Production of aminated peat from branched polyethylenimine and glycidyltrimethylammonium chloride for sulphate removal from mining water

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A B S T R A C T

A novel bio-based anion exchanger was developed to remove sulphate from synthetic solutions and mine water. Different modification parameters such as chemical dosage and reaction time were tested when using a unique combination of branched polyethylenimine (PEI) and glycidyltrimethylammonium chloride (GTMAC) to produce an aminated biosorbent (termed PG-Peat). The novel and environment-friendly modification method was shown by FTIR and XPS analyses to be able to introduce quaternary ammonium and N-H groups into PG-Peat. The optimal modification conditions (PEI: 0.26mmol/g, GTMAC: 0.0447mol/g, reaction time: 18h) resulted in the maximum sulphate uptake capacity (189.5 ± 2.7mg/g) with a partition coefficient value of 0.02mg/g/μM under acidic conditions. At low pH, amine groups on the peat surface became cationized, thereby resulting in a higher sulphate removal capacity. Batch sorption tests using PG-Peat exhibited rapid sulphate sorption after only five minutes of contact. The sulphate uptake by PG-Peat was unaffected by the presence of varying chloride concentrations, while slightly lower uptake capacity was observed when different concentrations of nitrate were present. The biosorbent showed high recyclability, which was revealed in regeneration studies. Tests were performed involving real mine water, where PG-Peat showed its potential to be a highly efficient biosorbent for sulphate removal at low pH values, indicating its suitability for treating acidic mine waters.

1. Introduction

Sulphate ions are major constituents in both natural and industrial wastewaters. Natural sources include the dissolution and chemical weathering of sulphur-containing minerals, the decomposition of plant and animal residue, and the oxidation of elemental sulphur and sulphides (Mulinari & da Silva, 2008). In contrast, major anthropogenic sources of sulphate in water bodies include chemical industry effluents and acid mine drainage (Cao et al., 2014). Although sulphate does not directly harm bodies of water as it is a non-toxic element, the natural sulphur cycles are affected by high sulphate concentrations (Silva et al., 2002). Sedimentation of sulphur in lakes, rivers and sea has harmful effects on the environment, such as salinization and the formation of hydrogen sulphide by the sulphate-reducing bacteria present in water bodies (Ghiglazza et al., 2000; van Dam et al., 2014; Miao et al., 2012).

Removal of sulphate with very high concentrations of sulphate is generally carried out using gypsum precipitation with lime or limestone, which is capable of reducing the residual sulphate concentration to 1500–2000 mg/L (Kinnunen et al., 2017), although additional treatment methods are required to reduce sulphate to even lower concentrations. Membrane filtration is a feasible alternative, but this entails high energy consumption and operational costs (Silva et al., 2002). Another conventional method is the biological treatment of wastewater for sulphate removal; however, this treatment method is highly sensitive to the environmental conditions around it due to the rigid growth conditions of microbes (Muyzer and Stams, 2008). Sulphate treatment using sulphate-reducing bacteria also requires an external carbon source, which further contributes to the major operational cost (Rezadehbash and Baldwin, 2018).

Ion exchange and sorption technology using anion exchange resins are effective methods for the removal of anionic pollutants (Bhatnagar and Sillanpää, 2011; Xu et al., 2016). However, these commercial materials are expensive, which hinders their industrial application (Xu et al., 2016). Sorption using bio-based anion exchangers is a sustainable alternative, as they are cost-effective, the raw material is renewable and abundantly available, and the mechanism displays rapidity and a highly selective nature (Cao et al., 2011; Keränen et al., 2013). Several surface modification methods have been reported to introduce specific
functional groups onto a biosorbent surface so as to enhance its pol-
lutant uptake capacity (Duan et al., 2017a) and overcome certain
possible pitfalls of low-cost sorbents such as low yield, longer proces-
sing times and low regeneration capability (Awual et al., 2017; Duan
et al., 2017b). For example, the mango stone biocomposite developed
by Shoukat et al. (2017), Akram et al. (2017) and Bhatti et al. (2018)
was shown to be highly efficient in the removal of crystal violet
by Shoukat et al. (2017), Akram et al. (2017) and Bhatti et al. (2018).
Similarly, up to 17.18 mg/g Rose FRN dye removal was achieved
(352.79 mg/g), Cr(VI) (320 mg/g) and phosphate (95 mg/g), respec-
tively, was shown to be highly efficient in the removal of crystal violet
by Shoukat et al. (2017), Akram et al. (2017) and Bhatti et al. (2018).

In order for biomass to act as an anion exchanger, cationic groups
need to be introduced into the structure. Crosslinking and introduction
of amine groups into the lignocellulosic structure is an efficient method
of enhancing the anion exchange capacity of bio-based sorbents
(Keränen et al., 2013). Biomass is principally made up of two poly-
saccharides: cellulose and hemicellulose. The reactive hydroxyl groups
present in constitutional anhydroglucose units can be modified using
chemicals in order to produce functional polymers (Orlando et al.,
2002).

Polyethylenimine (PEI) is a non-toxic polymer, which has also been
used for introducing amine groups into biomass (Shang et al., 2016;
Song et al., 2015; Won et al., 2011). Water-soluble polyethylenimine
consists of a large number of primary and secondary amines capable of
attaching onto the surfaces of biomass. PEI is also efficient in the re-
moval of anionic pollutants such as dyes (Shang et al., 2016) and ars-
enic (Song et al., 2015). Although a lot of research has been performed
with respect to the production of bio-based anion exchangers for an-
ionic pollutant removal, no literature has been published on the use
of biomass chemically modified with polyethylenimine (PEI) followed by
quaternization with glycidyl trimethylammonium chloride (GTMAC).

In the present work, a novel modification method was developed
with the aim of producing anion exchangers for sulphate removal using
economical and abundantly available biomass, such as sawdust and
peat, which are also cheap and renewable raw materials and comply
with the principles of sustainability and a bio-based economy. Bio-
based sorbents also support the cause of environment-friendly water
treatment methods. As the aim was to produce a biosorbent containing
both N-H and quaternary ammonium groups, a unique set of chemicals
was applied for biomass modification using branched PEI followed by
quaternization with GTMAC. The sulphate uptake capacity of each
biosorbent was compared. Different modification parameters such as
PEI and GTMAC dosage and reaction time were studied and a full-fac-
torial experimental design was used to optimize the sulphate uptake
capacity of the better performing sorbent (peat, in this case).

Following this, batch sorption studies were performed to examine the effect
of contact time, pH, initial SO4
2− concentration and sorbent dosage (in
the case of mine water). Besides the sorption capacity, the performance
of the developed sorbent was also evaluated using the partition coef-
ficient. Additionally, the effect of co-existing ions on sulphate capacity
and reuse potential was investigated. Characterization using Fourier-
transform infrared spectroscopy (FTIR), X-ray photoelectron spectro-
scopy (XPS) and elemental composition was carried out to study the
effect of cationization on the raw biomass. The other novelty of the
research was to test the developed biosorbent on real mine water to
justify the viability of the product for commercial application. Thus, the
optimal product was tested using real mine water, sampled after pro-
cessing in the mine’s water treatment plant.

