PHD THESIS

Humic acid and arsenic removal from well-water

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Budapest

2006

PhD School/Program

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Field: **Food Science**

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1. INTRODUCTION

In the 20th century the science and technology has developed to a great extent, but in parallel the problem of environmental pollution, including water pollution has increased in a large measure all over the world. So an increasing demand is reported for those processes which are able to purify the water without environmental pollution. Nowadays thousand of experts are working to decrease the degree of harmful procedures and to reduce the consequences. The traditional water treatment methods include the use of chemicals so during the purification they contaminate in some sort. To eliminate this problem membrane technology is applied increasingly worldwide.

In Hungary it is an important task to produce good quality drinking water. With the application of membrane filtration the high humic acid content could be removed from the waters of the Great Plain. Beside worsening the sensory quality of the drinking water it build carcinogenic by-products reacting with disinfection materials. So in the water treatment it is especially important the removal of humic acid.

In the main part of Hungary the high arsenic content of the well-waters is a great problem, because it is a well-known carcinogenic and toxic material. According to the statutory order [201/2001. (X. 25.)] – about the drinking water requirements and the order of monitoring – the maximum contaminant level of arsenic in drinking water was decreased and with the help of the traditional methods it is hard or not possible to meet the new drinking water safety standards. So there is a great need to find the methods to solve these problems. A promising way is the application of membrane filtration, which could replace the difficult, multi-stage methods decreasing the amount of the used chemicals where the wastewater production is also high.

The retentate of membrane filtration of well-waters is rich in arsenic so it has to be treated as hazardous waste matter. In the long run the deposition is not a solution of the problem, so it is also necessary to study the wastewater treatment possibilities.

2. AIM OF THE STUDY

a) Experiments for humic-acid removal:

- Membrane screening for humic acid removal from model-solutions and natural well-waters, on six ultrafiltration and two nanofiltration membranes, changing the operation parameters (transmembrane pressure, recirculation flow rate) at constant temperature
- Pilot-scale experiments on the chosen ultrafiltration membrane

b) Experiments for arsenic removal:

- Laboratory experiments for arsenic removal, examining the influence of oxidant agent ($KMnO_4$) and humic acid dosage on the rejection of arsenic
- Pilot scale experiments for arsenic removal with nanofiltration and reverse osmosis membranes, examination the influence of different oxidant agents (ozone, H_2O_2, NaOCl, air, $KMnO_4$)

c) Experiments for high arsenic content wastewater:

- Concentration experiments on nanofiltration and reverse osmosis membranes, examining the economical concentration rate
- Laboratory experiments for arsenic removal with lime softening, combine with oxidation ($KMnO_4$), NaOH dosage and microfiltration
- Arsenic precipitation with H_2S dosage in laboratory scale

d) Modeling

- Determination of mass transfer coefficients in case of humic acid containing well-waters, with filtration and concentration experiments in laboratory and pilot scale

- Validation of criterial equation for mass transfer model in case of humic acid containing well-water in laminar flow regime, establishment of a new criterial equation for transient flow regime
- Modeling the microfiltration of precipitation in case of the wastewater treatment with lime softening combining microfiltration, using the resistance model

e) Economic analysis

- Economic examination of arsenic and humic acid removal by membrane filtration
- Economic examination of the treatment of arsenic containing wastewater
- Economic analysis of the complex water and wastewater treatment

3. MATERIALS AND METHODS

In the humic acid and arsenic removal experiments deionized water, model-solutions and natural well-waters were used in laboratory and pilot scale. For the humic acid removal experiments in laboratory scale the high humic acid containing well-waters were used (humic acid content: 10-21 mg/L) originated from Békéscsaba, Orosháza and Zenta (Serbia), the pilot experiments were done in Békéscsaba. The applied flat sheet and hollow fiber membranes were chosen in wide molecular weight cut-off range (MWCO: 100-0,3 kDa),

For the arsenic removal experiments well-waters originated from Gyöngyfa (Baranya-district) and Békéscsaba (Békés-district) were used as feed solutions, the pilot scale experiments were done at the same places (Arsenic content of the well-waters were: 110-220 μg/L). The applied oxidants were as follows: ozone, air, NaOCl, H_2O_2 and $KMnO_4$, changing the dosage and the reaction time. The cross-flow filtration experiment were performed on nanofiltration and reverse osmosis membranes.

In the wastewater treatment experiment the retentate of the nanofiltration of well-water (Békéscsaba) was used as feed solution (arsenic content. 500-700 μg/L). As a possibility for the wastewater treatment lime softening was tested, using pure $Ca(OH)_2$ and commercial slaked lime. The changing of pH and oxidation conditions were analyzed by NaOH and $KMnO_4$ dosage, the formed precipitation was removed by microfiltration and sedimentation.

