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THE REMOVAL OF SULPHATE IONS FROM MODEL SOLUTIONS AND THEIR INFLUENCE ON ION EXCHANGE RESINS

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ABSTRACT: There is a growing tendency for industries around the globe to diminish the contents of pollutants in industrial wastewaters to an acceptable level. Conventional methods are unfavourable and economically unacceptable, especially for large volumes of wastewaters with a high content of undesirable compounds. In contrast, ion–exchange is a very powerful technology capable of removing contamination from water.

This paper analyses a study of ion exchange in Amberlite MB20 and Purolite MB400 resins after sulphate removal from a model solution. For the characterisation of ion exchange in resins, infrared spectroscopy was used. The IR spectra of both ion exchange resins show a similar composition after adsorption. Experiments that are due to this same used matrix in producing. The efficiency of sulphate ion removal and pH changes were also measured. Amberlite MB20 has proven to be a suitable ion exchange resin due to its high efficiency (about 86%) for the removal of sulphates from solutions with initial concentrations of 100 and 500 mg.L^{-1}, respectively.

KEY WORDS: ion exchange, resins, sulphate, water treatment

No. 2(73) 2020 • pages: 59-70 https://doi.org/10.34659/2020/2/16 JEL: Q25, Q52

Introduction

Sulphates are commonly found in many bodies of water, some of which have concentrations exceeding recommended limits. However, most sulphate discharges are found in industrial wastewaters (Johnson and Hallberg, 2005). These anthropogenic sources are responsible for enhanced concentrations of sulphates, but there are industries such as metallurgy, tanneries, agriculture, and mainly mining that load/burden the aquatic environment with sulphates (Balintova et al., 2012; Macingova and Luptakova, 2012). Water pollution by sulphates is causing an array of problems such as ecological damage, disease, and disorders for living organisms. Sulphates affect people by inducing headaches, digestive problems, diarrhoea and at higher concentrations may be lethal (Fernando et al., 2018).

Acid mine drainage (AMD) is responsible for wide environmental deterioration as a result of the microbial oxidation of iron pyrite ore. The whole process occurs in the presence of water and air, creating an acidic solution that contains a high concentration of different kinds of toxic metals and sulphates. Generally, inhibiting the formation or transportation of AMD from its source to the surrounding environment is the preferable option, but unfortunately, it is not applicable in many affected locations.

Thus, various options are available for remediating AMD, which may be categorised into those that use either chemical or biological mechanisms to neutralise AMD and remove heavy metals and sulphates (Akcil and Koldas, 2006). These include methods such as chemical precipitation, ion exchange, membrane separation, reverse osmosis, electro-dialysis, sorption techniques, and sulphate reducing bacteria (Runtti et al., 2016; Chernysh et al., 2019).

The most commonly used method for sulphate removal is chemical precipitation with soluble barium, magnesium or calcium salts as alternatives, especially for the treatment of wastewaters with high sulphate concentrations. The limitation of sulphate precipitation is due to the high cost of the input materials (Silva et al., 2002). An effective sulphate precipitation process is influenced by a suitable pH, temperature and appropriate stirring intensity (Sánchez-Andrea et al., 2014). Frequently after the final step (filtration), the concentration of sulphate in the filtrate still remains at a level of a few mg.L^{-1} (Balintova et al., 2016). The presence of sulphate in wastewater is often accompanied with pollution with other elements, mainly heavy metals. For this reason, systems for the separation and appropriate removal of solid components are necessary. Filtration using membranes is another possibility, but in the case of this study the significant economic aspect due to the price of the membranes and energy consumption, proportional to the sulphate concentration, must be taken into account (Silva et al., 2002).

Over the last decades, sulphate reducing bacteria was studied as a suitable technique for sulphate removal (Muyzer and Stams, 2008). The disadvantages of biochemical methods are the large areas required for biochemical treatment and the slowness of these processes (Hybska et al., 2017). These processes are based on the ability of anaerobic sulphate, reducing bacteria to reduce the sulphate contents of hydrogen sulphide (Luptakova et al., 2012). The produced H_2S must be pumped out, for example to the bioreactor, because of heavy metals precipitation with hydrogen sulphide that can inhibit the reduction processes. The limitations of biochemical processes are strongly affected with pH values where failure to optimise values inhibits sulphate reducing bacteria or their extinction (Silva et al., 2002; Dolla et al., 2006; Al Zuhair et al., 2008).