2. Materials and methods

2.1. Chemicals and materials used and water analysis

All chemicals used were of analytical grade. Polyethylenimine
(≥99% purity, Mw 25 000 by LS, branched, Sigma-Aldrich) and glyci-
dyltrimethylammonium chloride (≥90% purity, Sigma-Aldrich) were
used for biomass modification. Sulphate solutions were prepared using
Na2SO4 (99% purity, Baker). Stock solutions of nitrate (5000 mg/L) and
chloride (5000 mg/L) were prepared by dissolving NaNO3 (Merck) and
NaCl (Merck). The pH values of the SO4
2− solutions were adjusted
using 0.1 and 2 M HCl and 0.1 M NaOH, whereby the solutions were
made by diluting concentrated HCl (37%, Merck) and NaOH (99.1%)
purity pellets, Sigma-Aldrich) in Milli-Q water (Merck Millipore).

Scots pine sawdust (Pinus sylvestris) and peat were obtained from
Stora Enso Veitsiluoto, which is a pulp mill in Kemi (Finland) using peat
for energy production purposes. Following the method by Keränen et al.
(2013), sawdust was pre-treated by drying the biomass at 80 °C and
then grinding it using a Retsch SK100 cross beater mill with a 0.5 mm
sieve. The properties of the raw peat can be found in the study by
Leiviskä et al. (2018). Both sawdust and peat were sieved to a particular
size fraction (90–250 μm) so as to ensure a uniform size fraction
throughout the studies. Smaller-sized fractions might have affected the
settling behaviour of peat, due to its inherent poor settling properties,
whereas larger-sized particles (> 250 μm) might have constrained the
modification procedure (Gogoî et al., 2018).

The mine water was obtained from a Finnish mine site. The water
sample was collected after water treatment. The precipitation-neu-
tralization process of the mine aims to reduce sulphate to about
2000 mg/L. The characteristics of the sampled mine water are listed
in Table 1.

The pH measurement was made using a VWR Phenomenal pH
1000L, whereas conductivity was measured using a VWR Phenomenal
PC 5000H. Initial and residual SO4
2− analysis for the synthetic mine
water was performed using Hach Lange cuvette tests (LCK 153 for
40–150 mg/L and LCK 353 150–900 mg/L) and a Hach Lange DR8200
spectrophotometer. The samples were prepared for analysis according
to the respective cuvette test kit instructions. To prepare samples to
detect SO4
2− concentrations in the range of 40–150 mg/L, a 5 mL

Table 1. Characteristics of mine water.

| Parameter          | Mine water |
|--------------------|------------|
| pH                 | 6.7        |
| Conductivity (mS/cm)| 3.6        |
| Chloride (mg/L)    | 30.4       |
| Fluoride (mg/L)    | 0.1        |
| Sulphate (mg/L)    | 1970       |
| Nitrite (mg/L)     | 1.1        |
| Nitrate (mg/L)     | 40         |
| Ammonium (mg/L)    | 26         |
| Phosphate (mg/L)   | < 0.0060   |

Elements:

| Element          | Concentration (ug/L) |
|------------------|---------------------|
| Aluminium        | 102                 |
| Arsenic          | 3.2                 |
| Boron            | 90.1                |
| Barium           | 92.4                |
| Chromium         | 7.4                 |
| Copper           | 2.9                 |
| Iron             | 123                 |
| Manganese        | 62.7                |
| Molybdenum       | 20.2                |
| Nickel           | 2.8                 |
| Antimony         | 1.2                 |
| Selenium         | 5.1                 |
| Strontium        | 1460                |
| Zinc             | 1.3                 |
sample was pipetted into a bar-coded cuvette (LCK 153), after which a spoonful of barium chloride was added. The cuvette was then shaken for 2 min. Samples for detecting sulphate concentrations in the range of 150–900 mg/L were prepared by pipetting 2 mL into the bar-coded cuvette (LCK 353), adding a spoonful of barium chloride, shaking for 1 min and then letting the cuvette stand for 30 s. The cuvettes were then inserted into the cuvette slot of the spectrophotometer to measure the respective sulphate concentrations. Analysis of the raw mine water and synthetic solutions was performed as follows: Cl⁻, F⁻ and SO₄²⁻ were analysed using ion chromatography (SFS-EN ISO 10304-1:2009) and NO₂⁻, NO₃⁻, NH₄⁺ and PO₄³⁻ using a continuous flow analyser (SFS-EN ISO 13395:1997, SFS-EN ISO 11732:2005, SFS-EN ISO 15681-2:2005). The metals were analysed using inductively coupled plasma mass spectrometry (ICP-MS) (SFS-EN ISO 17294-2:2016). The initial SO₄²⁻ concentration of 1970 mg/L listed in Table 1, as detected by the ion chromatography method, is quite close to the concentration obtained (2168 mg/L) through measurement using the SO₄²⁻ cuvette test (LCK 153).

2.2. Preparation of anion exchangers

2.2.1. Preliminary modification studies

Preliminary modification studies were conducted using peat and sawdust under different experimental conditions to identify favourable modification conditions to obtain a bio-based product with improved sulphate uptake capacity. The aim was to compare the sulphate uptake efficiency of modified sawdust and peat under different chemical dosages and combinations. Different dosages of PEI (0.16 and 0.26 mmol/g of biomass) and GTMAC (0.0224 and 0.0447 mol/g of biomass) were used in combination or alone at different reaction times in a water bath under reflux, at a specific temperature controlled by a JP Selecta Tectron Bio immersion thermostat. Two repetitions, weighing 2 g each, were prepared for each product and the samples were stirred in round-bottom flasks under reflux at 60 °C for specific reaction times (RT). PEI modification was made by adding 20 mL of PEI solution (0.16 or 0.26 mmol/g of biomass) to the biomass (3 h or 6 h RT). Similarly, biomass modification using GTMAC was conducted by adding 20 mL GTMAC solution (0.0224 or 0.0447 mol/g of biomass) to the biomass (6 h or 12 h RT). Certain tests involving GTMAC were carried out using NaOH (constant 1.2 NaOH/GTMAC ratio; 30 min stirring) prior to the addition of GTMAC to verify whether the sorption efficiency of the cationized biomass is enhanced by the presence of a catalyst. When using both PEI and GTMAC, the biomass was stirred for 3 h with a PEI solution (0.16 or 0.26 mmol/g of biomass), followed by the washing of samples 2–3 times with MilliQ water to remove the unreacted PEI. Finally, 20 mL of GTMAC solution (0.0224 or 0.0447 mol/g of biomass) was added to the wet samples and stirred again under similar conditions for 6 h.

