

# Sulfate Removal from Water Streams Down to ppm Level by Using Recyclable Biopolymer

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**Abstract** Sulfate is not highly toxic to life, but nowadays sulfate concentrations in water are under increasing inspection from regulatory authorities. Typical sulfate drinking water limit in Finland is 250 mg/L, but places like Minnesota future waste water sulfate discharge limit is expected to be as low as 10 mg/L. Several methods to remove sulfate from aqueous solutions have been developed, but most of these methods do not fulfill the criteria of circular economy. This study focuses on sulfate removal by using chitosan as adsorbent in the laboratory and pilot scale.

**Key words** sulfate removal, biopolymer, recycling, ion exchange material

## Introduction

One of the main problems in industrial waste waters are sulfur compounds. Sulfur has several oxidation states between -2 and +6 and most common in the nature are the pure elementary sulfur (S<sub>8</sub>), sulfide (S<sup>2-</sup>) and sulfate (SO<sub>4</sub><sup>2-</sup>). The sulfate or sulphate ion is a polyatomic anion with the formula SO<sub>4</sub><sup>2-</sup>. Sulfates occur widely in everyday life, like in sea water (ca. 2.5 g/L) and sulfate salts and sulfuric acid are also widely used in industry. Many examples of ionic sulfates are known, and most of these are highly soluble in water, like FeSO<sub>4</sub>. Poorly soluble compounds are only CaSO<sub>4</sub>, SrSO<sub>4</sub>, PbSO<sub>4</sub> and BaSO<sub>4</sub>, while radium sulfate is the most insoluble sulfate known.

As such sulfate is not highly toxic to life, but sulfate increases salinity in receiving waters and may cause secondary toxic effect when sulfate is biologically reduced to toxic hydrogen sulfide (H<sub>2</sub>S). Nowadays, sulfate concentrations in water are under increasing inspection from regulatory authorities based mainly on public demands. Compared to other contaminants like nitrate, arsenic, and metals, sulfate has no strict standard for drinking water or aquatic life. Typical drinking water limit in Finland and many other countries is 250 mg/L, for livestock drinking water sulfate limits are higher e.g. in Canada, Australia and EU 1000 mg/L, while concentrations above 600 mg/L may create laxative effects. However, in some places like Minnesota, future sulfate discharges may be limited to as low as 10 mg/L. Several methods, like lime precipitation (CaSO<sub>4</sub>), barium precipitation (BaSO<sub>4</sub>), membrane techniques (e.g. reverse osmosis), ion-exchange and biological processes have been developed. The simplest method for sulfate removal is precipitation as gypsum, which is used widely as fertilizer or plaster. The main problem is gypsum's moderate solubility (~2.0–2.5 g/L at 25 °C) to water. Solubility is increased if sodium cations are present in the same solution, but in contrast to most other salts, it exhibits retrograde solubility, becoming less soluble at higher temperatures. BaSO<sub>4</sub> has lower solubility to water, but the problem is that water-soluble barium compounds are poisonous.

Outotec has developed ettringite ( $3\text{CaO}\cdot 3\text{CaSO}_4\cdot \text{Al}_2\text{O}_3\cdot 31\text{H}_2\text{O}$ ) precipitation process, in which lime and  $\text{Al}(\text{OH})_3$  can be used to remove sulphate and metals. Ettringite has very low water solubility (200-1000 mg/L) and therefore the resulting sulphate concentrations are low. Disadvantages are the large amount of sludge generated, highly basic solutions and the fact that high sodium concentrations inhibit the process.

Also several other processes have been developed like reverse osmosis (RO) and biological processes. RO is a water purification technology that uses a semipermeable membrane to remove ions (e.g. sulfate), molecules, and larger particles from water. RO is effective but a costly method to purify waste waters and results significant amount of reject water needing additional treatment. Biological process under anaerobic conditions convert sulfates into sulfides. Biological processes are cost effective but rather slow, difficult to control and formation of highly toxic  $\text{H}_2\text{S}$  cause additional problems.

Most of these methods mentioned above do not fulfill the criteria of circular economy. Recently, we have developed environmentally friendly method for the removal of inorganic sulfur compounds based on a generally available biopolymers, like chitosan which is prepared from shrimp shells as shown in Fig. 1. Here, preliminary results from our laboratory and pilot experiments are shown.



