

## HEAVY METAL ELIMINATION FROM WASTE WATER BY ION EXCHANGE WITH MODIFIED WOOD CHOPS

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### Abstract

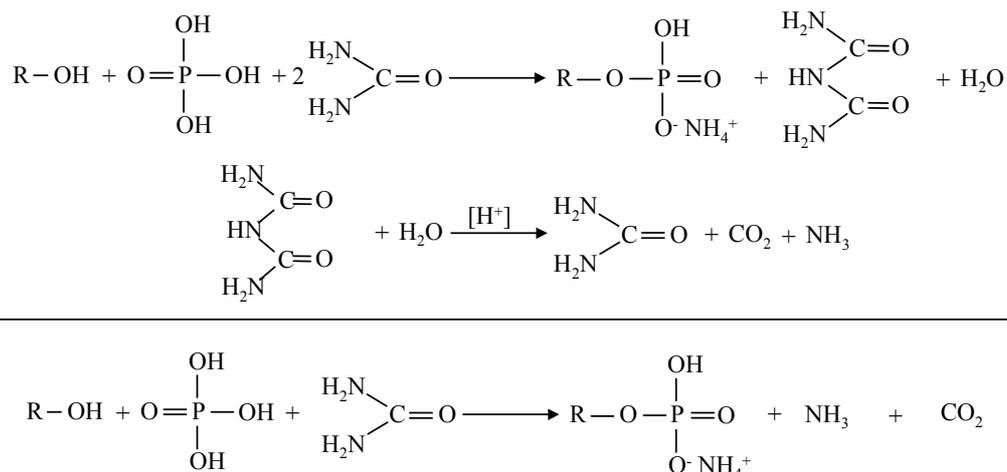
For elimination and reduction of heavy metal ions from (waste) waters a number of special artificial polymeric ion exchangers (IE) are offered. However, also natural polymeric products (wood, other cellulose fibres) or their modifications are capable to exchange heavy metal ions – usually with a reduced capacity. In a joint project (among others) pinewood chops were chemically modified to increase the ion exchange capacity (IEC). The wood chops were phosphorylated with a special microwave method. The different modified chops and competitive commercial ion exchangers were then tested in a number of laboratory and pilot scale experiments with model and real waste waters. IEC, breakthrough, regeneration and hydraulic parameters (e.g. porosity, blocking behaviour, pressure drop) were determined. The modified pinewood IE had moderate to good IEC (of 2 to 4.3 meq/g DW), about half of IEC of artificial polymeric IE. They proved to be competitive with commercial polymeric IE, especially for waste water with higher organic content and a reduced number of regeneration-loading-cycles. The results are now transferred to a pilot application for the treatment of waste water from waste gasification. There the special advantage is, that the organic wood IE loaded with heavy metals, can directly be fed back into the gasification process.

### Introduction

Heavy metals belong to the major environmental concerns in waste waters and effluents, because of their toxic or even cancerogenic characteristics. Among other methods (e.g. membrane separation, solvent or reactive extraction), ion exchange processes have been established for the treatment of industrial waste waters with low to moderate heavy metal concentrations (less than 1000 mg/L); for instance flushing or etching effluents. For elimination and reduction of heavy metal ions from waste waters, a number of special artificial polymeric ion exchangers (IE) are offered. However, also natural polymeric products (wood, other cellulose fibres) or their modifications are capable to exchange heavy metal ions – usually with a reduced ion exchange capacity (IEC).

In a joint project (besides others) pinewood chops were chemically modified to increase the IEC. Among various other reactions to produce derivatives (with carboxylic, amino, imino-diacetate groups), the phosphorylation proved to be an effective modification method for wood (ligno-)cellulose [1 - 4]. Figure 1 shows the phosphorylation reaction of ligno-cellulose chains (R). The free OH-groups are etherified with phosphoric acid in the presence of urea at temperatures above 140 °C. At these temperatures the urea is reacting to biuret. In the presence of water, the biuret decays immediately into urea, ammonia and carbon dioxide (reaction 2). Thus, the generated water from the etherification is directly removed, driving the equilibrium reaction towards the phosphorylated product (giving the cited net reaction). In the project, the wood chops were phosphorylated with a special microwave method [3]. This allows an effective, homogeneous and accelerated heat introduction into the wood chops. The microwave couples directly into the polar molecules; thus transferring the heat directly to the chops. The ammonium form of the ligno-cellulose IE after phosphorylation can be transformed into the sodium form by conditioning in sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and/or sodium hydroxide (NaOH) [3, 5].