2.2.2. Optimization of the modification of PEI-GTMAC peat

The most efficient biomass, i.e. PEI+GTMAC modified peat, was selected for further optimization of the modification conditions. A full-factorial design was used to study the effect of the modification parameters on peat. The three factors investigated were PEI dosage (0.16 and 0.26 mmol/g of biomass), GTMAC dosage (0.0224 and 0.0447 mol/g of biomass) and reaction time (3 h PEI + 6 h GTMAC = 9 h and 6 h PEI + 12 h GTMAC = 18 h). The chemical dosages and reaction times were selected based on the preliminary modification studies. The sulphate removal capacity of the modified peat product was chosen as the experimental variable. The results were evaluated through computation of the coefficients using multiple linear regressions (Modde 11.0 software, Umetrics UB). If the p value was below 0.05, the coefficient was considered significant.

A separate set of (PEI+GTMAC) modification experiments was conducted for peat using two PEI dosages (0.16 mmol/g and 0.26 mmol/g of peat), a constant GTMAC dosage (0.0447 mol/g of peat) and constant reaction time (18 h) in order to check whether the presence of NaOH enhanced the sulphate sorption efficiency of the modified peat. After modification with PEI for 6 h, the peat samples were washed with MilliQ water 2–3 times to remove unreacted chemical, followed by stirring with NaOH (1.2 NaOH/GTMAC ratio) for 1 h. Finally, GTMAC was added and the reaction was allowed to proceed for 12 h. The entire reaction was conducted at a constant temperature (60 °C), as in all the previous modifications. Once the reaction time was over, the samples were washed carefully with deionized water to remove the excess chemical residues and dried at 60 °C for 1–2 days.

2.3. Characterization of modified peat

Fresh and recovered biosorbents from the batch sorption experiments were prepared for FTIR analysis by grinding them into a fine powder using a hand mortar. About 50 mg of each sample was poured and pressed into the sample holder, which was then mounted onto the equipment tray of a Bruker Vertex V80 vacuum FTIR spectrometer connected to a computer containing the OPUS program to display the recorded spectra. The spectra were recorded in the 400-4000 cm⁻¹ wave number region.

The XPS spectra for fresh and recovered sorbents from batch experiments (washed a few times with deionized water and dried overnight at 60 °C) were obtained using a Thermo Fischer Scientific ESCALAB 250Xi with a monochromatic Al Kα source (1486.6 eV) mounted on indium foil. Advantage software was used to analyse the XPS data while using the Shirley function to subtract the background. The charge correction was made by setting the binding energy of the adventitious carbon to 284.8 eV. The N 1s and S 2p spectra were fitted using a Shirley background and a Gaussian-Lorentzian sum function.

The elemental composition, i.e. C, H and N, was determined for the raw peat (R-Peat) and modified peat (P-Peat, G-Peat, PG-Peat) samples. The analysis was performed using a 2400 Series II CHNS/O analyser (PerkinElmer). The results are presented as the average of three repetitions of each analysed sample.

2.4. Batch sorption tests

The efficiency of the cationized biomass was tested and compared through batch sorption tests using synthetic sulphate solutions (1000 mg/L SO₄²⁻). The biomass products (0.2 g) were weighed into 50 mL Falcon tubes and 50 mL of prepared sulphate solutions were added (4 g/L dosage). The tubes were shaken in a horizontal rotary shaker for 24 h at room temperature (21 ± 3 °C), after which the sorbents were separated from the solutions by centrifugation (Jouan C4.12, 2500 rpm, 10 min). The residual sulphate concentration was measured using the sulphate cuvette testing method mentioned in section 2.1. The initial and final pH values of the solutions were measured. The sulphate removal capacity q (mg/g) was calculated using the following equation:

$$q = \frac{(C_i - C_f)V}{m}$$

where $C_i$ and $C_f$ are the initial and residual sulphate concentrations (mg/L) respectively, V is the sample volume (0.050 L) and m is the adsorbent mass (g) used in the batch sorption sample.

Based on the initial sulphate removal results, the sorbent with the optimal modification conditions resulting in the highest sulphate removal capacity was identified as PEI + GTMAC modified peat (PG-Peat). The decision was made to study different sorption parameters using the selected biosorbent, i.e. PG-Peat. Thereafter a larger batch using 20 g of raw peat (R-Peat) was made to produce PG-Peat for studying the effect of different sorption conditions. To estimate the effect of modification on sulphate removal, the prepared batch of modified sorbent (PG-Peat) was compared for its sulphate uptake capacity with raw peat under similar batch sorption conditions as those mentioned earlier in this...
section.

2.4.1. Effect of contact time

Studies involving the effect of contact time were performed using 50 mL of sulphate solution (~1000 mg/L; pH_{initial}: 6.7) and 0.2 g of PG-Peat (4 g/L dosage) over varying time periods (1 min, 2 min, 5 min, 10 min, 30 min, 1 h, 4 h, 8 h and 24 h) to check the sorption rate of PG-Peat. The samples having sorption times of 1 min and 2 min were separated from the sorbent using 0.45 μm syringe filters immediately after removal from the shaker in an attempt to keep the overall contact times as accurate as possible. For the subsequent contact times, the solutions were separated from the biosorbent by centrifugation. The residual sulphate concentration and equilibrium pH were then measured.

2.4.2. Effect of pH

The effect of pH was studied to analyse how different pH conditions would affect the sulphate uptake capacity of PG-Peat and to check the type of mining effluent it was capable of treating, as this study aims to develop a bio-based anion exchanger with potential for commercial sulphate removal from mining effluents. The studies were performed by mixing 0.2 g of the biosorbent (4 g/L dosage) with 50 mL of the sulphate solutions (~1000 mg/L; pH_{initial}: 6.3). The pH of the solutions was adjusted in the pH 2–10 range, prior to sorbent addition. The solutions were then subjected to a sorption test for 4 h (stable contact time) and then centrifugation to obtain separated solutions for the measurement of residual sulphate and equilibrium pH.

2.4.3. Maximum sulphate uptake capacity

The maximum sulphate sorption capacity of PG-Peat was studied using varying sulphate concentrations (450–2515 mg/L; pH_{initial}: 5.6–6.4), prepared by diluting stock Na_{2}SO_{4} solution. The sorption studies were performed using 50 mL of each sulphate solution (with and without pH adjustment to 2; two repetitions for each pH value) and 0.2 g of biosorbent (4 g/L dosage) in 50 mL Falcon tubes, shaken for 4 h. The maximum sorption capacity q (mg/g) was measured using the same formula as equation (1) and the experimental data was fitted into nonlinear forms of the Langmuir (1916), Freundlich (1906) and Redlich-Peterson (Redlich and Peterson, 1959) adsorption isotherm models (see supplementary material). In addition to the coefficient of determination (R^2) used to assess the goodness-of-fit of the sorption data to the isotherm models presented, the χ^2 test (chi-square) was used to confirm the reliability of the results (see supplementary material). The performance of PG-Peat was also evaluated at different levels at which equilibrium was attained (i.e. 50% and 100% of maximum uptake level) using the partition coefficient (K_{D}), which was calculated using the following equation as described by Hu et al. (2014):

\[ K_{D} = \frac{q}{C_{o}} \]  (2)

where q is the equilibrium sorption capacity (mg/g). The unit of K_{D} is mg/g/μM (the calculation of the partition coefficient value can be found in supplementary material).