**Figure 1.** Chitosan used in this study is prepared from shrimp shells.

### General methods

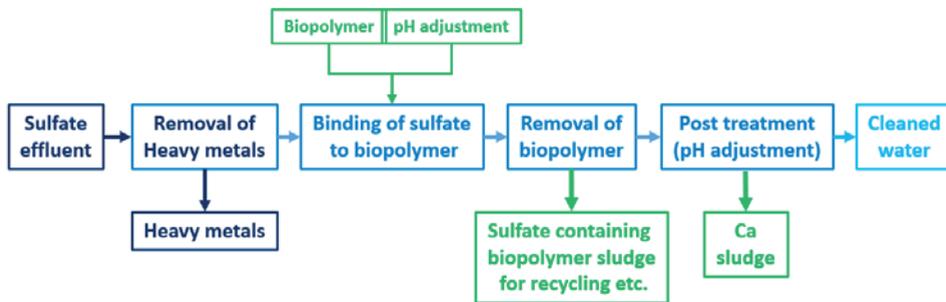
Most of our sulfate containing solutions were taken from mining sites and paper mills in Finland. We also studied samples from Huelva area (Rio Tinto) in southwest Spain and drinking water from Kuopio town. Sulfur concentrations from samples were measured before and after treatment with different adsorbents by using either PANalytical Epsilon 3<sup>XLE</sup>

energy dispersive X-ray fluorescence (EDXRF) spectrometer or S2 Picofox Total Reflection X-ray Fluorescence spectrometer (TXRF, Bruker). Also, ion chromatography methods was tested to determine sulfate concentrations during one pilot session. Reagents here were commercial p.a. quality.

In a typical laboratory scale experiment weighted amount (1-20 g/L) adsorbent was added with stirring to sulfur containing water (800-8000 mL). Reaction pH was controlled during mixing and contact time varied depending on experiments being typically from minutes to an hour. After reaction was completed adsorbent was filtered off and sulfur concentration was measured from the treated solutions and the filtered adsorbent.

### Pilot scale experiments

Sulfate removal has been demonstrated also in pilot scale (ca. 0.25-1.0 m<sup>3</sup>/h) on field using two different water source: 1) metal ore mine dewatering water and 2) non-metal mineral mine infiltration water. Typical flow chart of our pilot experiments are shown in Fig. 2 and typical experimental condition with additional supervisors in Fig. 3.



**Figure 2.** Flow chart of biopolymer based sulphate removal process.  
The sulphate binding step lasts typically 5 to 30 min.

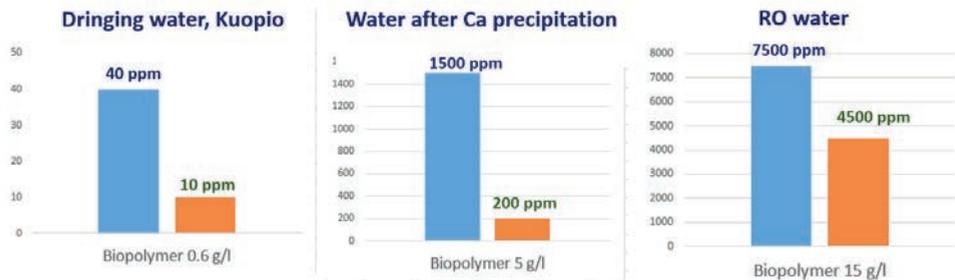
### Result and discussion

Our sulfate removal method (FI and PTC patents pending) is based on the reaction between positively charged functionalities in solid material containing modified sugar units and dissolved negatively charged sulfur substances in acidic waters and subsequent separation of the SO<sub>4</sub><sup>2-</sup> containing solid material from the aqueous medium.

In the beginning of the project we tested in laboratory scale different types of waters containing variable amount sulfur starting from Kuopio town drinking water (40 mg/L) and ending up to RO water (40 000 mg/L). However, mostly we concentrated on water samples 1) obtained from lime precipitation processes and 2) water samples from which sulfate cannot be removed with lime. The results of some of these tests are shown in fig. 4.