There is a tendency for all types of industry to diminish the contents of sulphates in wastewaters to an acceptable level. Compared with other methods, ion exchange provides benefits because either the ions can be completely removed from a solution or substances separated (Dąbrowski et al., 2004). Likewise, we can divide ion exchange resins into two separate groups. The first is designed for selective ion removal and the latter for complete purification of wastewaters. The decision is based on the contamination characteristics and also expected extent of the whole decontamination process. Selectivity is achieved by the application of ion exchangers with a specific affinity to selected ions or groups of cations and anions. During the purification process, the undesirable ion or group is replaced by another one which is neutral within the aquatic environment (Dąbrowski et al., 2004; Fu and Wang, 2011).

Sulphate pollution can be treated with a combination of different methods, but they are often limited. The use of ion exchange is promising due to its capability to reduce sulphate ion to very low concentration levels (Lens et al., 1998). Moreover, its economic impact can be reduced by selecting an appropriate resin and propose proper conditions that maximise the purification process and also improve regeneration after using. Feng et al. (2000) proposed a two-step process for AMD treatment based on metal precipitation in the first step and subsequent sulphate reduction on ion exchange resins Amberlyst A21. Guimarães and Leão (2014) showed a detailed application of the resin Amberlyst A21 for sulphate removal to conclude that the process has positive features that make it a good candidate for these applications (11.6 mg of sulphate on 1 mL of resin). Its adsorption capacity exhibit lower results compared to other resins commercially designed for sulphate removal, but on the other hand, almost 100% of the resin elution was achieved by increasing the pH to 10 and 12 with NaOH solution.

The Ion exchange resins are materials that contain large polar exchange groups that removal ions or molecules between solid and liquid with no substantial change to the solid structure. Sulphate ions in the wastewater interfere heavily to the other ions removal and result in short service runs (Runtti et al., 2018). From this reason must be applied resins capable of removing not only high sulphate concentrations but also other present ions in wastewaters as Amberlite MB20 and Purolite MB400.

The aim of this paper is a study of ion exchange in Amberlite MB20 and Purolite MB400 resins after sulphate removal from acidic model solutions. For the characterisation changes of ion exchange resins, infrared spectroscopy was used. The efficiency of sulphate ion removal and pH changes were also measured.

Research methods

The ion exchange resins, Amberlite MB20 and Purolite MB400, were obtained from a commercial resin supplier in Slovakia and were used for static adsorption experiments. Purolite MB400 is a mixture of high-quality ion-exchange resin used for water purification. It is suitable for usage in both regenerable and non-regenerable cartridges and large ion exchange units. The mixture is composed of an ion-balanced mixed resin in a ratio of 40% catex to 60% anex. Amberlite MB20 is an ion-balanced mixed resin containing 38-44% catex and 56-62% anex. This resin was developed for the preparation of high purity water where 97% of the ionex resin has a grain <0.3 mm. It is also most commonly used for the preparation of demineralised water free of silica and carbon dioxide.

1 g of resin was mixed with 100 mL of each model solution containing 100, 500, and 1000 mg.L^{-1} of sulphates, respectively (laboratory temperature t = 20±1 °C). The model solutions were prepared by concentrated sulphuric acid and deionised water. The reaction was carried out under static conditions in a batch adsorption system with an interaction time of 24 h. After absorption, resins were filtrated. Colorimetric method (Colorimeter DR 890, HACH company, Loveland, USA) was applied for the determination of residual sulphate concentration. The pH values of solutions were also measured with a pH meter inoLab pH 730 (WTW, Weilheim, Germany). The IR spectra of resins before and after adsorption experiments were studied for the characterisation of present functional groups that can be responsible for sulphate binding. Measures were performed by an Alpha spectrometer with a Platinum-ATR module (Bruker Optik, Ettlingen, Germany).

In addition, the efficiency of ion removal was calculated using the following equation (Eq. 1):

$$\eta = \frac{(c_0 - c_e)}{c_0} \cdot 100\,, \tag{1}$$

where:
η – sorption efficiency [%],
c_o – the initial concentration of appropriate ions [mg.L^{-1}],
c_e – equilibrium concentration of ions [mg.L^{-1}].

All adsorption experiments were performed in triplicate under batch conditions, and the results are expressed as arithmetic mean values with standard deviations.

Results of the research

Infrared spectra

The ability of ion exchange could be influenced by different factors but is closely linked to selective or multi-componential removal of pollutants. The functional groups of Amberlite MB20 and Purolite MB400 ion exchange resins were determined using Fourier Transform Infrared Spectroscopy (FTIR). The IR spectra of resins before and after adsorption experiments are shown in Figures 1 and 2. The FTIR spectrum of the studied resins revealed several major intense bands which could be observed within wavenumbers of 3,600–2,800 cm^{-1}; and 1,750–650 cm^{-1}.