2.4.4. Effect of co-existing ions

The effect of co-existing ions, i.e. chloride and nitrate, on the sulphate uptake capacity of PG-Peat was studied by adding varying concentrations of chloride (0–100 mg/L) and nitrate (0–100 mg/L) to sulphate solutions having a constant concentration (1046 mg/L). The chloride and nitrate concentrations were chosen based on their respective concentrations (30.4 mg/L Cl^- and 40 mg/L NO_3^-) in the mine water used in the study. A few higher concentrations (50 mg/L and 100 mg/L) of the anionic solutions were also selected to study how the sulphate uptake capacity of PG-Peat was affected under different concentrations of co-existing ions. The sorbent dosage was 4 g/L and the solutions were shaken for 4 h. They were then centrifuged (10 min) to separate the solution from the sorbent in order to measure the residual sulphate, chloride and nitrate concentration, and the equilibrium pH.

2.4.5. Regeneration studies

In order to assess the reusability of the developed sorbent, regeneration studies were performed using 0.2 g of PG-Peat for three batch sorption-desorption cycles. Fifty millilitres of sulphate solution (1046 mg/L SO_4^{2-}; pH_{initial}: 5.5) was used in each sorption cycle. The sorbent was regenerated using 25 mL of 1 M NaCl solution where the Cl^- acted as the exchanging ion in PG-Peat. Samples were shaken in a horizontal rotary shaker for 2 h at room temperature (21 ± 3 °C) in both the sorption and desorption tests, after which the sorbent was separated from the solution by centrifugation (10 min). The sulphate sorption capacity during each cycle was measured using equation (1). The desorption efficiency (%) was calculated using the following equation:

\[ \text{Desorption (\%)} = \left( \frac{m_{f}}{m_{i}} \right) \times 100 \]  (3)

where m_{f} is the sulphate amount (mg) released from the sorbent and m_{i} is the initially sorbed sulphate amount (mg). It should be noted that between each sorption-desorption cycle, the sorbent was rinsed with water and then the desorbed sulphate fraction in the rinsing solution was analysed and taken into account in the desorption efficiency calculations.

2.4.6. Preliminary tests with real mine water

In order to confirm whether the developed biosorbent (PG-Peat) would be applicable for actual wastewaters, selected dosages of the biosorbent (4, 8 and 12 g/L) were tested for sulphate removal from real mine water. Samples were shaken under similar conditions as described in section 2.4 with 4 h contact time at pH 2 and at the original pH value of 6.7.

3. Results and discussion

3.1. Development of anion exchangers

3.1.1. Preliminary modification studies

Different kinds of biomass (sawdust and peat) were modified under several experimental conditions and compared in order to identify the product possessing the highest sulphate removal efficiency (SO_4^{2-} uptake capacity).

Similarly, when both biomasses were modified using both PEI (dosage 0.16 mmol/g) and GTMAC (dosage 0.0447 mol/g) for 9 h, the PEI + GTMAC-modified peat (PG-Peat) achieved a much higher sulphate removal capacity of up to 63.6 mg/g and 59.7 mg/g when modified with PEI dosages of 0.16 mmol/g and 0.26 mmol/g of sawdust, respectively. However, under the same conditions, PEI-modified peat exhibited a much higher sulphate removal capacity of up to 63.6 mg/g and 59.7 mg/g when modified with PEI dosages of 0.16 mmol/g and 0.26 mmol/g of peat, respectively. Similarly, when both biomasses were modified using both PEI (dosage 0.16 mmol/g) and GTMAC (dosage 0.0447 mol/g) for 9 h, the PEI + GTMAC-modified peat (PG-Peat) achieved a removal capacity of up to 92 mg/g, whereas the modified sawdust (PG-Sawdust) could only reach a capacity of up to 56.1 mg/g. When PEI + GTMAC modification was conducted using a longer reaction time (18 h) and higher PEI dose (0.26 mmol/g of biomass) while keeping the GTMAC dosage constant (0.0447 mol/g biomass), PG-Peat (114.7 mg/g SO_4^{2-} uptake capacity) again proved to be more efficient than PG-Sawdust (80.2 mg/g SO_4^{2-} uptake capacity).

The attachment of PEI to the biomass structure mainly occurs through the interaction of the amine groups provided by PEI and the hydroxyl groups, as well as the N-containing functional groups present...
in the biomass. This interaction has also been reported in several studies involving biomass modification using PEI where FTIR and XPS analyses of modified sorbent revealed that the principal functional groups interacting with PEI were the OH and amine groups present in the raw biomass (Deng and Ting, 2005a; Sun et al., 2010; Song et al., 2015). In the current study, following PEI treatment, the biomass was modified using GTMAC where the quaternization of biomass occurred through the attachment of trimethylammonium groups provided by GTMAC, as was also reported in the study by Wahlström et al. (2017). Upon the addition of GTMAC, the N-H groups provided by PEI in the biomass may have reacted with the epoxy ring in GTMAC, thus resulting in a bio-based anion exchanger having both amine and quaternary amine groups. The modification scheme is shown in Fig. 1. Elwakeel (2010) suggested a similar reaction between tetraethylenepentamine (TEPA) and GTMAC in the modification of chitosan resin.

In the case of sawdust, the presence of NaOH as a catalyst in modifications involving GTMAC alone (0.0447 mol/g) substantially increased the sulphate uptake capacity, from 10.1 mg/g (without NaOH) to 67.8 mg/g (with NaOH). However, when NaOH was used in peat modification involving both PEI and GTMAC, the presence of NaOH led to a considerable decrease in the anion exchanging capacity of the peat (32.2–38.8 mg/g), compared to the capacity of the PG-Peat (92–114.7 mg/g) produced without the addition of NaOH. As reported by Kong et al. (2015), NaOH is commonly used in the cationization of biomass using GTMAC, as it acts as a catalyst and produces a nucleophilic intermediate. The intermediate reacts with the epoxy ring present in GTMAC, thereby resulting in an efficiently GTMAC-grafted cationized product. While this could have been the phenomenon taking place in the modification of sawdust using NaOH and GTMAC (1.2 NaOH/GTMAC ratio), the same chemical reaction was not favourable when the peat was modified using all three chemicals (i.e., PEI, NaOH and GTMAC). In the case of biomass modified first with PEI and then with GTMAC in the presence of NaOH, the quaternary ammonium groups from GTMAC were able to attach to the OH groups (under alkaline conditions). The NaOH-GTMAC reaction may have prevented the interaction between GTMAC and PEI (added during the first modification step), inhibiting the quaternary ammonium groups (from GTMAC) from interacting with the amine groups (provided by PEI) that had previously been grafted onto the peat surface.

