corresponds to the regenerant consumption of 20 moles NaOH / 1 L anion exchanger. After a contact time of 20 minutes the filtration was performed. The filtrate had finally a concentration of 150 mg As/l.

The regenerated sorbent was washed with water and finally activated (protonated) by using 0,5 M HCl according the following formula.

$$-NH_2 + HCl \rightleftharpoons NH_3^+ Cl^-$$

This regenerated resin was re-used successfully. The re-used resin shows no different kinetics also after re-use of more than 10 times.

5.2.1.4 Conclusions

The present studies lead to the following conclusions:

- The newly developed hybrid process of sorption and cross flow microfiltration, using a modified weak-base anion exchanger in the form of very fine particles (40 – 60 µm), was proved to be efficient in removal of monovalent anion AsF_6^- down to As-concentration < 0.1 mg/l from groundwater containing a high excess of bivalent sulphate anion.
- Extremely high concentrations of bonding agents in the bleed of about 90 g/l were achieved, making regeneration or disposal easier.
- The membrane performance in these experiments with real wastewater was always high. Even in one week of continouous experiments no fouling was observed that could not be eliminated by backflushing.

5.2.2 Study of the hybrid process consisting of sorption, flotation and submerged membranfiltration in the semiconductor industry

5.2.2.1 Definition of the problems to be solved

For these experiments real industrial wastewater was used, provided by a company, producer of copper foil, which are used in the electronic industry**.**

Description of the copper foil production process

The manufacturing process begins by using high grade copper, selected for its purity and cleanliness, and dissolving it in acid to produce a copper electrolyte solution. The subsequently controlled introduction of chemical additives to the solution allows modification of the mechanical properties of the base copper foils. The electrolytes are monitored by a computerised process automation system and supervised by the process control department in order to ensure the integrity of the solutions. When the electrolyte solution meets all the chemical and quality standards, it is pumped through filtering systems into large plating tanks, containing partially immersed titanium drums. Each of them slowly rotates and is polarised against a conforming anode. As the drum rotates, a thin film of very pure copper is electro-deposited onto its surface. At this stage, one side of the foil is smooth and shiny, the other one has a precisely controlled micro – crystalline structure with a matte appearance. The rolls of base foil, or drum foil, are now processed through a sequence of chemical and electro – chemical processing steps. Bonding treatments are applied to the foil and provide an enhanced surface for wetting by resin systems during laminations, thus ensuring the integrity of adhesion to the dielectric substrate. The final processes apply protective chemical conversion coatings that prevent corrosion to both the shiny and matte surfaces during storage or laminations. These treatment produce a base foil with all the specific final product attributes, required by the customer. Automatical visual inspection using CCD cameras and laser scanners further ensures consistent and reliable products. After the foil has been treated, samples are cut from each roll and rigorously tested for quality. If the customer requires, treated foils can be coated with either acrylic or epoxy – based adhesives applied in our specially designed coating facility. After a series of stringent manufacturing control tests, the foil is taken to the slitting department for final inspection and slit to the precise widths required by the customer. Pinhole detectors and beta gauges are fitted to the slitting machines in order to enhance strict quality control and ensure that no product leaves the plant before receiving final approval and certification. All the produced foils pass through surface cleaning equipment that removes any loose microscopic particles immediately prior to the final protective packaging.

During the production process of copper foil some wastewater streams with different chemical stuff are obtained. The treatment of two of the basic ones, marked as C and D, is shown on the figure below (Figure 5-24). The process consists of the following stages:

- Filtering the water by ion-exchange columns for metal removing
- Adding of $NaHSO_3$
- Adding of CaO and NaOH
- Adding of flocculant
- Filtering by sand- and carbon filtation