The FTIR spectrum of Amberlite MB20 resin recorded before and after sulphate adsorption is shown in figure 1. The strong broad band at around wavenumbers 3,353 cm^{-1} and 1,634 cm^{-1} was assigned to the hydroxyl functional groups (Demcak et al., 2017). The peak intensity at wavenumber around 1,634 cm^{-1} on the adsorbed resins shows that the -OH functional groups was released into the solution but the peak at wavenumber about 3,353 cm^{-1} was only slightly decreased due to the natural water adsorption process. The end of the strong broad peak centred at a wavenumber around 3,353 cm^{-1} could also be attributed to amine (–NH) functional groups. The deformation bands at wavenumber 2,928 cm^{-1} were due to the stretching mode of C–H (Nguyen et al., 2010; Kovacova et al., 2019). The three bands that followed each other at 1,599; 1,450 and 1,411 cm^{-1} are assigned to the ring vibration of benzene rings, which also contribute to bending observed at wavenumbers 830 and 773 cm^{-1} assigned to an out of plane ring C–H bonding vibrations (Merdivan et al., 2001). The deformation peak at wavenumber 1,357 cm^{-1} could be attributed to C–H vibrations of the aliphatic group. The band at 1,150 cm^{-1} was assigned to the vibration involving the ester oxygen and the next two carbons attached to it in the hydrocarbon chain. Amberlite MB20 could be containing ester group O–C=O as all esters give IR bands at approximately 1,700; 1,200; and 1,100 cm^{-1} wavenumbers. Ghosh et al. (2015) found that the peaks at wavenumbers 1,031; 1,003; and 667 cm-1 belong to the presence of $–SO_3H$ groups in the catex component of the resin. On the other hand, they observed that the strong deformation at 890 cm^{-1} is due to the presence of $–N(CH_3)_3$ group in the annex component of resin.

In figure 2 the IR spectra of Purolite MB400 before and after the sorption experiment are depicted. In comparison with Amberlite MB20, IR spectrum reveals changes in the composition and slight shifting of band positions of the same functional groups. The spectrum exhibits a band at 2,926 cm^{-1} ascribed to the asymmetric stretching modes of aliphatic C–H groups but also presented symmetrical C–H stretching at wavenumber 3,032 cm^{-1}. The stretching vibrations observed at wavenumber 2,652 cm^{-1} could be attributed to OH bonded to $N(CH_3)_3$. The four bands that following each other at 1,612; 1,512; 1,478 and 1,454 cm^{-1} are assigned to ring vibration of benzene rings, which also contain a contribution due to bending observed at 923 and 834 cm^{-1} assigned to the out of plane ring C–H bonding vibrations. The peak at 1,089 cm^{-1} could represent the content of an ester group O–C=O (Kerkez et al., 2012; Ghosh et al., 2015). Deformation vibrations of C–H out-of-plane functional groups of monosubstituted benzene rings was observed at wavenumber 976 and 857 cm^{-1} (Kerkez et al., 2012; Lazar et al., 2014; Ghosh et al., 2015).