A common trend observed in both forms (i.e. sawdust and peat) of anion exchangers is that higher chemical dosages and longer reaction times are more conducive to better sulphate uptake capacity. It has been reported in the study by Elwakeel (2010) that anion exchangers cationized using both amine and quaternary ammonium groups are much more efficient than products cationized by introducing amine groups alone, due to the presence of the trimethylammonium chloride moiety. This is also evident in the present study comparing different modification parameters, where the most efficient cationized biosorbent was PG-Peat modified using both PEI and GTMAC. Based on preliminary modification studies using both peat and sawdust as well as the overall higher sulphate sorption efficiency of PEI+GTMAC-modified peat, the decision was made to continue with the peat in order to identify the optimal modification conditions by testing different dosages of PEI and GTMAC and reaction times.

### 3.1.2. Optimization of modification conditions

Optimization of peat modification using PEI and GTMAC using different chemical dosages (PEI dosage: 0.16–0.26 mmol/g and GTMAC dosage: 0.0224–0.0447 mol/g) and reaction times (9–18 h) revealed that the highest sulphate removal capacity obtained was 114.7 mg/g (at pH 5.8) using the higher chemical dosages and longer reaction time. Peat modified using lower chemical dosages and shorter reaction times yielded a much lower sulphate removal capacity of 73.8 mg/g. The statistical analysis backed up the experimental data on the interactions between all three variables: PEI dosage (PEI), GTMAC dosage (GTMAC) and reaction time (RT). As can be seen in Table 2, all the parameters analysed, including the main interactions PEI*GTMAC, PEI*RT and GTMAC*RT, were significant where the p value was < 0.05. The interaction between the chemical dosages of PEI and GTMAC was highly significant as a p value of 5.93e−007 was obtained. Another significant interaction observed was between PEI and reaction time (p value: 6.21e−005). Higher dosages of chemicals facilitated a higher concentration of cationic groups attaching to the biomass surface, whereas a prolonged reaction time ensured strong interaction between the amine and quaternary ammonium groups (Fig. 2). At a longer reaction time (18 h), even peat modified with lower dosages of PEI and GTMAC was more efficient in sulphate sorption compared to the higher dosage counterparts modified for a shorter reaction time (9 h). For these reasons, the PG-Peat modified using higher dosages of PEI (0.26 mmol/g peat), GTMAC (0.0447 mol/g peat) at longer reaction times (6 h PEI; 12 h GTMAC) was selected as the most efficient sorbent (sulphate uptake capacity 114.7 mg/g) for studying the effect of different sorption parameters and also for preliminary tests using mine water.

### 3.2. Characterization of selected anion exchanger

#### 3.2.1. FTIR spectra

The FTIR spectra of raw peat (R-Peat) and modified peat (P-Peat, G-Peat and PG-Peat) are presented in Fig. 3. In all the materials analysed, a broad band can be observed at 3409 cm−1. This is proof of the presence of hydroxyl and hydrogen bonds, as they appear as peaks between

| Table 2 | Magnitude of coefficients (scaled and centred, extended format) and significance of factor effects on the response variable of sulphate removal capacity (mg/g). Variables: PEI dosage, GTMAC dosage and reaction time. |
|---------|--------------------------------------------------------------------------------------------------|
| Sulphate removal capacity | Coef. SC | Std. Err | P | Conf. int (±) |
| Coefficient | 97.5 | 0.72 | 2.34e-037 | 1.48 |
| Constant | | | | |
| DF = 25 | | | | |
| PEI dosage (PEI) | 3.34 | 0.72 | 9.36e-005 | 1.48 |
| GTMAC dosage (GTMAC) | 9.16 | 0.72 | 1.98e-012 | 1.48 |
| Reaction time (RT) | 7.74 | 0.72 | 7.13e-011 | 1.48 |
| PEI*GTMAC | 4.78 | 0.72 | 5.92e-007 | 1.48 |
| PEI*RT | −3.46 | 0.72 | 6.21e-005 | 1.48 |
| GTMAC*RT | −4.46 | 0.72 | 1.73e-006 | 1.48 |
3400 and 3600 cm\(^{-1}\) in the spectra (Nakanishi, 1962; Williams and Fleming, 1995). According to Deng and Ting (2005b), these bands also overlap with N-H stretching, appearing with strong intensity for the modified sorbents at 3424 cm\(^{-1}\). The two bands around 2854 cm\(^{-1}\) and 2919 cm\(^{-1}\) are attributed to the stretching vibrations of C-H of the methoxyl groups, -OCH\(_3\), which are present abundantly in lignin-containing materials (Hergert, 1960). One of the most interesting peaks, verifying the presence of a quaternary ammonium group, is the peak at 2123 cm\(^{-1}\) in the case of G-Peat and P-Peat. In PG-Peat, the same quaternary ammonium groups appear at a significantly stronger intensity band at 2094 cm\(^{-1}\), as reported by Alves de Lima et al. (2012), due to the grafting of PEI-attached GTMAC onto the PG-Peat surface. Additionally, the more prominent peak at 1652 cm\(^{-1}\) observed in P-Peat is due to N-H bending induced by the PEI treatment, as reported by Sowmya and Meenakshi (2014). In the case of PG-Peat, since GTMAC reacted with the amine groups of PEI (at neutral pH), the intensity of the same peak decreased in the sample. Bartczak et al. (2018) reported that C-O bond stretching vibrations in peat appear in the 1100-1200 cm\(^{-1}\) spectral region, and these appear in a similar range (1089 cm\(^{-1}\)) for all the peat samples studied in Fig. 3. The region below 1000 cm\(^{-1}\) is difficult to identify due to the complex structures (cellulose, hemicellulose, lignin and extractives) present in peat.

3.2.2. XPS spectra

The XPS data of the raw and modified peat surfaces revealed that the biosorbents mainly contained carbon followed by oxygen (Table 3). The nitrogen content increased with PEI and PEI+GTMAC modification, with the highest amount found in PEI-modified peat. The decrease in oxygen was observed in all the modified products, which indicates the bonding of chemicals through an oxygen-related functional group.

Table 3

| Biosorbent type | Atomic percentage of the elements (%) |
|-----------------|--------------------------------------|
|                 | C  | O  | N  | S  |
| R-Peat*         | 73.8 | 22.8 | 3.2 | -  |
| G-Peat**        | 79.3 | 16.9 | 3.4 | -  |
| P-Peat          | 76.3 | 11.6 | 12.2 | -  |
| PG-Peat**       | 78.1 | 12.1 | 7.3 | -  |
| PG-Peat (recovered from synthetic water)** | 73.4 | 17.0 | 8.2 | 1.1 |
| PG-Peat (recovered from mine water)** | 74.2 | 16.6 | 7.7 | 1.3 |

* R-Peat also contained 0.3 at.% of silicon. ** Samples contained traces of chlorine.