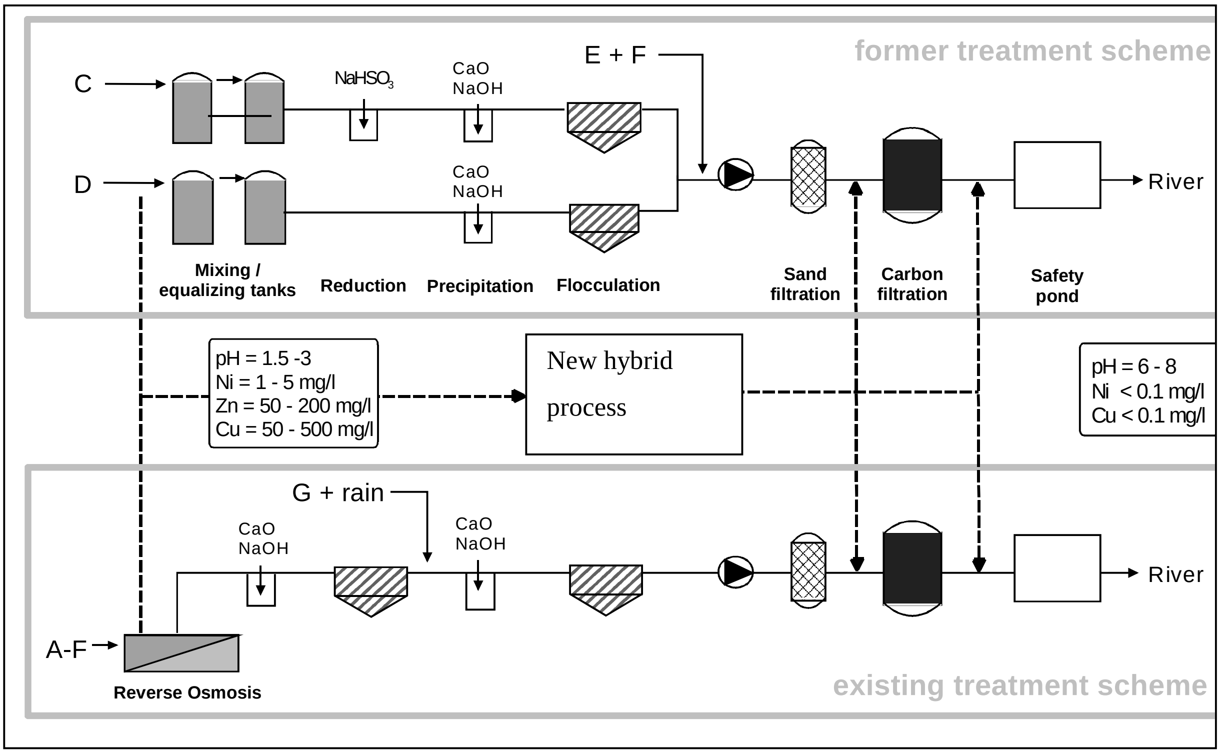

Figure 5-24: Flow sheet of the present waste water treatment

Finally as a result from this treatment a lot of sludge is produced. Another disadvantage of this process is that it is not always possible the requirements for low heavy metal concentration to be achieved. On the scheme it is also shown how the new treatment process will be applied. It may replace entirely the process, which is used presently.

Table 5-10: Heavy metals concentration in the wastewater and the required concentrations

Parameters	Concentration in the wastewater [mg/l]	Required concentration [mg/l]
Ni^{2+}	3,3	< 0.1
Zn^{2+}	167	< 0.1
Cu^{2+}	474	< 0.1
pH	2.2	6-8

5.2.2.2 Methodology

In order to solve this kind of problem the hybrid process consisting of sorption, flotation and submerged membrane filtration was used (Figure 5-25).

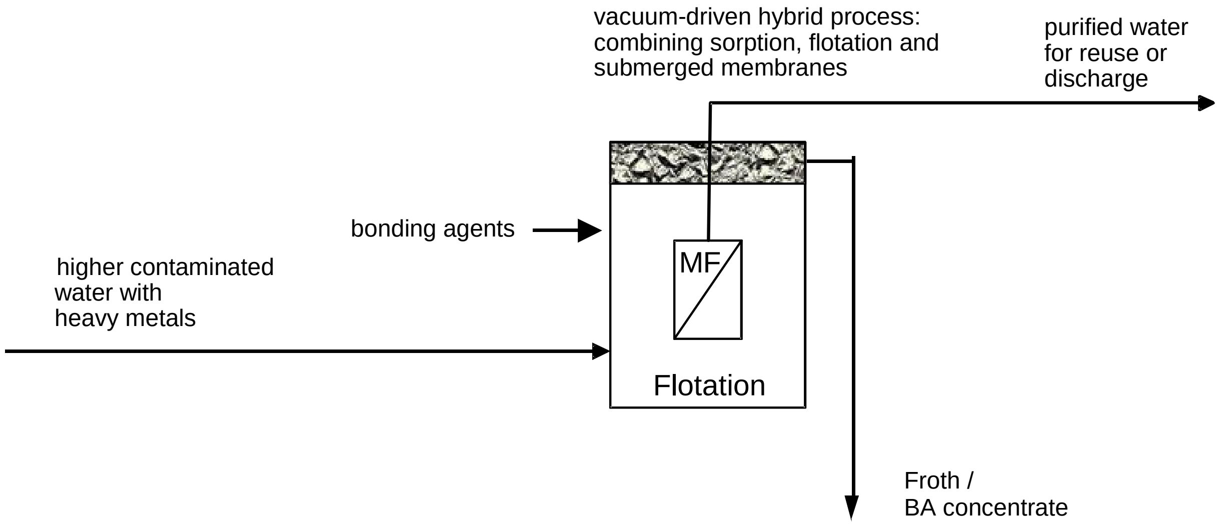

Figure 5-25: Flow sheet of the integrated processes combining metal bonding and separation of the loaded BA by a new hybrid process (membrane microfiltration and flotation) for highly contaminated wastewater

5.2.2.3 Results and discussion

As bonding agent for this hybrid process were used the Advanced zeolite P and the modified ion exchanger Lewatit TP208.