Figure 1: Phosphorylisation of ligno-cellulose with phosphoric acid and urea [1]



### Materials and Methods

For the tests discussed here, pinewood ligno-cellulose was phosphorylated by the microwave [3] and (for comparison) the classical method [1] with the following parameters: mass ratio ligno-cellulose :  $\text{H}_3\text{PO}_4$  :  $\text{CO}(\text{NH}_2)_2$  = 1.0:0.63:1.56; reaction temperature 160 to 180 °C; reaction time 5 (for microwave) and 60 minutes (for classical method).

The IE characteristics were determined in simple batch (equilibrium) and percolation (break-through) experiments. In addition artificial polymeric IE and commercial ligno-cellulose IE were tested under the same conditions for comparison. Figures 2 and 3 are photographs of the batch and percolation test equipment, respectively.

Figure 2: Photograph of batch test equipment



Figure 3: Photograph of percolation test equipment



For the batch experiments 100 (or 500) mg DW of IE were brought into contact with an intensively stirred or shaken solution of heavy metals (Ni, Cu, Ca ...) in 50 or 100 (or 400) mL deionised or real industrial water. After the contact time (1 to 240 minutes) the IE was removed by filtration. Then the solution was analysed for the residual heavy metal concentrations.

For the percolation experiments the 24 h swollen IE was packed in columns. The heavy metal solution usually percolated from column top to bottom. Also some up-stream experiments were carried out. The column outflow was collected in an automatic sampler and subsequently analysed.

Generally double experiments were performed. Figure 4 gives an overview over the parameter variations. In Table 1 the analytical methods and devices are summarised.

Figure 4: Variations of experimental parameters

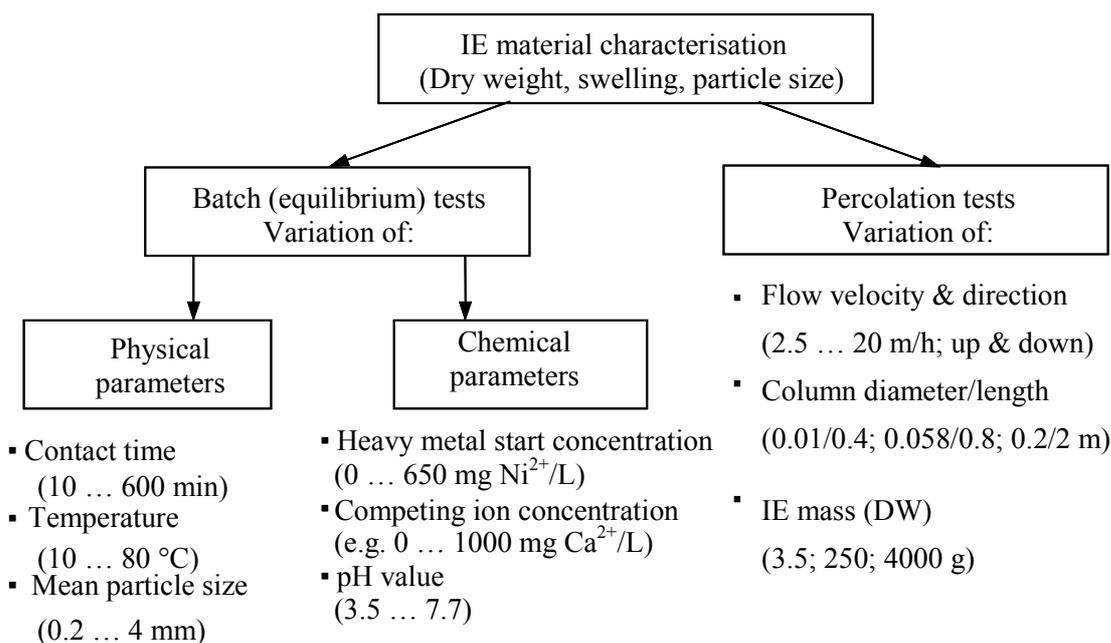


Table 1: Analytical methods and devices

Parameter	Method; Device
Dry weight / Moisture content	DIN ISO 11465
Heavy metals (Ni, Cu, Ca ...)	DIN 38406 E 11; (flame) atomic absorption spectrometer (Perkin Elmer 3100) with air - acetylene
pH value	DIN 38404 C5; Multi Lab 540, WTW, Sen Tix 41
Ortho- / total phosphate	DIN EN 1189; Merck Spektroquant (photometry)
TOC – total organic carbon	Cuvette test LCK 380, Dr. Bruno Lange GmbH