XPS analysis was conducted of the PG-Peat samples recovered from the sorption tests, involving synthetic as well as mine waters, to check the binding of sulphate ions to the PG-Peat surface. Both samples exhibited identical peaks to those of the XPS analysis of PG-Peat samples.

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3.2.2. XPS spectra

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The N1s spectra of the raw (R-peat) and modified peat (P-peat, G-Peat and PG-Peat) showed interesting changes. As can be seen in Fig. 4, the modification clearly led to the introduction of additional nitrogen-based functional groups to the peat. Kelemen et al. (2006) showed that amide forms of nitrogen present a dominant peak in unmodified peat at 400.2 eV. The same peak can be seen at 400.1 eV in the R-peat sample (Fig. 4a). Although raw peat contains pyridinic nitrogen (398.6 eV) and quaternary nitrogen, they are present in very small quantities (Kelemen et al., 2006), and as such cannot be seen in Fig. 4a. The peaks at 398.8 eV in P-peat (Fig. 4b) and at 399 eV in PG-Peat (Fig. 4d) could be attributed to the amide and/or N-H bonds of the primary and secondary amine groups present in PEI. The peak at 399.8 eV in G-Peat could be attributed to amide groups (Gengenbach et al., 1996), which were already present in the raw peat samples. The most interesting peaks were the additional peaks seen with G-Peat and PG-Peat at 402.5 eV, which clearly indicated the presence of quaternary ammonium cations in the modified samples (Kistamah et al., 2009). The N 1s spectrum of PG-Peat was fitted (data not shown) and approximately 44% of the nitrogen was contributed by the quaternary ammonium groups.

XPS analysis was conducted of the PG-Peat samples recovered from the sorption tests, involving synthetic as well as mine waters, to check the binding of sulphate ions to the PG-Peat surface. Both samples exhibited identical peaks to those of the XPS analysis of PG-Peat samples.
recovered from synthetic water (presented in the supplementary material, Fig. S1). The sulphate doublet could be seen at 167.0 eV and 168.1 eV for the S2p3/2 and S2p1/2 transitions respectively and the doublet was separated by an energy level of 1.1 eV. The peak at 167 eV for S2p3/2, representing the sulphate species, was fairly close to the results of studies by Hood et al. (2018) and Suresh (2015), who reported sulphate peaks at ≈168 eV.

3.2.3. Elemental composition

The elemental analysis of raw and modified peat revealed a significant increase in nitrogen content, especially in the case of PEI-modified and PEI+GTMAC-modified peat (Table 4). The nitrogen content increased from 2.2% in raw peat to up to 10.7% in P-Peat, which could be attributed to the introduction of amine groups during PEI treatment. The nitrogen content in PG-Peat originated from the attachment of amine and quaternary ammonium groups, which were attached to the biosorbent structure during PEI and GTMAC treatment, respectively. However, the nitrogen content of PG-Peat was slightly less (9.4%) than that of the P-Peat indicating that some of the PEI might have desorbed from the biomass surface during GTMAC treatment. The presence of both amine and quaternary ammonium groups in the modified sorbent was supported by the XPS results (section 3.2.2).

Table 4

| Parameter | R-Peat | P-Peat | G-Peat | PG-Peat |
|-----------|--------|--------|--------|---------|
| C (%)     | 48.4 ± 0.6 | 51.3 ± 0.2 | 51.5 ± 0.1 | 46.1 ± 0.1 |
| H (%)     | 4.5 ± 0.9  | 7.2 ± 0.1  | 6.4 ± 0.6  | 8.4 ± 0.3  |
| N (%)     | 2.2 ± 0.0  | 10.7 ± 0.1 | 3.3 ± 0.0  | 9.4 ± 0.1  |

3.3. Batch sorption experiments

Sorption experiments using raw and modified peat (PG-Peat), performed under similar conditions, revealed that the cationized biomass exhibited a much higher sulphate uptake capacity (114.1 mg/g) than the removal efficiency achieved by raw peat (34.5 mg/g). The higher sorption capacity of PG-Peat could be attributed to the presence of attached amine and quaternary ammonium groups on the sorbent surface, introduced by the chemical modification using polyethylenimine and glycidyltrimethylammonium chloride.

3.3.1. Effect of contact time

The effect of contact time on the sulphate removal capacity of PG-Peat at varying sorption times (from 2 min to 24 h) was studied. The equilibrium pH was measured and found to be ≈ 7.7. As can be seen in Fig. 5, there was a rapid increase in sulphate uptake capacity from the initial contact times of 1–2 min to 5 min, at which point a removal capacity of ≈ 100 mg/g could be achieved. The sorption mechanism was very effective as it achieved a removal capacity of ≈ 100 mg/g within 5 min. There was a slight increase in sulphate uptake capacity at a contact time of 4 h (114.1 mg/g), after which it remained > 100 mg/g throughout the tests with longer contact times (8–24 h). The results revealed that the main sorption mechanism was ion exchange whereby the cationic sites were quickly filled by anionic sulphate ions and the biosorbent attained equilibrium within a very short time period. Similar short contact times to achieve equilibrium have also been reported for other bio-based anion exchangers (Keränen et al., 2013).

3.3.2. Effect of pH

The effect of pH on the sulphate removal capacity of PG-Peat was studied using a contact time of 4 h. As can be seen in Fig. 6, pH played a significant role in the sulphate uptake capacity of the biosorbent. The removal capacity (171 mg/g) was the highest at the lowest pH studied (pH 2), after which it showed a steep decrease when the pH value was
increased to only 3. It should be noted that a further increase of pH from 4 to 11 did not significantly affect the sorption efficiency of PG-Peat and the sulphate removal capacity remained > 100 mg/g at all pH values. The high sulphate removal by PG-Peat at pH 2 is probably due to the high concentration of cationic amine groups under acidic conditions. The presence of cationized amine groups at low pH in addition to quaternary ammonium groups having an optimal uptake efficiency at pH = 2.8. Elwakeel (2010) further stated that the extent of protonation of the amine groups decreases with increasing pH value. Elwakeel (2010) also reported higher As(V) uptake capacity of the anion exchanger under acidic conditions due to the presence of protonated amine groups. In this study, highly acidic pH values (such as pH 2) were studied as the aim was to confirm whether the developed biosorbent, PG-Peat, would be efficient in sulphate removal from wastewaters under acidic conditions. As evident in Fig. 6, the developed biosorbent is highly efficient in sulphate uptake from water having a low pH and, as such, exhibits high potential for the treatment of acid mine water.