Using the advanced zeolite P

In the next figure (Figure 5-26) are shown the sorption results with this real waste water. For this experiment 8g of the synthetic zeolite were added to 1l of the waste water.

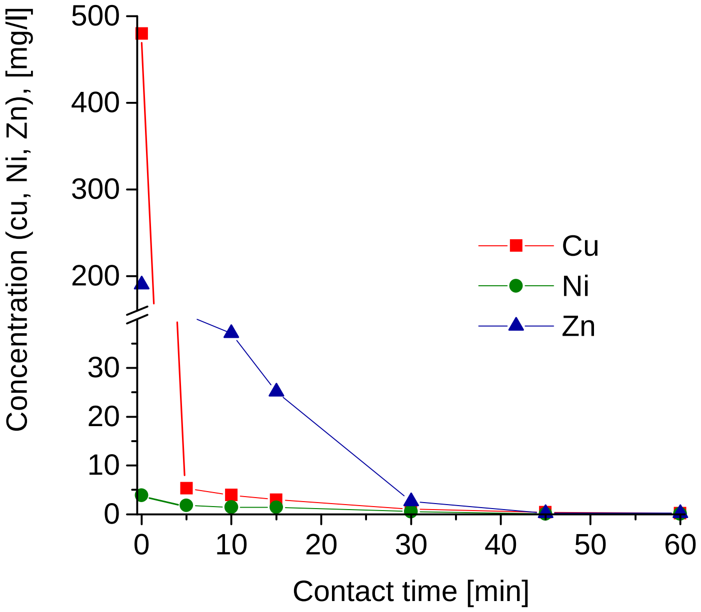

Figure 5-26: Change in heavy metal concentration with contact time; real waste water from a copper foil producer was used

No other chemicals were added to compensate for the low pH value (2.2) of the solution. However pH value increased to above 5 once the zeolite was added. The reason for this is the releasing of carbonate out of the zeolite as discussed in chapter 5.1.2.

Performance of the Hybrid Process for Zeolite / Heavy Metal Removal

The zeolite used is characterized by high capacity and fast kinetics for binding heavy metal ions such as zinc-, copper-, nickel-ions [48]. Therefore if capacity is not exceeded, almost 100 % of the heavy metals is sopted to the zeolite. This means that in terms of process efficiency there is virtually no difference between the removal of zeolites and that of the heavy metals. Considering the concentrations of heavy metals observed in industrial wastewater streams (up to 500 mg l^{-1} for several ions) and the capacity of the zeolites, the concentrations of practical importance that had to be investigated were around 10 g l^{-1}.

For initial zeolite concentrations of 8 and 12 g l^{-1} the removal efficiency for zeolites and heavy metals during two selected continuous experiments is presented in Figure 5-27.

