Study of Changes of Ion Exchange Resins after Sulphate Removal from Model Solutions

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Nowadays is a tendency for the world industry to diminish down contents of pollutants in industrial wastewaters to acceptable level. Conventional methods as chemical precipitation are unfavourable especially for large volumes of wastes with content of heavy metal. Ion–exchange is a very powerful technology to remove contamination from waters. This method is technologically simple and enables efficient removal of even traces of pollutants from solutions. 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 pH control. Compared with other usual methods ion exchange provides advantages as recovery of metal value, selectivity, less sludge volume produced. From these reasons is the using of ion exchange is a suitable method due to its ability to sulphate removal from wastewaters.

Paper deals with a study of changes of ion-exchange resins Amberlite MB20 and Purolite MB400 after sulphate removal from model solution. For characterization of ion-exchange resins changes, infrared spectroscopy was used. The IR spectra of both used ion exchange resins shows almost similar composition after adsorption an experiments that are due to this same used matrix in producing. Efficiency of sulphate ions removal and pH changes were also measured. Amberlite MB20 has been proven as suitable ion exchange resin for sulphate removal due to efficiency of ion removal about 86 % from sulphate concentrations 100 and 500 mg.L^{-1} respectively.

1. Introduction

Sulphate is a common constituent of many natural waters and wastewaters, and is sometimes present in high concentrations. The most of sulphate discharges have an origin in the 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 the aquatic environment with sulphates (Balintova et al., 2012; Macingova and Luptakova, 2012). Acid mine drainage (AMD) are causing the wide environmental pollution resulting from the microbial oxidation of iron pyrite ore in presence of water and air, affording an acidic solution that contains toxic metal ions and sulphates. Preventing the formation or the migration of AMD from its source is generally considered to be the preferable option, although this is not feasible in many locations. There are various options available for remediating AMD, which may be divided into those that use either chemical or biological mechanisms to neutralise AMD and remove of heavy metals and sulphates (Akcil and Koldas, 2006).

The water pollution by sulphates is causing various serious damages, diseases, and disorders for living organisms. For human bodies sulphates can cause headaches, digestive problems, diarrhoea and at the higher concentrations of sulphates they may be lethal dose (Fernando et al. 2018). There are a lot of physic-chemical and biochemical methods for sulphate removal such as chemical precipitation, ion-exchange, membrane separation, reverse osmosis, electrodialysis, sorption techniques, and sulphate reducing bacteria (Runtti et al., 2016).

The most commonly used method for sulphate removal is chemical precipitation with the soluble barium, magnesium or calcium salts as an alternative, mainly if it is applied to the treatment of wastewaters that

contain high sulphate concentrations. The limitation of sulphate precipitation is high costs of salts (Silva et al., 2002). For effective sulphate precipitation, suitable pH and temperature are required and in addition suitable concentration of sulphate and controlled stirring intensity (Sánchez-Andrea et al., 2014). Frequently after final filtration, concentration of sulphate in the filtrate still remains on the 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. In this case, systems for separation and appropriate disposal of the solid phase are necessary too. Filtration using membranes is another alternative. However, the relatively high cost and energy consumption, proportional to the sulphate concentration, should be taken into account (Silva et al., 2002).

In last decades, as a suitable technique for sulphate removal the using of sulphate reducing bacteria is studied (Muyzer and Stams, 2008). The disadvantages of biochemical method 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 reduction of sulphate on hydrogen sulphide (Luptakova et al., 2012). The produced H_2S must be pumped out, e.g. 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 optimal values results to inhibit sulphate reducing bacteria or their extinction (Silva et al., 2002; Dolla et al., 2006; Al Zuhair et al., 2008;).

All over the industrial branches, is the tendency to diminish down contents of sulphates in wastewaters to acceptable level. Compared with other usual methods ion exchange provides advantages. By ion exchange either all ions can be removed from a solution or substances are separated (Dąbrowski et al., 2004). Therefore we can divide ion exchange resins designed for selective ions removal of contamination and complete deionization of wastewaters. The choice of between both depends mainly on the composition of the solution and on the extent of decontamination required. Selectivity is achieved selected types of ion exchangers with specific affinity to definite metal ions or groups of metals. In the most cases ion exchange is replacing the undesirable ion by another one which is neutral within aquatic environment (Dąbrowski et al., 2004; Fu and Wang, 2011).