To reduce the amount of the wastewater nanofiltration and reverse osmosis were applied. From the concentrate the arsenic was precipitated with hydrogen sulphide, which was developed from iron sulphide with hydrochloric acid.

4. SUMMARY

To produce good quality drinking water is an important task all over the world, the solution for this problem can be the application of membrane filtration. In this study complex membrane filtration methods were worked out for the reduction of the the humic acid and arsenic content in the Hungarian well-waters to meet the drinking water requirements, and for the treatment of the by-product wastewater.

Humic acid cause some types of cancer, when they react with chlorine or other disinfection material composing disinfection by-products, e.g. trihalomethans. For the removal different flat sheet and hollow fiber membranes with a wide range of molecular weight cut off (MWCO: 100-0,3 kDa) were investigated, using different well-waters and model-solutions in laboratory experiments. On the basis of pilot scale experiments it could be established that the membranes with 1-2 kDa molecular weight cut off are proper for humic acid removal.

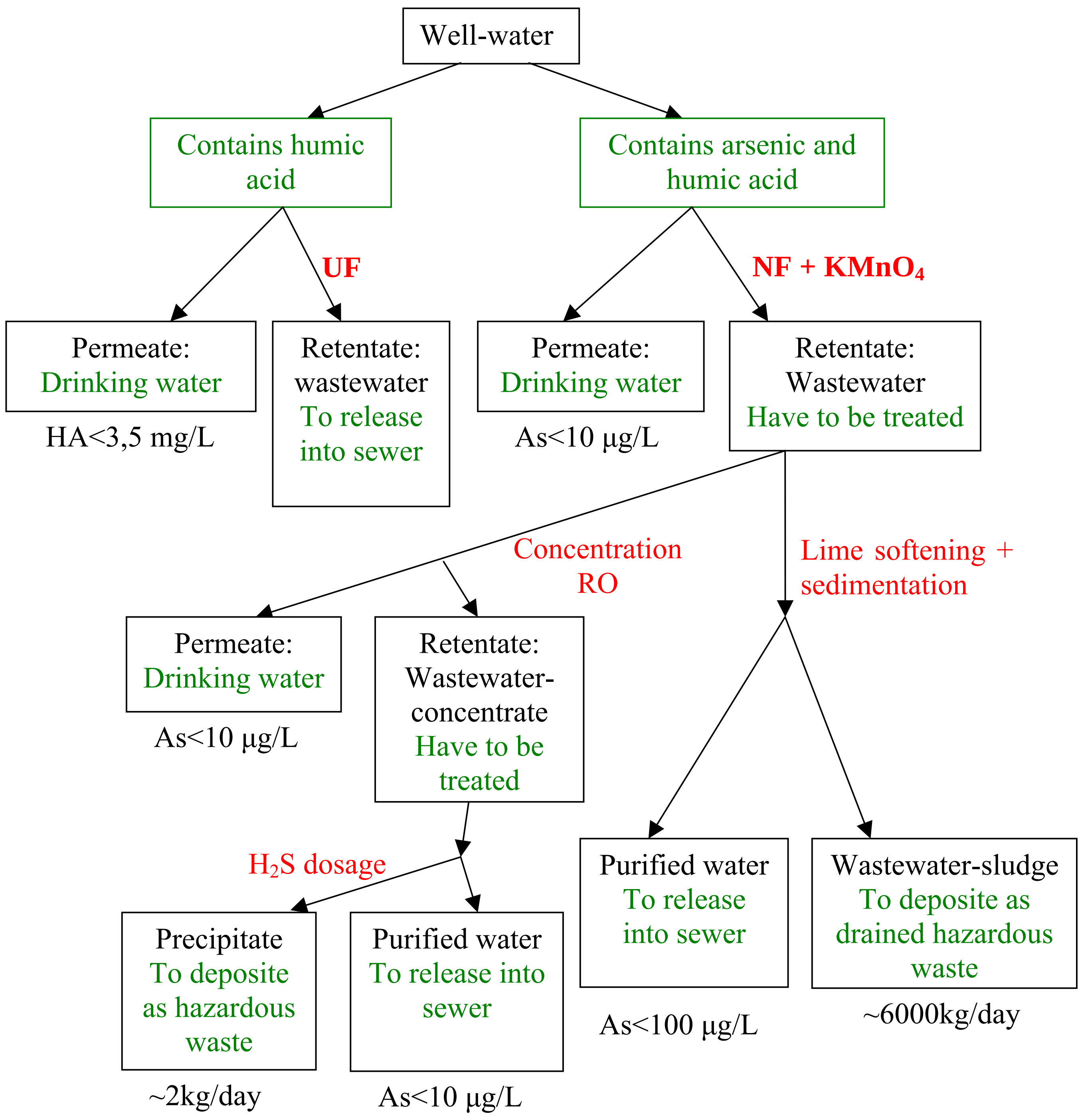
The arsenic content of well-waters in some part of Hungary is high, in these areas the drinking water quality does not meet the requirements (< 10 μg As/L). The membrane filtration of arsenic content waters are worldwide examined, it is proved that the removal of As(V) is more efficient than the removal of As(III). In this study different oxidizing agents (ozone, air, NaOCl, H_2O_2, $KMnO_4$) were tested in laboratory and pilot scale. It could be established that nanofiltration (NF) combined with $KMnO_4$ dosage is an efficient method to meet the drinking water standards.