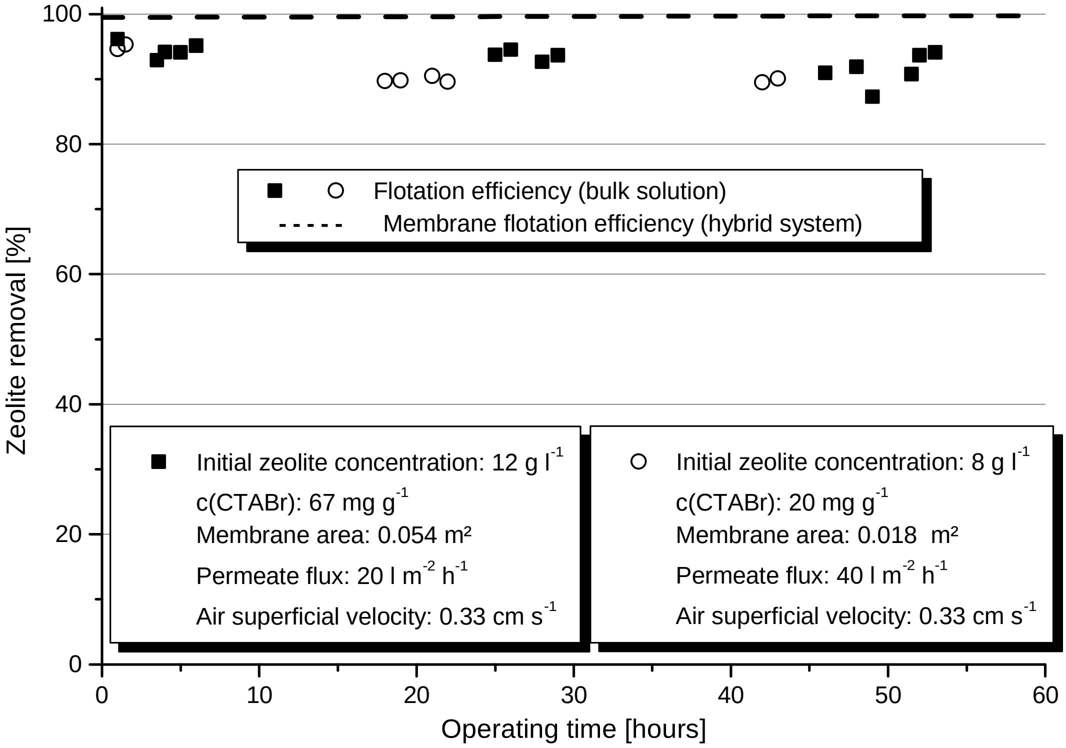

Figure 5-27: Removal efficiency of flotation and the hybrid system (membrane flotation) as a function of operating time for two selected experiments, heavy metal removal equals zeolite removal

As can be seen, the efficiency of flotation alone is 90 % on average, which means that 10 % of the heavy metals remain in the bulk solution (although they are sorbed to the zeolites), whereas the zeolite concentration in the membrane permeate is below the detection limit, leading to an efficiency > 99.9 %.

The developed process was used to treat wastewater from a company producing copper foils that is polluted with copper-, zinc- and nickel-ions in concentrations of 474, 167 and 3.3 mg l-1, respectively. Table 5-11 contains details of the heavy metals concentrations in the permeate, after 7 hours continuous operation. For all three metals, concentration was below the detection limit, consistently meeting the water re-use limit of the company. Corresponding removal efficiency was > 99.99 % for copper, > 99.97 % for zinc and > 98.5 % for nickel.

For a variety of one to three-day experiments, aimed at the investigation of different membrane operating modes, the results regarding zeolite/heavy metal removal were similar. Usually a slight decrease of flotation efficiency was observed in the beginning that stabilised after 24 hours of operation. Removal efficiency of flotation did not significantly depend upon initial zeolite concentration, on average it was 90.7 % for 8 g l^{-1} and 86.1 % for 12 g l^{-1} initial concentration, respectively.

Table 5-11: Concentrations of heavy metal ions in wastewater from the copper foil producing industry and in the treated water in relation to the limit required by the company for water re-use (in mg l^{-1})

Ion	Wastewater	Treated Water	Water Re-use Limit (required by the company)
Cu(II)	474	< 0.05	< 0.1
Zn(II)	167	< 0.05	< 0.1
Ni(II)	3.3	< 0.05	< 0.1

However, similar removal efficiency for different initial zeolite concentrations means that the concentration of zeolites in the bulk solution is higher, if higher concentrated zeolite solutions are used for binding the heavy metals. Generally, flotation efficiency could have been increased by using higher collector concentrations. However, this led to stronger foaming, making foam collection difficult and at the same time increasing the water content in the foam.

Besides the quality of the treated water the second important goal for nearly any separation process is to achieve high concentrations in the concentrate fraction, no matter if the bonding agents (e. g. zeolites) will either be regenerated or be disposed of. Therefore a high zeolite concentration in the froth is aimed at. Although the system was not optimised yet with respect to froth structure, average zeolite mass fractions of 61.5 and 83.0 % were achieved in experiments with 8 and 12 g l^{-1} initial zeolite concentration (approx. 0.8 – 1.2 %), respectively. Thus the concentrations in the froth were of nearly two magnitudes higher than those of the initial zeolite solution. It is considered a major advantage of this hybrid system investigated as similar fractions of bonding agents in the retentate cannot be achieved with a conventional membrane filtration stage, be it in cross-flow mode or in an immersed membrane system. It would mean operating the conventional membrane separation unit at concentrations of > 500 g l-1 which is neither practical nor economical.

The froth can be used in many applications of copper processing where the constituents of the zeolite (Al, Na, Si) do not interfere with the process.

Membranes Performance

Membranes were operated at constant flux in all experiments. For an initial zeolite concentration of 8 g l^{-1} the membranes could be operated at 20 l m^{-2} h^{-1} without backflushing. Resulting transmembrane pressure (TMP) was as low as 15 mbar. However, to achieve stable membrane performance with higher fluxes, backflushing proved to be necessary. A cycle of 10 s backflushing every 30 min was found to be sufficient, resulting in TMP of 45 and 90 mbar (mean of two cycles between backwashing) for imposed fluxes of 40 and 80 l m^{-2} h^{-1}, respectively (Fig. 5). The relatively long time between backflushing resulted in a permeate loss of less than 5 % by the backwashing.