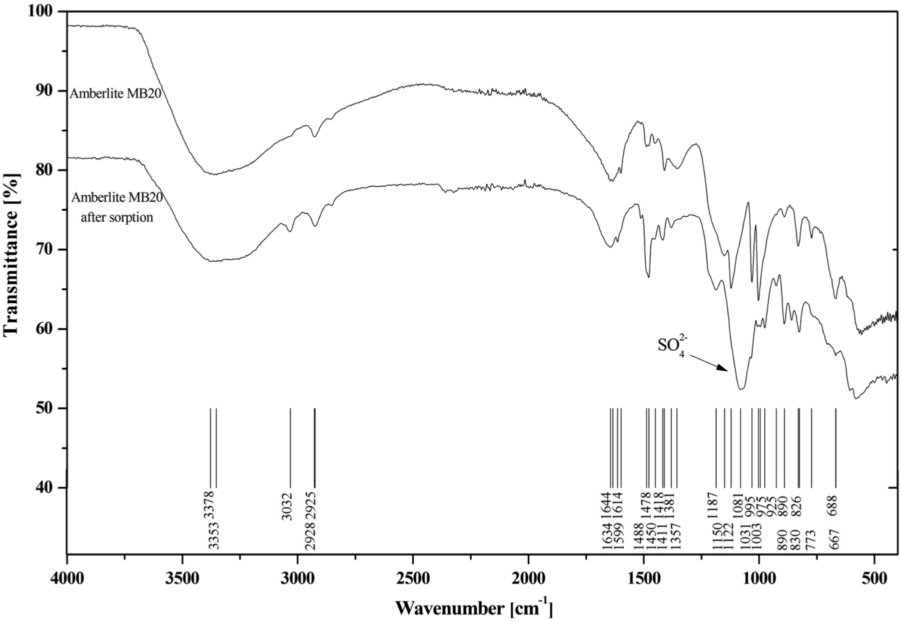

Figure 1. Infrared spectra of Amberlite MB20 before and after sorption experiments

Source: author's work.

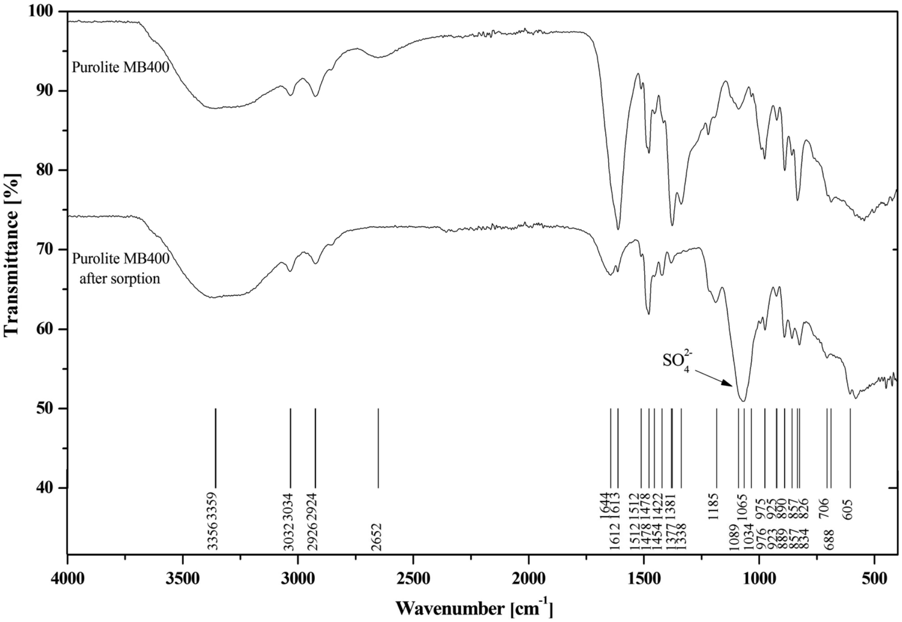

Figure 2. Infrared spectra of Purolite MB400 before and after sorption experiments

Source: author's work.

A difference was observed between the FTIR spectrum of both resins before and after sulphate adsorption. The strong broad band of OH functional groups increased due to water adsorption in resins. The sulphate sorption revealed symmetrical aliphatic C-H groups in the structure of the Amberlite MB20 resin around 3,032 cm^{-1} wavenumber. In both resins, significant changes were observed at wavenumbers between 1,500 to 1,300 cm^{-1} with ring vibration of benzene rings observed at (1,450 and 1,411 cm^{-1}) and C–H vibrations of the aliphatic group at (1,357 cm^{-1}). Anew wide band with a double-peak at wavenumber 1,187 cm^{-1} and 1,081 cm^{-1} (Amberlite MB20) and 1,183 cm^{-1} and 1,065 cm^{-1} (Purolite MB400) were observed. These deformations are visible for both spectra and are characteristic for the sulphate functional group that was adsorbed on both resins in the process of ion exchange. Clearly evident from figures 1 and 2, the IR spectra after sulphate adsorption are almost identical due to the same matrix used on for the production of the studied resins.

Ion exchange study

Results of sorption experiments for model solutions with different sulphate concentrations are shown in Table 1. The selected ion exchange resins used in these sorption experiments were capable of removing the sulphate from the solutions. Amberlite MB20 exhibits a similar efficiency (86.6%) of sulphate removal from the model solution with sulphate concentrations of 100 and 500 mg.L^{-1}. In the model solution with a sulphate concentration of 1000 mg.L^{-1}, the efficiency of sulphate removal was reduced to 70%. Table 1 presents the efficiency of sulphate removal using Purolite MB400 solutions, where the best efficiency (84.9%) of sulphate removal from the model solution with the initial concentration of 500 mg.L^{-1} was achieved. At the 1,000 mg.L^{-1} level of sulphate, Purolite MB400 reached an ion removal efficiency of only 48.0%. Both used ion exchange resins exhibit a suitable effect in experiments for sulphate removal, but have a limited absorption capacity as was observed in the case of Purolite MB400 at the higher level of sulphate in the model solution.