Sulphate pollution can be treated by combinations of different techniques but they are often limited. The usage of ion exchange is a promising method due to its ability to reduce sulphate ion concentrations to very low levels (Lens et al., 1998). Moreover, its relative cost can be reduced by selecting a suitable resin and working under conditions that maximize adsorption and also facilitate regeneration. Feng et al. (2000) devised a process for AMD treatment consisting of metal precipitation and sulphate sorption on ion exchange resins Amberlyst A21. Guimarães and Leão (2014) showed of detailed the application of the ion exchange resin Amberlyst A21 on sulphate removal to conclude that the process has positive features that make it a good candidate for use in sulphate removal applications (11.6 mg of sulphate on 1 mL of resin). Although this adsorption capacity is low compared to other resins commercially designed for sulphate removal, 100% resin elution by increasing the pH to 10 and 12 with NaOH solution easily accomplished was almost reached.

The aim of this article is a study of changes of ion-exchange resins (Amberlite MB20 and Purolite MB400) after sulphate removal from model solutions. For characterization of ion-exchange resins changes, infrared spectroscopy was used. Efficiency of sulphate ions removal and pH changes were also measured.

2. Material and methods

The ion exchange resins, Amberlite MB20 and Purolite MB400, were obtained from commercial resin supplier in Slovakia and they 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 from ion-balanced mixed resin in ratio 40% catex to 60% anex. Amberlite MB20 is an ion-balanced mixed resin containing of 38-44% catex and 56-62% anex. This resin was developed for preparation of high purity water where 97% of the ionex resin has size of grains <0.3 mm. It is also most commonly used for the preparation of demineralized water free from silica and carbon dioxide.

1 g of resin was mixed with 100 mL of each model solutions 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. Batch adsorption experiments were carried out on static conditions with interaction time 24 h. After absorption, resins were filtrated. A concentration of residual sulphate concentration was determined by colorimetric method by Colorimeter DR 890. The pH values of solutions were also measured by pH meter inoLab pH 730. The IR spectra of resins before and after adsorption experiments were studied for characterization of present functional groups, which can be responsible for sulphate binding by Bruker Alpha Platinum-ATR spectrometer (Bruker Optics, Ettingen, Germany). Also 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 is efficiency of ion removal (%), c_0 is the initial concentration of appropriate ions (mg.L^{-1}) and c_e is equilibrium concentration of ions (mg.L^{-1}).

3. Results and discussion

3.1 Infrared spectra of ion exchange resins

The ability of ion exchange could be influenced by various factors but is closely linked strongly with using to selective or multi-componental removal of pollutants. The functional groups of Amberlite MB20 and Purolite MB400 ion exchange resins were determined using FTIR spectroscopy. The IR spectra of resins before and after adsorption experiments are shown in Figures 1 and 2. The FTIR spectrum of studied resins showed several major intense bands that it could be divided to two significant areas around wavenumbers 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 about 1,634 cm^{-1} on the adsorbed resins shows that the -OH functional groups was released to solution but the peak at wavenumber about 3,353 cm^{-1} was only slightly decreased due to the water naturally adsorption process. The ending of strong boarded peak centred at wavenumber around 3,353 cm^{-1} could be also 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). The three bands that following each other at 1,599; 1,450; and 1,411 cm^{-1} assigned to ring vibration of benzene rings, which also contain contribution due to bending observed at wavenumbers 830 and 773 cm^{-1} assigned to 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 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 and all esters give IR bands at approximately at wavenumbers 1,700; 1,200; and 1,100 cm^{-1}. Ghosh et al. (2015) found that the peaks at wavenumbers 1,031; 1,003; and 667 cm^{-1} belong to presence of –SO3H groups in the catex component of resin. On the other hand, they observed that the strong deformation at 890 cm^{-1} is due to the presence of –N(CH3)3 group in the anex component of resin.
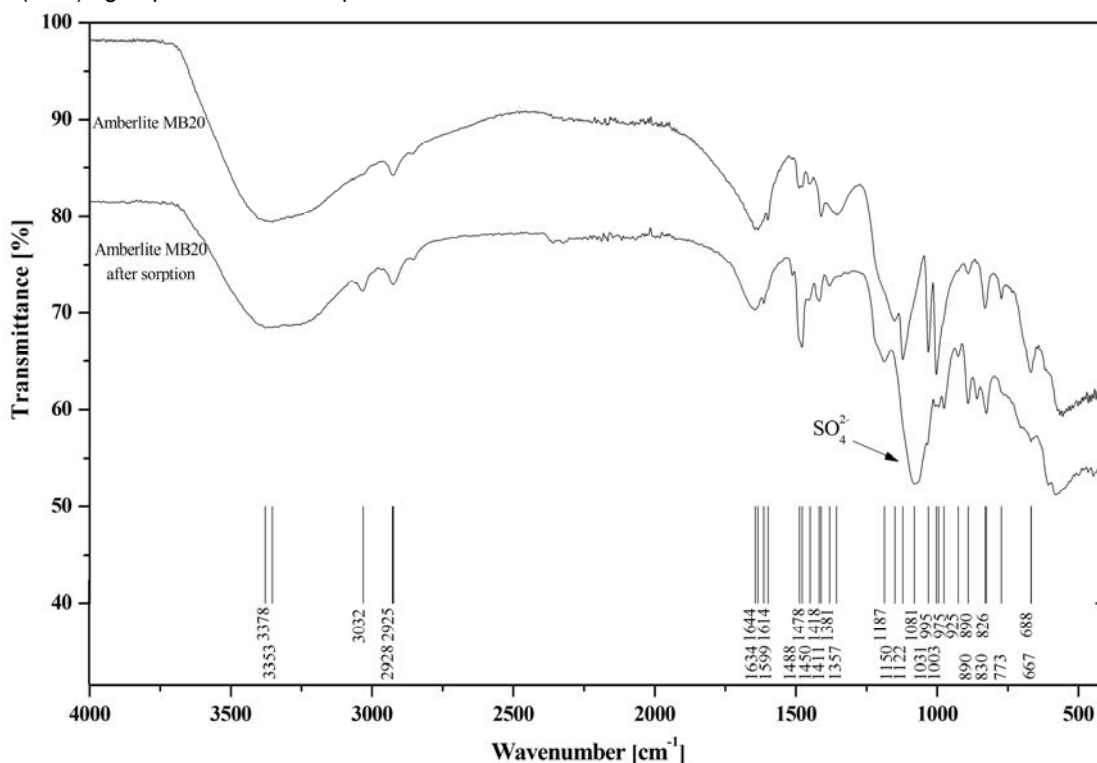