In Figure 5-28 it can also be seen that the increase in transmembrane pressure when operating the membranes at 40 l m^{-2} h^{-1} without backflushing is fully reversible. Switching the operating mode of a membrane, that had been operated in continuous permeate withdrawal for 24 hours, to backflushing resulted after less than one hour in the same transmembrane pressure as for a membrane that had been operated with backflushing from the beginning. This proves that the loss in membrane performance is attributed to an easily removable cake layer, which was also visually observed. Using the resistance-in-series-model (see chapter 3.2.2.1) the resistance of the cake layer can be evaluated according to Formula 3-19.

For the experiments with 40 and 80 l m^{-2} h^{-1} (resulting in TMP of 45 and 90 mbar, respectively) the same value for R_g of $2.9 \cdot 10^{11}$ m^{-1} is obtained which means that the higher imposed flux did not create a higher cake resistance. Cake resistance in general is of the same magnitude as membrane resistance and thus quite low, which can be attributed to a highly permeable cake layer the zeolite form. The results can also be considered in terms of the concept of “critical flux” (the flux up to which the relation between flux and TMP is linear), which is currently often applied for microfiltration processes ([81], [84]). Although this concept does basically not imply backflushes, from a process point of view it can also be concluded that the membranes in our process were operated in the subcritical flux region. Thus the flux of 80 l m^{-2} h^{-1} seems not to be the limiting flux for the process investigated.

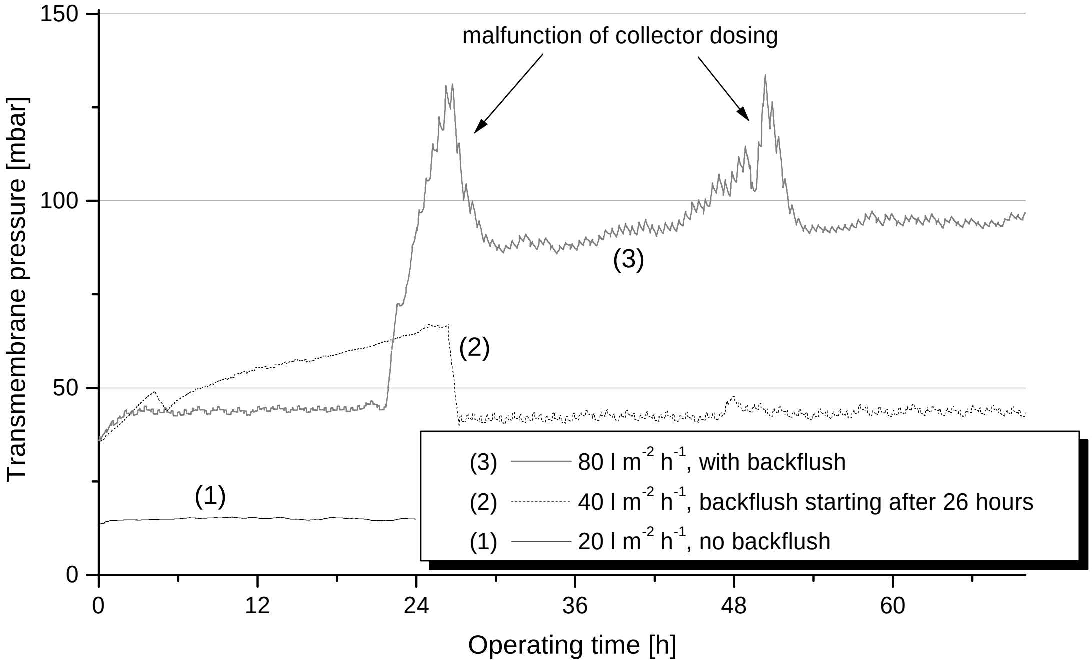

Figure 5-28: Transmembrane pressure as a function of time for the hybrid process at various operating modes, under the following conditions: c(zeolites) = 8 g l-1, c(CTABr) = 20 mg g-1, ug = 0.33 cm s-1, backflushing (if applied) every 30 min for 10 s

The influence of initial zeolite concentrations on hydraulic membrane performance is shown in Figure 5-29, where the resulting TMP for two different fluxes and operating modes is shown for 8 g l^{-1} and 12 g l^{-1}, respectively. Generally it can be said that higher initial zeolite concentrations led to higher TMP, yet stable hydraulic performance was achieved for both concentrations and imposed fluxes (with the respective operating mode).

