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Application of ion-exchange resins for removing sulphate ions from acidic solutions

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The removal of sulphate ions from different types of wastewater is an environmental challenge faced by several industrial sectors such as the mining, petrochemical or metallurgical industry. Most of the current existing options are inefficient and economically unviable, particularly for acid mine drainage (AMD), where the low *pH* and high concentrations of heavy metals and sulphates are limiting for these processes. This work is focused on ion-exchange as one of the most common treatment methods for AMD treatment.

Ion-exchange represents a very powerful technology where one or more undesirable contaminants are removed from the aqueous environment by exchange with another substance. The ideal ion-exchange solution for sulphate reduction is one that combines both anionic and cationic resins. The paper presents the results from ion-exchange experiments by the synthetic ion-exchange resin and the AMBERLITE MB20 for SO_4^{2-} removal from a model solution.

The efficiency of the AMBERLITE MB20 resin for SO_4^{2-} removal from the model solution H_2SO_4 was higher than of the PUROLITE MB400, and its efficiency decreased with increasing the concentration of sulphates from 86.6 % for the concentration 100 mg/L to 66.9 % for the concertation 1000 mg/L.

Key words: sulphates, ion-exchange, ion-exchange resin.

Introduction

Opencast mining activities have a serious environmental impact on soils and water streams, having generated millions of tons of sulphide-rich tailings [1]. Another most serious negative impact represents acid mine drainage (AMD), whether in the form of direct discharges or as a leachate from landfills [2].

Acid mine drainage (AMD) is a serious environmental problem resulting from the weathering of sulphide minerals, such as pyrite (FeS_2) and its polymorph marcasite (α-FeS). It is characterized by a low *pH* value and high levels of sulphate and metals [3]. In the treatment of AMD, little attention has been focused on the mitigation of the dissolved sulphate; this may be attributed to its lower environmental risks and regulatory standards when compared to those for acidity and dissolved metals [4].

Sulphate is invariably present in groundwater, but its mobility in natural systems is restricted by its conversion to organo-sulphur compounds and by precipitation with some inorganic cations. This sulphate is discharged into water from geological strata with the gypsum and anhydrite content, from acid mine waters (AMD) and from industrial wastewater. Although sulphate's health effects are relatively short-term, it causes acute diarrhoea and dehydration at concentrations of 1000–1200 mg/L [4]. The selection of treatment processes was based on applicability to sulphate removal and the availability of data on sulphate removal and costs. Some processes have been proposed for AMD treatment applying ion-exchange resins [5].

The removal of sulphate ions constitutes one of the main challenges in the mining, metallurgical and chemical industries. Sulphate removal from aqueous streams is by far one of the most difficult and onerous tasks in these industries, and most of the existing processes are inefficient and costly [6].

There are several possibilities to remove sulphates from water. The most known are precipitation, reverse osmosis, nanofiltration and sorption including biosorption. In the biosorption study [7], seven types of bio-adsorbents were chosen: poplar, hornbeam, ash, oak, cherry, pine, and spruce wood sawdust. Hornbeam decreased the concentration of a sulphate at the value less than 0.5 mg/L in a solution of $CuSO_4$ and $ZnSO_4$, representing the efficiency of 99.0 %. In solutions of $FeSO_4$, the sulphate was removed by ash and cherry with high efficiencies. Biological methods are also very popular. The treatment of AMD by SRB (sulphate-reducing bacteria) is based on the ability of SRB to reduce sulphates to hydrogen sulphide. In the study [8], using the cultivation of sulphate-reducing bacteria and a complete matrix with a nutrient medium, an about 40 % efficiency of sulphate elimination (or reduction) and in the case of a medium without sulphates the 100 % efficiency were achieved.

Ion-exchange is a very powerful technology to remove contamination from water and other solutions. Undesirable ions are replaced by others which do not contribute to the environment contamination. The method is technologically simple and enables an efficient removal of even traces of pollutants from solutions [9]. A wide range of materials is available for the ion-exchange treatment. These materials are available in a variety of forms, they have widely different chemical and physical properties and can be naturally occurring or synthetic. The type of the material to be used is selected based on its ability to remove undesirable ions and to control the *pH* [10]. To minimize the disposal costs, in any process for the removal of pollutants from a liquid waste it is important to minimize the volume of the secondary waste to be conditioned and disposed of in a final repository. Environmental aspects are also very important, since the regulations on discharges are becoming increasingly more stringent. Highly selective synthetic ion-exchangers play an important role in solving these problems [11].

This work studies the sulphate removal by two synthetic ion-exchange resins PUROLITE MB400 and AMBERLITE™ MB20 which have not yet been tested for AMD treatment.