## Results and Discussion

Detailed summaries of the tests are given in [5 - 7]. Here only the results for the particle size variations will be discussed. Figure 5 depicts the IEC for that variation in the batch experiments with the contact time as parameter. With an increase of the mean particle size from 0.35 to 3.25 mm, the IEC decreases by about 50 %, from 2.15 to 1.06 mmol Ni<sup>2+</sup>/g DW. This is probably due to a decrease of specific surface and effective exchange groups with increasing particle size. Obviously, the exchange groups of ligno-cellulose IE are mainly on the outer surface. Light and electronic scanning microscopic pictures support this assumption [5, 6]. However, there are also macro-pores with exchange groups. Their diffusion paths are also shorter for smaller IE in ion exchange at a fixed contact time. Though, contact times larger than 90 minutes do not remarkably improve IEC. In addition, the smaller particles show a better swelling behaviour. Both facts might contribute to the higher IEC of small particles. Very small particles (less than 0.3 mm) tended to become mechanically unstable. Thus, a particle range between 0.5 and 0.8 mm seems to be optimal for technical applications.

The particle size variation for the percolation tests is given in Figure 6. There, the ratio of the outlet to the feed concentration is depicted over the ratio of fed (or passed) volume to the bed volume. From this figure could be derived that again the mean particle size 0.65 mm shows an optimum IE behaviour. That particle fraction has a steep break-through curve with an usable IEC of about 2 mmol Ni<sup>2+</sup>/g DW (~ 4 meq/g DW). This is almost the value of the equilibrium experiments. Larger particles (> 1.3 mm) show a channelling in the column (i.e. an early break-through due to too large open channels and bed porosity) and a reduced IEC. Very small particles (< 0.5 mm) showed an increased pressure drop and also an IEC reduction. Both might be due to an abrasion of IE material and is disadvantageous for technical applications. Further pilot scale tests supported these facts [7].

Derived from specific re-finding as well as systematic and statistic error analyses, the total measuring errors could be indicated as less than 10 % for the batch and less than 15 % for the percolation test data.

Figure 5: Mean particle size variation in batch experiments; start concentration  $c_0 \sim 600 \text{ mg Ni}^{2+}/\text{L}$  [5]