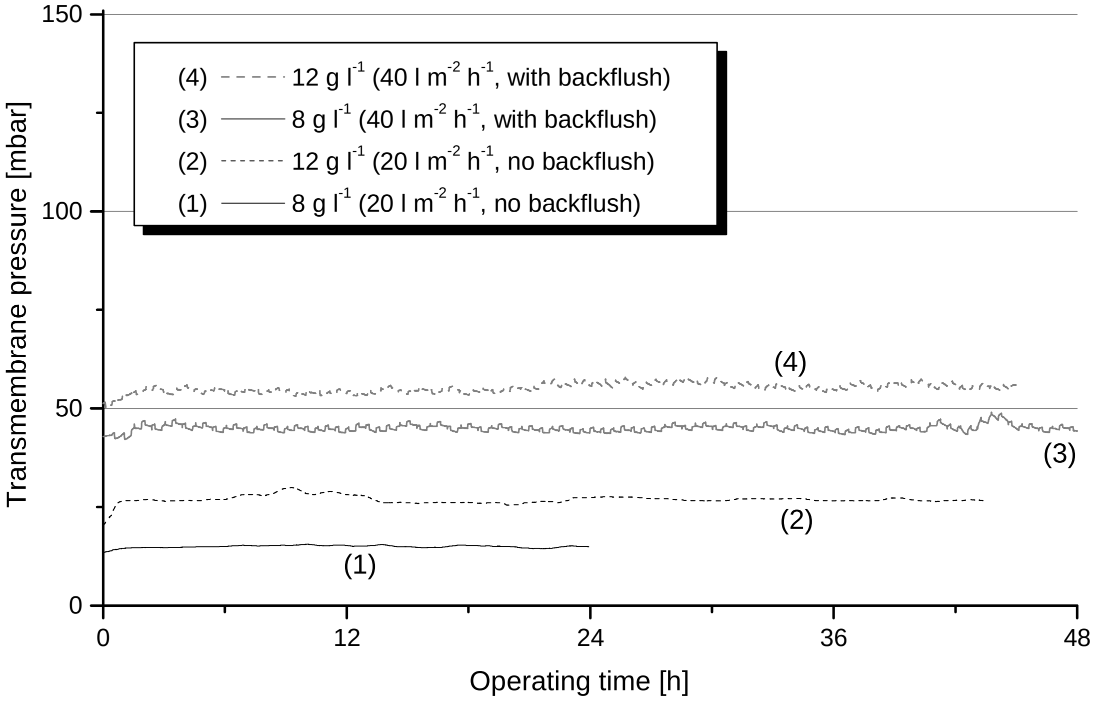

Figure 5-29: Transmembrane pressure as a function of time for the hybrid process at 8 and 12 g/L zeolite concentration, under the following conditions: c(CTABr) = 20 mg g-1, ug = 0.33 cm s-1, backflushing (if applied) every 30 min for 10 s

Using the modified Ion exchanger Lewatit TP 208

The modified ion exchange resin was added at a concentration of c_0(IX) = 8 g/L. Collector addition was c(CTABr) = 20 - 60 mg/g of IX. In Table 5-11 the results regarding water quality are presented.

Table 5-12: Heavy metals concentration in the wastewater and effluent quality with BA modified IX related to the requirements for re-use (set by the company)

	Wastewater	Hybrid process effluent	Water re-use limit
Cu [mg/L]	474	0.46	< 0.1
Zn [mg/L]	167	0.04	< 0.1
Ni [mg/L]	3.3	< 0.05	< 0.1

The only water re-use limit that was not met was the one for copper which indicates that a higher BA concentration might have been required. Nevertheless, also in this case removal efficiency was 99.9 %. In contrast to the flotation of zeolites, flotation efficiency for IX was considerably lower. Even with a collector (CTABr) dosing of 60 mg/g of IX only 60 % removal was achieved (Fig. 7). This example shows the advantage of the hybrid system, as with pure flotation the remaining 40 % of BA in the bulk solution would mean 40 % of the initial heavy metals concentration in the effluent.