Materials and methods

For the study of SO_4^{2-} ions removal from model solutions by the ion-exchange process, two inorganic ion-exchange resins – PUROLITE MB400 (No. 1) and AMBERLITE MB20 (No. 2) – were used.

PUROLITE MB400 (Fig. 1) is a high-quality resin mixture for the direct purification of water. It is suitable for use in regenerable or non-regenerable cartridges and in large ion-exchange units. The passage of water at recommended flow rates through the resin as supplied can achieve an almost complete reduction of the total dissolved solids. The residuals produce the average conductivity values of about 0.1 μs/cm for a major portion of the service run which may be extended depending upon the final water quality acceptable. The equivalent volumes of ultra-pure water may be obtained after regeneration, but only if sufficient regenerant quantities are employed to achieve the percentage conversion levels equivalent to those of the "as supplied" resin. The generally acceptable capacity and quality are obtained economically at a lower regeneration. The theoretical total combined capacity in the regenerated form is 0.55 eq/L.

Fig. 1. PUROLITE MB400 resin.

The AMBERLITE™ MB20 resin (Fig. 2) is an ionically equilibrated mixed bed resin. It is a fully regenerated, ready-to-use mixture of a strong acid cation-exchanger with a strong base type 1 anion-exchanger. The AMBERLITE MB20 resin has been developed for the production of high-purity water. It can be used for all applications requiring totally demineralised water free of silica and of carbon dioxide.

Fig. 2. AMBERLITE MB20 resin.

Single synthetic solutions containing sulphate anions were prepared from sulphuric acid puriss. p.a. 93 %.

Working solutions were prepared by further dilution to the desired initial concentration of the sulphates. The initial *pH* of each solution was not adjusted. The anion removal efficiency by the ion-exchange process was tested at a laboratory temperature (23 ± 0.2 °C) under static conditions.

1 g of resins No. 1 and 1 g No. 2 were mixed with 100 mL of each solution. After 24 hours of reaction the resins were removed by filtration through a laboratory filter paper for the qualitative analysis. The concentrations of ions before and after the experiments were determined in filtrates by the X-ray fluorescence method, Spectra iQ II (Ametek, Germany). The *pH* values were determined with a *pH* meter inoLab pH 730 (WTW, Germany). All data are presented as the mean ± SD of triplicate results.

The percentage of efficiency (%) was calculated using the following equation:

$$Efficiency = \frac{(C_0 - C_e)}{C_0} x100\% ; \qquad (1)$$

where C_0 – initial concentration, mg/L; C_e – concentration after sorption, mg/L.

Results and discussion

The initial and residual concentrations of sulphate removal by resin No. 1 from model solutions are presented in Table 1.

Table 1. The initial concentration of SO_4^{2-} and its concentration after 24 h of contact with the PUROLITE MB400 resin; H_2SO_4 solutions; batching 1 g/100 mL

	Concentration of SO_4^{2-}, mg/L		
Initial	100	500	1000
After 24 hours of contact	25.4 ± 3.3	84.9 ± 7.1	519.7 ± 17.4

The efficiency of the PUROLITE MB400 resin for sulphate removal from the model solution H_2SO_4 was 74.6 % for the concentration 100 mg/L, 83.2 % for the concentration 500 mg/L and 48.03 % for the concertation 1000 mg/L.

The initial and the residual concentrations of sulphate removal by resin No. 2 from model solutions are presented in Table 2.

Table 2. The initial concentration of SO_4^{2-} and its concentration after 24 h of contact with the AMBERLITE MB20 resin; H_2SO_4 solutions; batching 1g/100 mL

	Concentration of SO_4^{2-}, mg/L		
Initial	100	500	1000
After 24 hours of contact	13.4 ± 1.9	67.1 ± 7.8	330.8 ± 12.3

The efficiency of the AMBERLITE MB20 resin for SO_4^{2-} removal from the model solution H_2SO_4 was 86.6 % for the concentration 100 mg/L, 85.5 % for the concentration 500 mg/L and 66.9 % for the concertation 1000 mg/L.

One can see that the ion-exchange resin AMBERLITE MB20 seems to be more effective for sulphate removal in these acidic solutions. A comparison of removal efficiencies is presented in Fig. 3.