### 3.3.3. Sulphate uptake capacity and adsorption isotherms

The maximum sulphate sorption capacity of the solutions with no pH adjustment was 138.2 mg/g, whereas for solutions where the initial pH was adjusted to 2 the maximum sorption capacity was 189.5 mg/g. The higher uptake capacity of the pH-adjusted solutions was probably caused by the higher concentration of protonated amine groups under the acidic conditions in addition to the quaternary ammonium groups, as stated in section 3.3.2. The maximum sulphate sorption capacity and the partition coefficient (K_H) of PG-Peat (under acidic conditions) was compared to that obtained by other sorbents reported previously in the literature (Table 5). The partition coefficient is a valuable parameter in assessing the sorption performance of sorbents as it is the ratio of the target analyte concentration sorbed onto the solid sorbent to its residual concentration in the liquid phase at equilibrium (Hu et al., 2014; Vikrant and Kim, 2019). In order to assess the true performance of a sorbent, it is essential to evaluate both the sorption capacity and partition coefficient of the sorbent. In this case, the partition coefficients were higher when sorption was halfway to the saturation level compared to the partition coefficient values obtained at the maximum sorption capacity point (Tables 5 and S1). This phenomenon is directly dependent on the initial concentration of the target species. When the initial adsorbate concentration is higher, the active sorption sites of the sorbents rapidly become saturated, thus leaving behind a significant number of unadsorbed contaminant ions in the solution (Vikram and Kim, 2019). Although a low partition coefficient value was obtained for PG-Peat at high initial sulphate concentration, the residual concentration of around 1000 mg/L SO_4^{2−} was satisfactory because such a level

![Fig. 5. The effect of contact time on sulphate (SO_4^{2−}) removal capacity with PG-Peat (not shown: 24 h contact time; 105.4 mg/g sulphate removal capacity). Initial sulphate concentration 1174 mg/L, pH_{initial} 6.7, PG-Peat dosage 4 g/L; temperature 22 ± 2 °C. Error bars represent the deviation of two repetitions.](image1)

![Fig. 6. Effect of pH on sulphate removal capacity with PG-Peat. Initial sulphate concentration 1182 mg/L; PG-Peat dosage 4 g/L; contact time 4 h; temperature 22 ± 2 °C. Error bars represent the deviation of two repetitions.](image2)

| Anion exchanger                          | C_o (mg/L) | C_e (mg/L) | R (%) | q_e (mg/g) | K_H (mg/g/μM) | pH | Reference                      |
|------------------------------------------|------------|------------|-------|------------|---------------|----|--------------------------------|
| Chitosan-grafted-Polyacrylamide copolymer| –          | –          | –     | 277.8^a    | –             | –  | Fosso-Kanke et al. (2015)      |
| Epichlorohydrin and trimethylamine modified rice straw | –          | 270        | –     | 74.8^a     | 0.03          | 6.4 | Cao et al. (2011)              |
| Surfactant-modified palygorskite          | –          | –          | –     | 3.2^a      | –             | –  | Dong et al. (2011)             |
| Chitin-based shells                       | –          | 650        | –     | 156.0^a    | 0.02          | 4.3 | Moret and Rubio (2003)         |
| Barium modified blast-furnace slag geopolymer | –          | 750        | –     | 90.0^b     | 0.01          | 7–8| Runtti et al. (2016)           |
| Polypyrrole-grafted granular activated carbon | 250        | 140        | 44    | 44.7^b     | 0.03          | –  | Hong et al. (2014)             |
| Organono-clay                            | –          | 200        | –     | 20.0^b     | 0.01          | 7.0| Chen and Lui (2014)            |
| PG-Peat                                 | 1835       | 1050       | 43    | 189.5^b    | 0.02          | 2.4| Present study                  |

^a Langmuir isotherm maximum sorption capacity.
^b Experimental maximum sorption capacity.
of sulphate concentration is currently permissible in industrial effluents such as mining waters, unlike concentrations of toxic metals. When comparing the sulphate removal performance of PG-Peat to that of previously reported sorbents (Table 5), the partition coefficients of the respective sorbents were quite similar, whereas the sorption capacity of PG-Peat was higher in some cases. This supports the feasibility of applying PG-Peat in sulphate treatment.

The experimental sorption capacities of PG-Peat obtained from the pH-adjusted sulphate solutions were fitted into non-linear Langmuir, Freundlich and Redlich-Peterson models. The parameters together with $\chi$ values shown in Table 6. The calculated maximum sorption capacity value (188.5 mg/g) provided by the Langmuir model is quite close to the experimental maximum sorption capacity (189.5 mg/g). The Redlich-Peterson model, however, provided the best fit in terms of the $R^2$ value (0.95) and $\chi^2$ value (5.77). Additionally, the $g$ values obtained from the Redlich-Peterson isotherm model were quite close to unity (0.95). This indicates that the model is closer to the Langmuir model than the Freundlich model (Tran et al., 2017), thus inferring a monolayer adsorption phenomenon (Langmuir, 1916). Since Redlich-Peterson was the model with the best fit to the experimental data, the graphical form of the Redlich-Peterson model is presented in Fig. 7, together with the experimental data. The experimental sorption capacity at 50% of the maximum uptake level was also compared to values obtained from the isotherm models (supplementary material, Table S2). At 50% of the maximum uptake value, the experimental sorption capacity of PG-Peat (94.8 mg/g) was closest to the value given by the Freundlich model (94.8 mg/g) at the same level (50%).

The partition coefficients calculated from the isotherm models are also shown in Table S2. At the maximum uptake value, the experimental value of partition coefficient (0.02 mg/g/μM) was the same as the values obtained from the isotherm models. However, at 50% of the maximum uptake, the experimental partition coefficient value (0.19 mg/g/μM) was closest to the value given by the Freundlich model (0.20 mg/g/μM). The partition coefficient value for the Langmuir model was 0.16 mg/g/μM at 50% of the maximum uptake, whereas it was 0.17 mg/g/μM for the Redlich-Peterson model at the same level.

### 3.3.4. Effect of co-existing ions

The effect of co-existing ions, i.e. chloride and nitrate, on the sulphate uptake capacity of PG-Peat was investigated (Table 7) because the most commonly found anions in mining effluents are sulphate, chloride and nitrate. The sulphate uptake capacity of the modified sorbent was unaffected by the presence of chloride ions at all the concentrations tested. However, since PG-Peat is in Cl form, chlorine was released into the solution (up to 435 ± 5mg/L Cl⁻, Cl⁻ on the presence of other counter ions and their respective valences. In the absence of sulphate, chloride was still released into the solution by PG-Peat, albeit at a lower concentration (185 ± 5 mg/L).

In the case of nitrate, the sulphate uptake capacity slightly decreased with increasing nitrate concentrations as both anions competed with each other for the cationic sorption sites of PG-Peat (Table 7). In general, divalent sulphate has stronger electrostatic interactions and higher affinity than monovalent ions, which plays an important role in the ion-exchange capacities of sorbents (Awual et al., 2011a, 2012; Blaney et al., 2007). In the absence of sulphate, the nitrate removal of PG-Peat was higher due to lack of competition for binding sites.