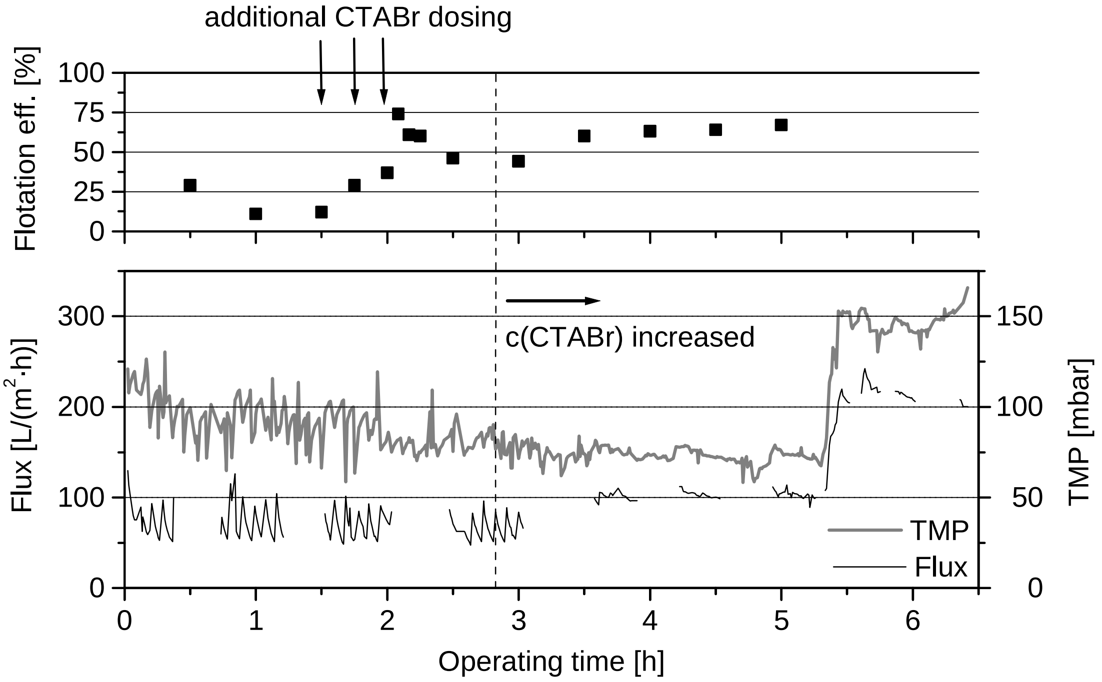

Figure 5-30: Hydraulic membrane performance with bonding agent modified IX

Mass fractions of the modified ion exchanger in the froth were 21 to 23 w-% (grab samples) which equals a heavy metal mass fraction of 2.1-2.3 w-%. As the modified IX can be regenerated to a certain extent [6], the feasibility of copper re-use will depend on the concentration of copper in the solution from regeneration.

The hydraulic performance of the membranes with the modified IX is shown in Figure 5-30. Despite the high solids concentration in the bulk due to the lower flotation efficiency (compared to the one with zeolite) a high permeability was still achieved. The flux could be increased up to 200 L/(m²·h) at a TMP of 150 mbar.

In all investigations the air supply was determined by what was required for the flotation process. No additional aeration of the membranes was carried out. This has to be considered when relating the membrane performance to conventional immersed membrane systems, as the air superficial velocity used in the hybrid system was about ten times lower than that usually applied in these systems ([85], [81]). This results in an equally lower energy consumption which, generally, still makes up a great portion of operating costs in microfiltration systems. In the hybrid system, these energy costs for membrane operation were eliminated.

From these results it can be concluded that the basic idea of operating microfiltration membranes integrated with flotation was proven to have beneficial effects in terms of membrane performance and energy efficiency.

5.2.2.4 Conclusions

The investigations presented prove that the concept of a hybrid system of sorption, flotation and immersed microfiltration membranes is promising. Tests were conducted for the separation of zeolites within the process of heavy metal removal from industrial wastewater with the following conclusions:

- The beneficial interaction of flotation and immersed membranes was shown: Membranes guarantee an almost 100 % removal of the zeolites while flotation maintains a low concentration of bonding agents in the bulk solution where the membranes are placed. This allows high membrane fluxes despite the low turbulence created by the flotation air.
- No energy in addition to that needed for flotation was necessary for fouling control of the membranes, leading to low operating costs of the process if compared to conventional membrane filtration.
- Extremely high concentrations of bonding agents in the froth were achieved, making regeneration or disposal easier.
- It was shown that the process is capable of treating wastewater from copper foil production to obtain a quality that allows water re-use.
- Membrane performance in these experiments with real wastewater were always high.. Even in one week of continouous experiments no fouling was observed that could not be eliminated by backflushing.

6 Summary

The main scope of the work was to study the hybrid membrane processes for separation of heavy metals from water and wastewater leading to less disadvantages than the state-of-the-art processes. These new hybrid processes consist of one treatment step containing the sorption of the heavy metals on suitable bonding agents and the separation of the loaded bonding agents.

In this context two bonding agents - namely a synthetic zeolite P and a modified ionexchanger were examined for their sorption ability. The bonding agents showed significant higher sorption dynamics, higher sorption equilibrium and higher selectivity against accompagnying ions than commercial bonding agents.