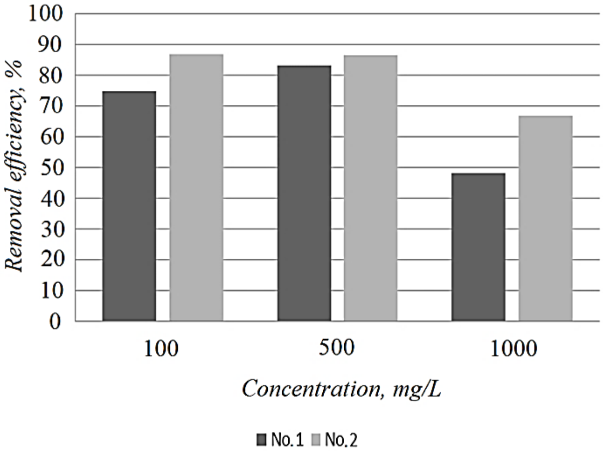

Fig. 3. Comparison of removal efficiencies.

The initial and the final *pH* values after the ion-exchange process of the H_2SO_4 solution are presented in Tables 3 and 4. One can see that both adsorbents caused an increase of the *pH* values in these solutions.

Table 3. The initial *pH* values and its values after 24 h of contact with the PUROLITE MB 400 resin

Initial concentration of SO_4^{2-}, mg/L	100	500	1000
Initial *pH*	2.45	1.95	1.54
pH after 24 hours of contact	6.42 ± 0.3	2.96 ± 0.4	1.98 ± 0.3

Table 4. The initial *pH* values and the *pH* values after 24 h of contact with the AMBERLITE MB20 resin

Initial concentration of SO_4^{2-}, mg/L	100	500	1000
Initial *pH*	2.45	1.95	1.54
pH after 24 hours of contact	7.88 ± 0.4	3.5 ± 0.5	2.11 ± 0.2

The *pH* is one of the most important parameters to control the uptake of sulphates from aqueous solutions. In both solutions the ion-exchange resins PUROLITE MB400 and AMBERLITE MB20 caused an increase of the initial *pH* values (see Tables 3 and 4).

The increase of *pH* was caused by the OH^- ions exchange from the resin with sulphate ions and their release into the solution.

According to the presented results, AMBERLITE MB20 will be used as a potential resin for sulphate removal under dynamic conditions using a column setup with the aim of its using for a partial acid mine drainage treatment.

An appropriate combination of sorption and ion-exchange materials in this case has a high potential for a complex treatment of AMD in real conditions.

Conclusions

1. This study has shown the possibility of using two synthetic ion-exchange resins PUROLITE MB400 and AMBERLITE MB20 for SO_4^{2-} removal from a model acidic solution.
2. In general, AMBERLITE MB20 exhibits better ion-exchange properties than PUROLITE MB400.
3. The decrease of the SO_4^{2-} concentration using AMBERLITE MB20 is about 86.6 %, 85.5 % and 66.9 % for solutions containing SO_4^{2-} ions at the initial concentration of 100 mg/L, 500 mg/L and 1000 mg/L, respectively.
4. The obtained results show that both types of ion-exchange resins could be used for sulphate removal in acidic conditions and for AMD treatment.

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JONŲ MAINŲ DERVŲ PRITAIKYMAS SULFATO JONAMS PAŠALINTI IŠ RŪGŠČIŲ TIRPALŲ

Santrauka

Sulfato jonų pašalinimas iš užteršto vandens (nuotekų) yra aplinkosaugos problema, su kuria susiduria įvairios pramonės šakos: kasyba (kalnakasyba), naftos ar metalurgijos pramonė. Labiausiai paplitę būdai neveiksmingi (neefektyvūs) ir ekonomiškai įgyvendinami (perspektyvūs), ypač valant rūgščius telkinius, kurių mažas *pH* ir didelės sunkiųjų metalų ir sulfatų koncentracijos. Šiame darbe pateikiama, kad jonų mainų metodas, kuris yra vienas labiausiai paplitusių apdorojimo būdų, gali būti panaudotas rūgščių nuotekoms valyti.

Vykstant jonų mainams (metodas – tai labai efektyvi technologija), vienas ar keli nepageidaujami teršalai pašalinami iš užteršto vandens (nuotekų), sukeičiant juos su kitomis medžiagomis. Sulfatų kiekiui sumažinti galima kartu naudoti anijonines ir katijonines dervas. Darbe sulfato jonams pašalinti iš modelinio H_2SO_4 tirpalo buvo panaudotos dvi sintetinės jonų mainų dervos PUROLITE MB400 ir AMBERLITE MB20. Gauti rezultatai parodė, kad AMBERLITE MB20 derva yra veiksmingesnė šalinant sulfato jonus iš modelinio rūgštaus tirpalo nei PUROLITE MB400 derva. Tačiau sulfato jonų koncentracijai padidėjus nuo 100 mg/l iki 1000 mg/l, šis efektyvumas sumažėja nuo 86,6 % iki 66,9 %.

Reikšminiai žodžiai: sulfatai, jonų mainai, jonų mainų derva.