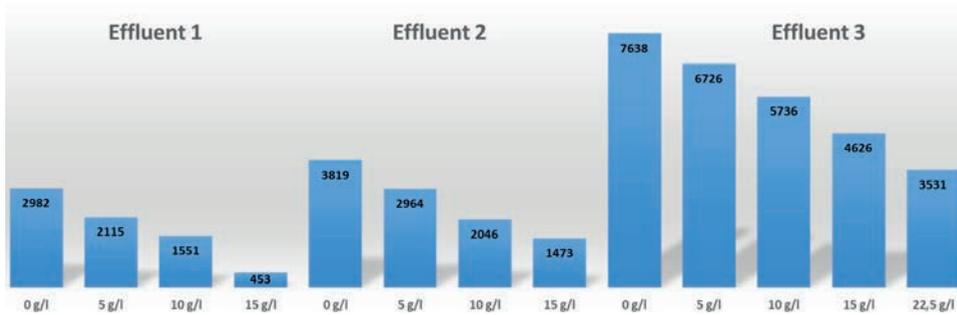
**Figure 3.** Pilot testing of biopolymer based sulfate removal system: part of used pilot equipment (left), pilot supervisors (top right) and sulfate containing biopolymer sludge (bottom right).



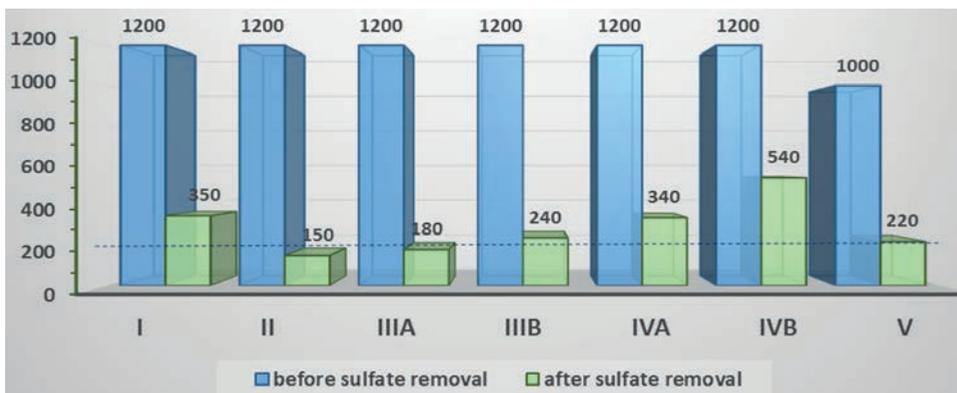
**Figure 4.** Chitosan is effective adsorbent to purify different type of real water and waste water samples regardless of sulfate concentration.

As expected, adsorption is quite directly dose dependent and binding capacity for sulfate compared to adsorbent weight is typically ca. 20%. The tests in Fig. 5 were carried out using Kemwater Flocculator 2000 JAR equipment at 10°C - 14°C with 15 min mixing time.

The pilot tests results shown here were done at a metal mine site using two different dewatering waters (five separate tests). Each test was continuous and lasted 5 to 8 hours. Water flow was varied between 0.25 - 0.4 m<sup>3</sup>/h and retention time in mixing from 22 to 36 min between tests. Under normal adsorption conditions, when pH and adsorbent amount is well controlled there is no problem to reduce sulfate concentration under drinking water limit (see fig. 6 case II, IIIA and V). If pH is not controlled results are poor (see fig. 6 case IV A and IVB).



**Figure 5.** Effect of biopolymer dosing on sulfate removal in three different mining industry effluents.



**Figure 6.** Results of sulfate removal pilot tests. Target  $SO_4^{2-}$  level was 200 mg/L (dotted line).

Based on our laboratory and pilot scale testing, our method has following advances compared to many traditional methods: 1) effective under large sulfate concentration range, 40 – 36 000 mg/L; 2) effective also under low temperatures +4...+50°C; 3) removal of sulfur species is not inhibited by high sodium, potassium, magnesium or calcium concentrations; 4) process is fast and robust; 5) sulfate binding biopolymer can be recycled (>10 times); 6) method is safe for humans and environment, all materials are non-toxic; 7) binding capacity compared to adsorbent weight is high, typically ca. 20%; and 8) cast-off polymer is possible to use as fertilizer.

## Conclusions

The method efficiently removes sulfate from cold and diluted water streams from which sulfate cannot be removed by using gypsum precipitation (sulfate <1500 mg/L) method or from water streams containing high concentrations of sodium. Exceptionally low residual sulfate levels can be reached (sulfate <250 mg/L). Removed sulfate can be recycled: sulfate biopolymer sludge from pilot tests fulfilled the requirements set for harmful substances on the decree of the Ministry of Agriculture and Forestry on fertilizer products 24/11.

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