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Study of sulphate ions removal from acidic waters using ion exchange resin

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Abstract

Acid Mine Drainage (AMD) is the most common pollution related to mining. It consists of an aqueous solution containing high metals and sulphate concentration, which impact surface and groundwater and lead to serious environmental problems. Low pH and high concentrations of heavy metals and sulphates are limiting for many various treatment technologies in these acidic waters. Ion - exchange is a very powerful technology where one or more undesirable contaminants are removed from water by exchange with another non-objectionable or less objectionable substance. Many of materials for the ion - exchange treatment is available in a variety forms and have widely differing chemical and physical properties.
The paper deals with study of ion – exchange process under static and dynamic conditions for sulphate removal from acidic waters using ion - exchange resin with the aim to apply the results for treatment of acid mine drainage.
Two types of experiments were performed under static and dynamic conditions. The efficiency of AMBERLITE MB20 resin for SO_4^{2-} removal from model solution H_2SO_4 under static conditions decreases from 86.6 % for concentration 100 mg/L to efficiency 66.9 % for concertation 1000 mg/L. The efficiency for sulphate removal from AMD was only 41%. The study also presents three experiments under dynamic conditions, one with new ion – exchange resin a two experiments with its regenerated form. It was find that ion-exchange capacity decreases numbers of regeneration steps.

Key words: sulphates, ion – exchange, waste water treatment, acidic solution.

1 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 leachate from landfills [2]. 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]. Sulphate is a major anion occurring in natural water and industrial effluent, such as inorganic chemical industry waste water and acid mine drainage. 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 gypsum and anhydrite content, from acid mine waters (AMD) and from industrial wastewater [4].

Naturally, it mainly originates from the processes of chemical weathering of sulphur containing minerals and the oxidation of sulphides and sulphur. Sulphate is nontoxic, and sulphur is a necessary nutrient element for many kinds of living systems, however, high sulphate concentrations can cause unbalance of the natural sulphur cycle [5] and also endanger human health when excessive ingestion [6]. Recently, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Adsorption has become one of the alternative treatments, in recent years the search for low-cost adsorbents that have metal-binding capacities has intensified [7]. Some processes have been proposed for AMD treatment applying ion exchange resins [8]. Although many techniques can be employed for the treatment of inorganic effluent, the ideal treatment should be not only suitable, appropriate and applicable to the local conditions, but also able to meet the maximum contaminant level standards established [9]. 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 contamination of the environment. The method is technologically simple and enables efficient removal of even traces of pollutants from solutions [10]. A wide range of materials is available for the ion–exchange treatment. These materials are available in a variety forms, they have widely different chemical and physical properties and can be naturally occurring or synthetic. The type of material to be used is selected based on its ability to remove undesirable ions and to control pH [11].

This study showed the possibility of ion exchange resins AMBERLITE MB20 for sulphate removal under static and dynamic conditions.

2   Material and method

For study of SO_4^{2-} removal from acidic waters, ion exchange resin AMBERLITE MB20 was used. For these study two types of experiments was prepared: removal of SO_4^{2-} ions from model solutions and AMD under static conditions and removal of SO_4^{2-} from model solution under dynamic conditions.

AMBERLITE MB20 resin 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. AMBERLITE MB20 resin has been developed for the production of high purity water. It can be used for all applications requiring totally demineralized water, free of silica and of carbon dioxide. If required, AMBERLITE MB20 resin can be regenerated after exhaustion.

2.1 Static conditions experiments

Model solutions containing sulphate anions were prepared from sulphuric acid, puriss. p.a., 93%. Working model solutions of concentration 1000, 500 and 100 mg/L SO_4^{2-} ions were prepared by next dilution to the desired initial concentration of sulphates. The initial pH of each model solution was not adjusted. 1 g of resin AMBERLITE MB20 was mixed with 100 ml of each solutions and AMD. After 24 hours' reaction time resin were removed by filtration through a laboratory filter paper for quatitative analysis. Concentrations of ions before and after the experiment in model solution and AMD were determined by colorimeter DR890 (HACH LANGE, Germany). pH values were determined by pH meter inoLab pH 730 (WTW, Germany). The cations removal efficiency by ion-exchange process was tested at laboratory temperature (23 ± 0.2 °C).
The percentage of efficiency (%) was calculated using the following equation:

$$Efficiency = \frac{(C_0 - C_e)}{C_0} \; x \, 100\% . \tag{1}$$

C_0 – initial concentration
C_e – concentration after sorption

This resin was also used in AMD. Sample of AMD containing a high level of sulphates and heavy metals (concentration of monitored pollutants are listed in Table 1) was taken from the shaft Pech (Smolnik, Slovakia).