During the nanofiltration high arsenic content retentate (volume: ~20 %) is arising which have to be treated. The examined methods were as follows: concentration by nanofiltration and reverse osmosis (RO) membranes, lime softening and H_2S precipitation.

Based on the experimental results mass-transfer model was applied for the ultrafiltration of humic acid content well-water, furthermore resistance model was applied for the microfiltration of precipitation of lime softening.

Complex well- and wastewater treatment method was worked out, analyzing the operation parameters and the economic conditions. The overall production costs of the two complex methods (NF well-water treatment + concentration of retentate + H_2S precipitation; and NF well-water treatment + lime softening) are equal, but considering the yield (93 and 80 % respectively) and the arising quantity of hazardous waste matter (2 and 6000 kg respectively) NF filtration + RO concentration + H_2S precipitation can be recommended (the calculation was worked out for a settlement with 10000 m^3/day drinking water demand).

Diagram of the complex well- and wastewater treatment method



NEW SCIENTIFIC RESULTS

I. Based on laboratory membrane screening experiments (test of 8 different membranes with molecular weight cut off: MWCO = 0,3 – 100 kDa) for humic acid content reduction under the limit value (<3,5 mg/L) in well-waters and model-solutions, and based on pilot scale experiments it can be established:

- In the permeates of NF membranes (NMWCO = 0,3 – 0,4 kDa) no humic acid was detected, so the rejection of the nanofiltration membranes were ~100%, but they have also removed other compounds (e. g. total hardness), which are important for the drinking water quality.
- UF membranes with NMWCO of 5 kDa or higher could not decrease the humic acid content of natural well-waters under the limit value.
- The UF membranes with NMWCO 1 – 2 kDa are suitable for the removal of humic substances, (rejection: 81-85 %, transmembrane pressure: 1,1 – 2,5 bar, yield: 33 – 92 %, laminar and transient flow regime: Re = 288-5192).

Based on these results the application of membranes with 1-2 kDa molecular weight cut-off can be recommended for humic acid removal.

II. Results of experiments for arsenic content reduction below limit value (<10 μg/L) in well-waters:

- The humic acid content of model- and well-water did not influence the arsenic rejection (laboratory experiments, well-water: 110-220 μg As/L, model-solution: 200 μg As/L)
- With reverse osmosis (RO) combined with a small amount oxidant dosage (e.g. H_2O_2) arsenic can be removed (<10 μg/L).
- In the case of nanofiltration (NF) only the dosage of $KMnO_4$ (0,15 mg/L) reduced the arsenic content reliably below 10 μg/L (the examined oxidants: ozone, air,

H_2O_2, $KMnO_4$, NaOCl; the arsenic rejection with $KMnO_4$ dosage and nanofiltration: 94-97 %).

(It has to be remarked that without oxidants neither nanofiltration nor reverse osmosis could lower the arsenic content of well-waters below 10 µg/L.)

III. On the basis of experiment for wastewater (retentate of nanofiltration of arsenic content well-waters, As concentration: 500-700 µg/L) treatment it could be established:

- Using nanofiltration for the reduction of wastewater-volume it could be decreased with 35 %, the permeate can be released into sewer (<100 µg/L arsenic content); in case of reverse osmosis – considering the flux decline – the optimal concentration rate is 2,7 (yield = 63 %), the arsenic content of the permeate meets the drinking water requirements (<10 µg As/L).
- Using lime softening for wastewater treatment in case of model solutions (adding 600 mg/L $Ca(OH)_2$) the arsenic rejection is 94-99 %. At low arsenic content wastewaters (As: 600 µg/L) with 2400 mg/L $Ca(OH)_2$ the rejection is about 75 %, while at high arsenic content wastewaters (As: 1280 µg/L) the $Ca(OH)_2$ dosage is not effective.
- For arsenic precipitation from high arsenic content wastewaters H_2S dosage is proper, the arsenic content decreased from 1020 µg/L to 10,3 µg/L, so the rejection is 99 %.

IV. Based on the laboratory and pilot scale experimental results mathematical models were worked out to describe the mass transfer process:

- Modeling the ultrafiltration of humic acid it could be established that for laminar flow regime the Sherwood criterial equation describes well the mass transfer coefficient of the humic acid containig well-water. For transient flow regime in the literature no equation could be found, so a new mathematical model was found based on pilot scale experiments determining the new invariants of the model for turbulent flow regime:

$$Sh = 0,276 \cdot \mathrm{Re}^{0,41} \cdot Sc^{0,33} \qquad (R^2 = 0,886)$$

the formula is valid: Re = 2401 – 5192.