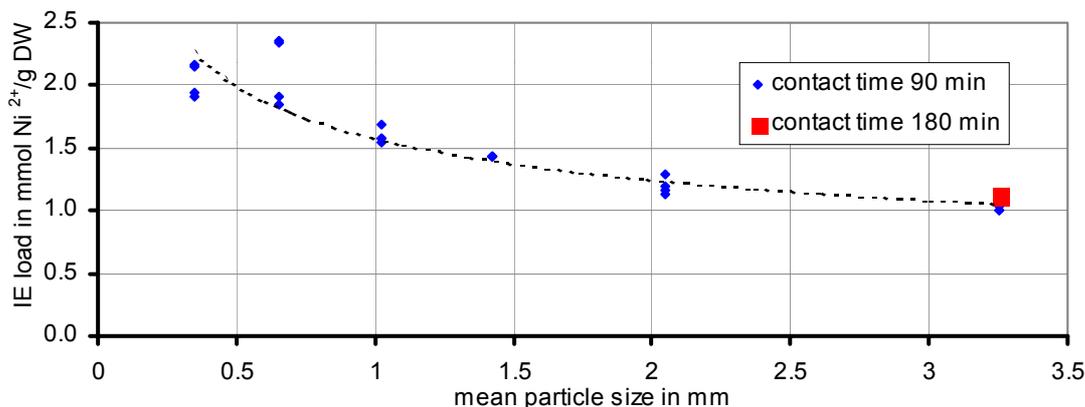
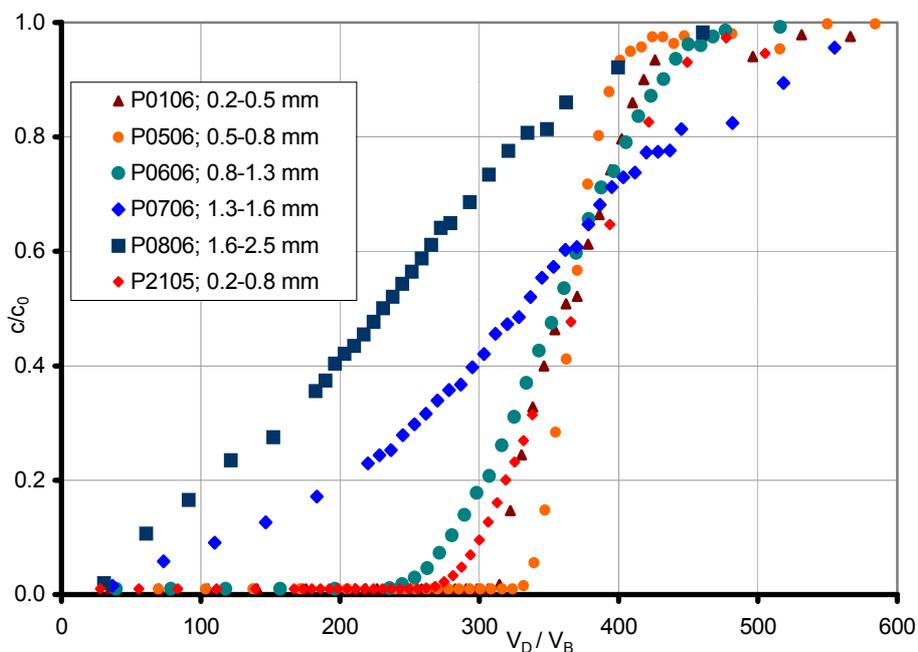


Figure 6: Mean particle size variation in percolation experiments; feed concentration  $c_0 \sim 50 \text{ mg Ni}^{2+}/\text{L}$ ; IE mass 3.5 g DW; bed volume  $V_B$  18 ... 21.7 mL; mean flow velocity  $\sim 12 \text{ m/h}$  [6, 7]



## Conclusions

By chemical modification, i.e. phosphorylation, ligno-cellulose IE from pinewood with good cation exchange performance could be produced in laboratory scale. These IE proved to be competitive to commercial IE from artificial polymers and ligno-cellulose, produced by other methods [8]. The IEC of about 2.5 ... 4.3 meq/g DW (i.e. about 60 ... 140 mg Ni<sup>2+</sup>/g DW) was very much improved, compared to the unmodified ligno-cellulose (with IEC less than 0.2 meq/g DW). Thus, the developed and applied microwave heating method proved to be effective.

Optimum IEC values were achieved for relatively low temperatures (10 °C), a pH of 7.5 (due to the dissociation behaviour of phosphoric acid) and a mean particle size of about 0.65 mm. The usable IEC in percolation experiments was (for the particle size variation at minimum 5 %) lower than in batch experiments, depending on the percolation parameters and IE characteristics. The selectivity of the produced IE is similar to other ligno-cellulose IE [8]: e.g.: Pb<sup>2+</sup> > (Me<sup>3+</sup>) > ... Cu<sup>2+</sup> > ... Ni<sup>2+</sup> ~ Ca<sup>2+</sup> ... > (Me<sup>+</sup>) > Na<sup>+</sup>.

A major advantage is that IE is derived from renewable (wood) sources. It is relatively cheap, despite of the chemical modification procedure. That is why it can be readily applied for the treatment of waste gasification effluent water. There, the IE removes, collects and buffers heavy metals. After the utilisation

it can directly be charged into the gasifier. Thus the IE generates gas and energy. Furthermore, the separated heavy metals are tightly bound into the vitrified gasification slag. At present, pilot scale tests and a scale-up for that application are performed.

The general application of the ligno-cellulose IE is, however, restricted by some disadvantages. Regeneration is limited to a maximum of about 5 cycles; with an IEC loss of at least 50 to even 90 %. The abrasion of small particles and fractions might cause column blocking and increasing pressure drop. In long-term applications (longer one year) there might be the risk of an- and/or aerobic degradation in a respective microbiological milieu.

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