Figure 1: Infrared spectra of Amberlite MB20 before and after sorption experiments

In the Figure 2 are shown IR spectra of Purolite MB400 before and after sorption experiment. In comparison with Amberlite MB20 FT-IR spectrum was found some changes in composition and slightly shifting of band positions of this 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 was 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 of 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 assigned to ring vibration of benzene rings, which also contain contribution due to bending observed at 923 and 834 cm⁻¹ assigned to out of plane ring C–H bonding vibrations. The peak at 1,089 cm⁻¹ could represent a 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).
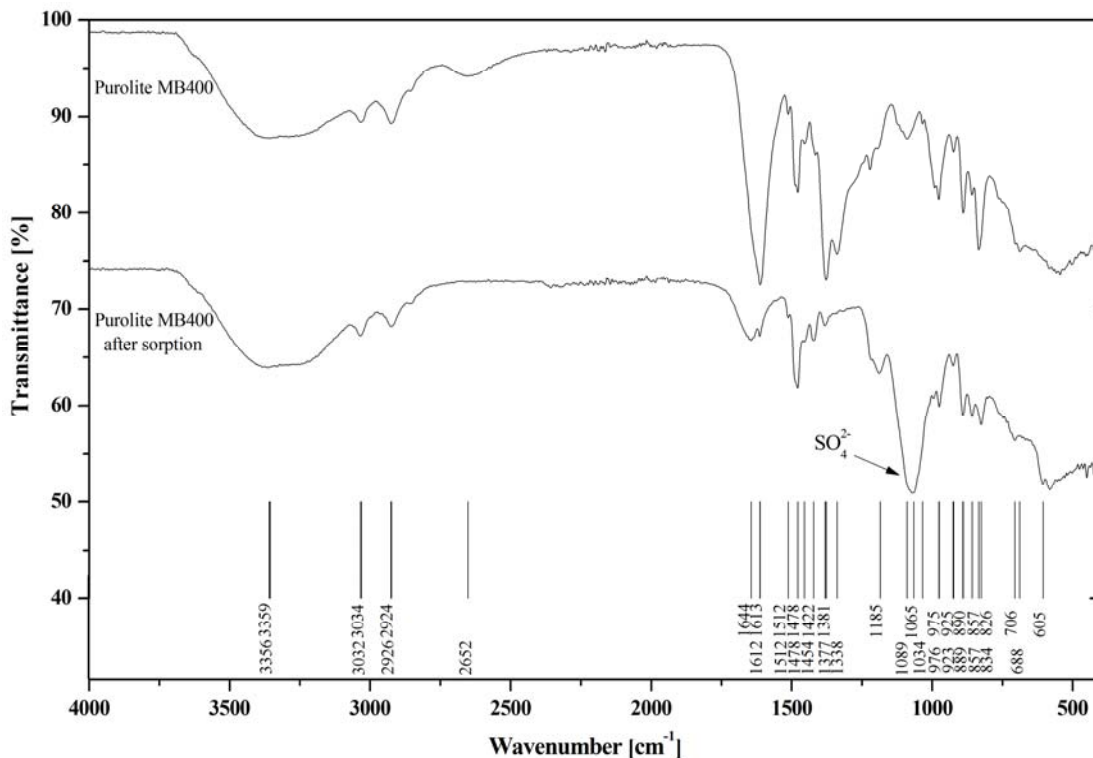