Based on the results of FTIR analysis and Ion exchange experiments, we can suppose weak base anion resins character that is suitable for sulphate removal. On the other hand Runtti et al. (2018) mention, that ion exchange may not be suitable as a primary technology, but it has potential to be used in combination with other processes like chemical precipitation. Robertson and Rohrs (1995) show the ion exchange processes could be used as an alternative for chemical precipitation or as a post-treatment process to lime precipitation. Additionally, the technique may also serve as a suitable pre-treatment method. For example, Robertson et al. (1993) found that combination the gypsum precipitation and ion exchange enhance the efficiency of sulphate removal from 75.3 to 97.5%.

As shown in table 1, changes of pH values were also observed during batch experiments. In all cases, both resins influenced increasing pH values. As is clearly observed from IR spectra after the sorption experiment, the deformation peak at wavenumber about 1,644 cm^{-1} represents the hydroxyl functional group and confirmed weak base anion resins character. In both cases, the intensity of the deformation peak decreased (significantly at ion exchange resin Purolite MB400). This was caused due to ion exchange between the hydroxyl functional group (released to model solutions) and sulphate ions (caught on ion exchange resins). With increasing, initial sulphate concentrations in model solutions, less pronounced pH changes were also observed (Holub et al., 2014).

Guimarães and Leão (2014) study the utilisation of a weak base resin for sulphate removal confers the advantage of easy elution via pH as an important parameter in the treatment of sulphate-loaded waters is elution resin. Although this adsorption capacity is low compared to strong base resins, almost 100% resin elution is easily accomplished by increasing the pH to 10 and 12 with sodium hydroxide solutions. Conversely, although chloride was also loaded, it was later desorbed as the bed became saturated with sulphate, which had a higher affinity for the resin.

Table 1. Results of the sorption experiments with ion exchange resins for the sulphate removal from the model solutions

	Input values of model solutions at different sulphate concentration								
	=100 mg.L^{-1}; pH= 2.5			=500 mg.L^{-1}; pH= 2.0			=1000 mg.L^{-1}; pH=1.5		
Ion exchange resins	η		pH	η		pH	η		pH
	[mg.L^{-1}]	[%]		[mg.L^{-1}]	[%]		[mg.L^{-1}]	[%]	
Amberlite MB20	13.4±0.20	86.6	7.9	67.1±0.83	86.6	3.5	330.8±1,44	66.9	2.1
Purolite MB400	25.4±0.06	74.6	6.4	84.9±0.26	83.0	3.0	519.7±0.64	48.0	2.0

Source: author's work.

Conclusions

This study shows that using ion exchange resins Amberlite MB20 and Purolite MB400 for sulphate removal from model solutions is applicable. Based on experimental results, Amberlite MB20 was a more effective adsorbent than Purolite MB400. The efficiencies of both ion exchange resins were similar (about 80%) for sulphate removal from model solutions with the lower concentrations (100 and 500 mg.L^{-1}). At a concentration of 1,000 mg L^{-1}, the efficiency of Amberlite MB20 for sulphate removal from the model solution was about 68% in comparison to Purolite MB400 (only 48%).

It was observed that there is a difference between the FTIR spectra of both resins before sulphate adsorption. The IR spectra after sulphate adsorption are almost identical due to the same matrix used in the production of the studied resins. Despite the fact that Purolite MB400 contains more kinds of functional groups, Amberlite MB20 exhibited better results for sulphate removal.

The FTIR and ion exchange experiments show weak base anion resins character. Despite the lower adsorption capacity compared to strong base resins this property is a promising potential of full regeneration resin by NaOH solution.

Acknowledgements

This work has been supported by the Slovak Grant Agency for Science (Grant No. 1/0419/19) and Slovak Grant Agency for Science (Grant No. 1/0326/18).

The contribution of the authors

Stefan Demcak – 40% (conceived and designed the experiments, performed the experiments, analysed the data, wrote the paper; measured and analysed the data from IR spectroscopy).

Magdalena Balintova – 30% (discussed and coordinated the research activities and paper structure; supervised the paper and made the final corrections of the paper).

Marian Holub – 30% (conceived and designed the experiments, performed the experiments, analysed the data, wrote the paper; measured and analysed the data from the colorimetric method).

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