- On the basis of membrane screening experiments new relation was determined describing the correlation between the molecular weight cut-off of the ultrafiltration membranes and the humic acid content of the permeates:

  Model-solution: HS (mg/L) = 0,45 ln MWCO + 0,58 (R^2=0,943)

  Well-water (Zenta): HS (mg/L) = 1,21 ln MWCO + 1,55 (R^2=0,955)

  where HS is the humic acid content of the permeate and MWCO is the molecular weight cut off of the membrane (0,3 – 15 kDa).

- The mass transfer coefficients calculated from the laboratory and pilot scale experiments carried out with humic acid containing well-waters (from Zenta, Békéscsaba, Orosháza) in case of the membrane with 1 kDa molecular weight cut-off (MWCO) varied between $3,60\cdot10^{-6}$ and $1,56\cdot10^{-5}$ m/s, in case of the membrane with 2 kDa MWCO between $6,20\cdot10^{-6}$ and $2,85\cdot10^{-5}$ m/s.

  These mass transfer coefficients fits to the range of mass transfer coefficients calculated with the criterial equations for laminar and turbulent flow regime from literature data based on the molecular weight ($2,08\cdot10^{-6}$ – $4,39\cdot10^{-5}$ m/s).

- The microfiltration of precipitate arise in the course of the lime softening of arsenic containing wastewater was described using the resistance model, it could be established that the resistance of the membrane, the polarization layer and the resistance caused by the fouling are in the same order of magnitude ($9,94\cdot10^{-7}$ – $19,87\cdot10^{-7}$ Pas/m).

V. Complex method was worked out for the treatment of high humic acid and arsenic content well-water, and for the treatment of the by-product wastewater (see the diagram of paragraph 4.):

- The essence of the process is the following: the arsenic content of the permeate of the oxidized ($KMnO_4$: 0,15 mg/L) and nanofiltrated well-water is below the limit value (<10 µg/L). The arising retentate (wastewater) will be concentrated with reverse osmosis, from the wastewater-concentrate the arsenic content can be precipitated with H_2S. The purified water is releasable into sewer.
- Costs of the complex processes:
    - The total cost of water treatment with nanofiltration (NF) + concentration with reverse osmosis (RO) + precipitation with H_2S (NF+RO+H_2S) is 41,45 Ft/m^3 drinking water, the drinking water yield of the complex process is 93 %, ~2 kg/day hazardous solid waste matter arise.
    - The total cost of nanofiltration (water treatment) combined with lime softening (wastewater treatment) (NF+$Ca(OH)_2$) is 41,40 Ft/m^3 drinking water, the drinking water yield of the complex process is 80 %, while ~6000 kg/day hazardous sludge arise.
    - Because of the difference of the yield and the amount of arising dangerous waste the NF+RO+H_2S complex process is more economical and environment-friendly.

The cost estimation of drinking water and wastewater treatment was worked out for a settlement with 40.000 inhabitants, about 10.000 m^3/day drinking water demand, where the well-water contains humic acid and arsenic in high concentration, on the basis of economical data of the year 2006.

5. CONCLUSIONS AND SUGGESTIONS

In this study complex method was worked out for the treatment of well-waters with high humic acid and arsenic concentration, and for the treatment of the by-product wastewater.

1. For the treatment of well-waters with high humic acid concentration membranes with 1-2 kDa molecular weight cut-off are proper. Based on the pilot scale experimental results (Békéscsaba) the 1 kDa polysulfon, hollow fiber membrane module can be operated at yield of 90 %.
2. For the arsenic removal below limit value (10 μg/L) of well-waters with high arsenic concentration (As: 110-130 μg/L) nanofiltration is only applicable combined with the proper oxidant: $KMnO_4$ dosage, the yield of the process is 80-90 %.
3. To reduce the volume of the wastewater (As: 500-700 μg/L), which is arising during the treatment of high arsenic content well-water (as retentate), concentration with reverse osmosis can be applied (yield: 63 %), from the wastewater-concentrate arsenic can be precipitated with H_2S dosage.
4. The complex drinking water and wastewater treatment method is as high as 93 %, the total cost is 41,5 Ft/m^3 drinking water. By the application of this method small amount of hazardous waste (high arsenic content precipitate) is arising, which has to be deposited.

Further tasks

1. Further experiments are necessary to optimize the amount of the applied ferric sulphide and hydrochloric acid for the precipitation of arsenic content.
2. It is considerably to recover the high humic acid content of the retentate arising during the ultrafiltration of well-waters, and possibly use as plant nutrition.

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