During the study the sorption mechanism of the synthetic zeolite could be explained as a combination of ion exchange, adsorption and precipitation. The sorption dynamic could be mathematicly described with the Pseudo Second Order Model and the sorption equilibrium with the Langmuir Isotherm.

Furthermore the new hybrid processes were studied in bench scale under real industrial conditions for two different applications.

It could be shown that the newly developed hybrid process containing sorption and cross flow microfiltration, using a modified weak-base anion exchanger in the form of very fine particles (40 – 60 µm), was efficient in removal of monovalent anion AsF_6^- down to As-concentration < 0.1 mg/l from groundwater containing a high excess of bivalent sulphate anion. The membrane performance in these experiments with real wastewater was always good. Even in one week of continuous experiments no fouling was observed that could not be eliminated by backflushing.

The second hybrid process containing sorption/submerged microfiltration and flotation were studied with water from the semiconductor industry contaminated mainly with copper by using the new developed powdered synthetic zeolite P.

The investigations proved that the concept of this hybrid system was promising. The beneficial interaction of flotation and immersed membranes was shown. The membranes guarantee an almost 100 % removal of the zeolites while flotation maintains a low concentration of bonding agents in the bulk solution where the membranes are placed. This allows high membrane fluxes despite the low turbulence created by the flotation air.

For the fouling control of the membranes no additional energy to that needed for flotation was necessary. This leads to low operating costs of the process if compared to conventional membrane filtration. The membrane performance in these experiments with real wastewater was always high. Even in one week of continuous experiments no fouling was observed that could not be eliminated by backflushing.

In the froth a high concentration of up to 83% mass fraction of the bonding agent were achieved which makes the process very interesting in term of re-use of the heavy metals or which leads at least to a more efficient disposal.

During this study the following publications were generated:

- Erwe T., Mavrov V., Chmiel H., "Characterization of a synthetic zeolite P as a heavy metal bonding agent", **Chemical Papers** 57 (1) (2003) S. 45-49
- Erwe, Torsten ; Blöcher, Christoph ; Britz, Thilo ; Mavrov, Valko; Chmiel, Horst, "Ein neuartiges integriertes Verfahren zur Entfernung von Schwermetallen aus Abwasser mittels Adsorption, Membranfiltration und Flotation", **IWW-Schriftenreihe** 40 (2004), 249-263
- Schlichter, Bernhard ; Mavrov, Valko ; Erwe, Torsten ; Chmiel, Horst," Regeneration of bonding agents loaded with heavy metals by electrodialysis with bipolar membranes", **Journal of Membrane Science** (2004) , 232, 99-105
- Mavrov V., Erwe T., Blöcher C., Chmiel H., "Study of a new integrated processes combining adsorption, membrane separation and flotation for heavy metal removal from wastewater" **Desalination** 157 (2003) S. 97-104
- Matis K. A., Zouboulis A. I., Gallios G. P., Erwe T. and Blöcher C., "Application of flotation for the separation of metal-loaded zeolites", **Chemosphere** 55 (2004) S. 65-72
- Kostas ; Peleka, E.N. ; Zamboulis, D. ; Erwe, Torsten ; Mavrov, Valko. , „Air sparging during the solid/liquid separation by microfiltration : Application of flotation**",** **Separation and Purification Technology** 40 (2004) , 1-7
- Mavrov, Valko ; Erwe, Torsten ; Chmiel, Horst," Selective separation of heavy metals from industrial wastewater streams by means of heavy metal bonding Agents", **Water, Air and Soil Pollution : Focus** 4 (2004) , 4/5, 147-155
- Mavrov, Valko ; Erwe, Torsten ; Blöcher, Christoph ; Chmiel, Horst," Selective separation of toxic metals from specific industrial wastewater streams for water and metal re-use"METASEP", **Proceedings: Permea** (2003) Slowakia , LK2.1
- Mavrov, Valko ; Erwe, Torsten; Chmiel, Horst, „Characterisation of a synthetic zeolite P as a heavy metal bonding agent ",**Proceedings: 29th International Conference of Slovak Society of Chemical Engineering**, CD_ROM. (2002), SEPA3

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- Mavrov, V. ; Stamenov, S. ; Todorova, E.; Chmiel, H.; Erwe, T, ”New hybrid electrocoagulation membrane process for removing selenium from industrial wastewater” Desalination 201 (2006), 290-296.

This work comprises a part of the research project METASEP (Selective Separation of Toxic Metals from Specific Industrial Waste Water Streams for Water and Metals Re-use), contract no. EVK1-CT-2000-00083 (project site http://www.eurice.de/METASEP), funded by the European Union within the 5th Framework Programme.

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