Table 1: Properties of experimental AMD samples

Initial concentration mg/L					
pH	Fe	Cu	Al	Mn	SO_4^{2-}
3.93	305	0.86	44.8	24.4	1600

2.2 Dynamic conditions experiments

For the purposes of the experiments a column of borosilicate glass having an internal diameter of 4 cm ending at the bottom of the frit was used. A 50 g of ion exchange resin AMBERLITE MB20 filled the column up to 9 cm. The ion – exchange resin AMBERLITE MB20 served as a filter. Synthetic solution H_2SO_4 containing 1000 mg/L sulphate anions were prepared from sulphuric acid. The solution flowed through the column using a Masterflex C/L dual-channel variable-speed tubing pump with flow 20 ml/min. The effluent was collected at regular intervals for sulphate concentration and pH measurements.

The sulphate removal efficiency by ion exchange process was tested under dynamic conditions at laboratory temperature (23±0.2°C). Concentrations of ions, before and after the experiments were determined by colorimetric method using Colorimeter DR890 (HACH LANGE, Germany) with combination of appropriate reagent. pH values were determined by pH meter inoLab pH 730 (WTW, Germany).

3 Results and discussion

3.1 Static experiments

The initial concentration of SO_4^{2-} in model solutions and concentration after 24h of contact time with AMBERLITE MB20 are presented in Table 2.

Table 2: The initial concentration of SO_4 and concentration after 24h of contact with AMBERLITE MB20 resin; H_2SO_4 solutions; batching 1g/100 mL

Initial concentration SO_4^{2-} mg/L	Initial pH	Concentration SO_4^{2-} after 24 hours contact time mg/L	pH after 24 hours contact time
100	2.45	13.4	7.88
500	1.95	67.1	3.5
1000	1.54	330.8	2.11

The efficiency of AMBERLITE MB20 resin for SO_4^{2-} removal from model solution H_2SO_4 was 86.6 % for concentration 100 mg/L, 86.6 % for concentration 500 mg/L and 66.9 % for concertation 1000 mg/L. As can be seen ion–exchange resin AMBERLITE MB20 seems to be effective for sulphate removal in model solution. It was expected, in comparison to model solution of 100 mg/L, decreasing of the sulphate removal efficiency for the model solution of 500 mg/L. The same results of efficiency can be due to influence of various pH, which is in accordance with data from the literature.

Authors [8] declared decreasing of total exchange capacity of polyacrylic anion exchange resin (Amberlite IRA458) expressed in equivalents per unit resin weight with increasing of pH. This fact was confirmed in our experiments. The figure 1. shows dependence of total exchange capacity of AMBERLITE MB20 resin q on pH.
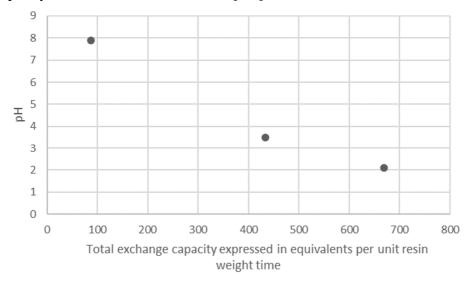

Figure 1: Dependence of total exchange capacity of AMBERLITE MB20 resin q on pH.

The initial concentration of SO_4^{2-} in AMD and concentration after 24h contact time with AMBERLITE MB20 resin is presented in Table 3.

Table 3: The concentration after 24h contact time with AMBERLITE MB20 resin

Initial concentration SO_4^{2-} mg/L	Initial pH	Concentration SO_4^{2-} after 24 hours contact time mg/L	pH after 24 hours contact time
1600	3.93	952	3.1

The efficiency for sulphate removal from AMD was only 40.5%. %. It can be affected by ion exchange processes with the other pollutants present in these acidic waters.