Figure 2: Infrared spectra of Purolite MB400 before and after sorption experiments

It was observed that there is a difference between the FTIR spectrum of both resins before and after sulphate adsorption. The strong broad band of OH functional groups was increased due to a water adsorption to resins. The sulphate sorption revealed symmetrical aliphatic C-H groups in structure of Amberlite MB20 resin around wavenumber 3,032 cm⁻¹. In both resins were observed significant changes at wavenumbers area from 1,500 to 1,300 cm⁻¹ where observed ring vibration of benzene rings (1,450 and 1,411 cm⁻¹) and C–H vibrations of aliphatic group (1,357 cm-1). The new wide band with 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 on both spectra and they are characteristic for sulphate functional group that was adsorbed on both resins in process of ion exchange. As it is clearly from figures 1 and 2, the IR spectra after sulphate adsorption are almost identical due to the same matrix used on production of studied resins.

3.2 Ion exchange study

Results of sorption experiments for model solution with different sulphate concentrations are shown in Table 1. The selected ion exchange resins used in these sorption experiments were capable to removal the sulphate from solutions. Amberlite MB20 exhibit almost similar efficiency (86.6 %) sulphate removal from model solution with sulphate concentration 100 and 500 mg.L⁻¹. In model solution with concentration of sulphate 1000 mg.L-1, slightly decreased efficiency of sulphate removal was observed, almost 70 %. Table 1 presents the efficiency of sulphate removal using Purolite MB400 solutions, where the best efficiency (84.9 %) of sulphate removal from model solution with the initial concentration 500 mg.L-1 was achieved. At the level of

sulphate 1,000 mg.L^{-1}, Purolite MB400 reached only 48.0 % efficiency ions removal. The both used ion exchange resins exhibits suitable effect in experiments for sulphate removal but they are limited of absorption capacity as was observed in case Purolite MB400 at the higher level of sulphate in model solution.

As shown in Table 1, the changes of pH values were also observed during static sorption experiments. In all cases, the both of resins had effect to increase of pH values. As is clearly from IR spectra after sorption experiment, the deformation peak at wavenumber about 1,644 cm^{-1} represent the hydroxyl functional group. In both cases was deformation peak decreased (significantly at ion exchange resin Purolite MB400). It was due to ion exchange between hydroxyl functional group (released to model solutions) and sulphate ions (caught on ion exchange resins). With the increasing of sulphate concentrations in model solutions were also observed that the pH change was less pronounced.

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

Ion exchange resins	Input values of model solutions at different sulphate concentration								
	c_0=100 mg.L-1; pH= 2.5			c_0=500 mg.L-1; pH= 2.0			c_0=1000 mg.L-1; pH=1.5		
	c_e [mg.L-1]	η [%]	pH	c_e [mg.L-1]	η [%]	pH	c_e [mg.L-1]	η [%]	pH
Amberlite MB20	13.4	86.6	7.9	67.1	86.6	3.5	330.8	66.9	2.1
Purolite MB400	25.4	74.6	6.4	84.9	83.0	3.0	519.7	48.0	2.0

4. Conclusions

Ion exchange is widely used to pollutant removal from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics. The ion exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations or anions with contaminants in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as effective materials to remove the impurities from the wastewaters.

The uptake of ions by ion-exchange resins is significantly affected by various factors such as pH, temperature, initial metal concentration and contact time, ionic charge of resins is also an important in treatment process. The most important factor of usage ion exchange resins are the high initial costs. On the other hand, the costs are compensated the ability of resins regenerate.

This study shows that using ion exchange resins Amberlite MB20 and Purolite MB400 for sulphates removal from model solutions is applicable. Based on experimental results Amberlite MB20 was more effective adsorbent than Purolite MB400. The efficiencies of both ion exchange resins was similar (about 80 %) for sulphate removal from model solutions with the lower concentrations (100 and 500 mg.L-1). At the concentration 1,000 mg.L-1, the efficiency of Amberlite MB20 for sulphate removal from 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 on production of studied resins. Despite the fact that Purolite MB400 contents more kinds of functional groups, Amberlite MB20 exhibited the better results for sulphate removal.

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