3.2 Dynamic experiments

The dependence of sulphate concentrations after contact time with ion – exchange resin under dynamic condition is presented in fig. 2. The initial concentration of sulphate in model solution H_2SO_4 was 1000 mg/L.
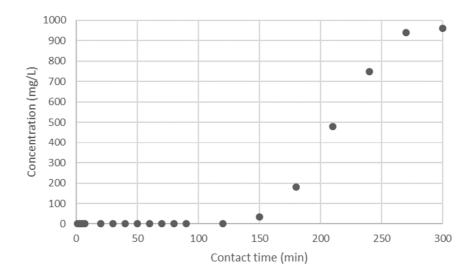

Figure 2: Dependence of SO_4^{2-} concentration on contact time

The efficiency of the ion – exchange resin for sulphate removal from model solution H_2SO_4 was ~ 100% at the beginning of the experiment. As can be seen in the fig. 3, the ion – exchange resin begins to deplete after 150 minutes of flow of model solution through the column. Efficiency after 150 minutes was 96.7% and then began to decrease rapidly. The AMBERLITE MB20 ion exchange resin was completely exhausted after 300 minutes.

After these experiments, the resin was first time regenerated with NaOH solution at a concentration of 1 mol/L. The influence of the regenerated ion – exchange resin on sulphate removal is presented in fig.3.
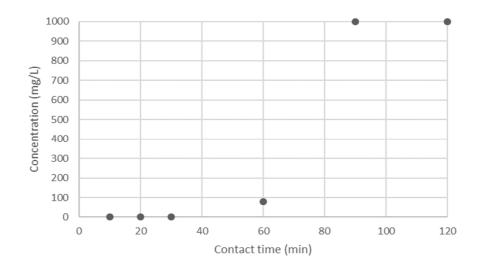
Figure 3: Concentration of SO_4^{2-} depends on contact time after first regeneration

As can be seen in the fig. 4 the ion – exchange resin begins to deplete after 60 minutes of flow of model solution through the column. The efficiency after 60 minutes was 92% and decreases. The regenerated ion – exchange resin AMBERLITE MB20 is completely exhausted after 90 minutes.

After first regeneration the resin was second time regenerated with NaOH solution at a concentration of 0,1 mol/L. The concentration sulphates after passing through a second regenerated ion – exchange resin is shown in fig.4.
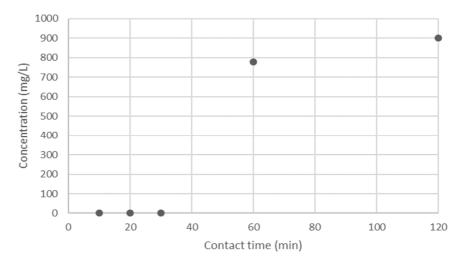

Figure 4: Dependence of SO_4^{2-} concentration on contact time with the second regenerated resin

As can be seen in the fig. 5 the capacity of the ion – exchange resin regenerated second time begins to deplete after 30 minutes of flow of model solution through the column. The efficiency after 60 minutes was only 22% and decreases. The ion – exchange resin AMBERLITE MB20 was completely exhausted after 90 minutes.

4 Conclusion

This study showed the possibility of ion exchange resins AMBERLITE MB20 for sulphate removal under static and dynamic conditions. For statics experiments model solutions with concentrations of 1000 mg/L sulphate anions and experimental sample of AMD was used. The efficiency of AMBERLITE MB20 resin for SO_4^{2-} removal from model solution H_2SO_4 under static conditions was 86.6 % for concentration 100 mg/L, 85.5 % for concentration 500 mg/L and 66.9 % for concertation 1000 mg/L. The efficiency for sulphate removal from AMD was 41%.

Dynamics experiments were performed with the acidic model solutions with concentration of 1000 mg/L sulphate anions prepared from 93% sulphuric acid and tested at laboratory temperature (23±0.2°C) under dynamic conditions. The paper described three experiments under dynamic conditions, one with new ion – exchange resin a two experiments with its regenerated form. It was find that during the first experiment ion-exchange resin begins to deplete after 150 minutes and was completely exhausted after 300 minutes of flow of model solution through the column. After first regeneration ion – exchange resin begins to deplete after 60 minutes and was completely exhausted after 90 minutes. The second regeneration caused the capacity of ion- exchange resin depletion also after 90 minutes, but the decreasing of its efficiency starts sooner, after 30 minutes.

The ion–exchange process seems to be suitable for sulphate removal because of its simplicity, effectiveness, selectivity, and recovery and relatively low cost. These results will be used for study of the sorption capacity and the sorption kinetics of the ion – exchange resins for sulphate removal for acid mine drainage treatment.

Acknowledgements

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