The selectivity of anion exchangers towards a specific ion is dependent on the presence of other counter ions and their respective valences (Awual et al., 2011b). In general, ions with higher charge have higher affinity. However, the ion concentration as well as the structure of the resin (e.g. degree of crosslinking, material) also affect the selectivity. Commercial crosslinked copolymers tend to follow the Hofmeister anion

### Table 6

| Parameter | PG-Peat |
|-----------|---------|
| Maximum experimental capacity $q$ (mg/g) | 189.5 ± 2.7 |

### Table 7

| $SO_4^{2-}$ initial (mg/L) | $Cl^-$ initial (mg/L) | $SO_4^{2-}$ final (mg/L) | $SO_4^{2-}$ uptake capacity (mg/g) | $Cl^-$ final (mg/L) |
|---------------------------|-----------------------|--------------------------|-----------------------------------|---------------------|
| 1046                      | 0                     | 652 ± 6                  | 97.5 ± 1.7                        | 380 ± 10            |
| 1046                      | 30                    | 626 ± 4                  | 103.3 ± 0.9                       | 375 ± 5             |
| 1046                      | 50                    | 100.2 ± 19               | 100.2 ± 4.5                       | 400                 |
| 1046                      | 100                   | 102.6 ± 6                | 102.6 ± 1.6                       | 435 ± 5             |
| 0                        | 100                   | -                       | -                                 | 185 ± 5             |

| $SO_4^{2-}$ initial (mg/L) | $NO_3^-$ initial (mg/L) | $SO_4^{2-}$ final (mg/L) | $SO_4^{2-}$ uptake capacity (mg/g) | $NO_3^-$ final (mg/L) |
|---------------------------|------------------------|--------------------------|-----------------------------------|----------------------|
| 1046                      | 0                      | 652 ± 6                  | 97.5 ± 1.7                        | 0.17 ± 0.1           |
| 1046                      | 29                     | 682.5 ± 9.5              | 100.7 ± 3.6                       | 23.5 ± 2.5           |
| 1046                      | 48                     | 682.5 ± 9.5              | 89 ± 2.3                          | 36.5 ± 1.5           |
| 1046                      | 96                     | 684 ± 16                 | 88.6 ± 4                          | 76.5 ± 1.5           |
| 0                        | 96                     | -                       | -                                 | 40 ± 1               |
selectivity series (Aveston et al., 1958; Awual et al., 2008; Wheaton and Bauman, 1953), which for monovalent anions is as follows:

\[ \text{OH}^- \approx \text{F}^- < \text{H}_2\text{PO}_4^- < \text{HCO}_3^- < \text{Cl}^- < \text{HSO}_4^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{ClO}_4^- \]

This means that resin prefers poorly hydrated anions to highly hydrated anions when the charge of anions is equal (Awual et al., 2008; Awual and Jyo, 2011). Moreover, the following order has usually been found for dilute solutions in the case of strong anion exchangers (styrenic): \( \text{OH}^- < \text{F}^- < \text{HSiO}_3^- < \text{HCO}_3^- < \text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{HSO}_4^- < \text{SO}_4^{2-} \) (Harland, 1994). On the other hand, a hydrophilic, weak-base fibrous anion exchanger proved to have non-Hofmeister anion selectivity, and thus preferred phosphate in the presence of chloride and sulphate (Awual et al., 2011b). Although the exact selectivity trend was not studied in this work, the sorption tests performed in the presence of co-existing ions confirmed that PG-Peat was able to remove divalent sulphate ions efficiently (at neutral pH) in spite of the presence of monovalent chloride and nitrate ions (albeit in much lower concentrations).

### 3.3.5. Regeneration studies

Regeneration studies were performed to check the recyclability of the sorbent in order to support its potential application as a commercial sorbent in the future. The effect of recycling on the sulphate uptake capacity and desorption efficiency (%) of PG-Peat is presented in Fig. 8. The sulphate removal capacity of PG-Peat was not affected during the first two cycles tested where an uptake capacity of \( \approx 100 \text{mg/g SO}_4^{2-} \) was maintained. However, during the third cycle, there was a slight decrease in the performance of the sorbent (92.6 mg/g \( \text{SO}_4^{2-} \) uptake capacity) in comparison with the 98.6% and 100% desorption efficiency exhibited during cycle 1 and cycle 2, respectively. As with the sorption cycles, the desorption efficiency of PG-Peat slightly decreased during the third sorption cycle, although the sorbent still exhibited a high desorption efficiency of 92.5%. The release of \( \text{SO}_4^{2-} \) ions from the active binding sites of PG-Peat in exchange for \( \text{Cl}^- \) ions further proved that the main sorption mechanism involved was ion exchange. It could be inferred from these results that the developed bio-based anion exchanger, PG-Peat, exhibited high reuse potential. Thus, this recyclable product, possessing a high sulphate uptake capacity, can be considered highly cost-efficient.

### 3.3.6. Sulphate removal from mine water

The real mine water sampled after water treatment in the mine’s wastewater treatment plant contained 2168 mg/L sulphate. The aim was to conduct preliminary sorption studies with the mine water using the developed PG-Peat biosorbent and to reduce the sulphate concentration to \( \approx 1000 \text{mg/L} \). The target was set to about 1000 mg/L as this concentration was already feasible for release into the environment and, unless specifically required, reducing the sulphate concentration to a very low level would have been neither cost-efficient nor reasonable. PG-Peat performed more efficiently in sulphate removal under acidic conditions. This characteristic makes it a highly favourable candidate for sulphate treatment from acidic mine water, which contains a very low pH value (2–3). As previously discussed in section 3.3.2, the high efficiency of the sorbent at low pH values can be attributed to the amine groups (highly protonated under acidic conditions) and the additional quaternary ammonium groups grafted onto PG-Peat, which are thus able to attach \( \text{SO}_4^{2-} \) ions to their binding sites through the ion-exchange mechanism. At higher pH values, the amine groups are protonated to a lesser extent, leading to decreased anion uptake capacity (Elwakeel, 2010). This means that only the quaternary ammonium groups are responsible for anion uptake, which explains the lower efficiency of PG-Peat for sulphate removal from mine water without pH adjustment. As shown in Fig. 9, a dosage of 4 g/L exhibited the highest removal capacity (137 mg/g) under acidic conditions. The target residual concentration was only achieved the highest tested dosage: 12 g/L of PG-Peat (residual sulphate concentration: 1006 mg/L). However,
these preliminary tests with real mine water reveal that the developed biosorbent has great potential for the treatment of sulphate-contaminated waters as it is capable of reducing the sulphate concentration to below 1500 mg/L, which is the maximum achievable efficiency by gypsum precipitation (Runtti et al., 2018).

4. Conclusion

This study was conducted in order to develop a novel bio-based anion-exchanger using branched polyethyleneimine (PEI) and glyceld trimethylammonium chloride (GTMAC) for sulphate removal from mine water. FTIR and XPS analyses revealed the presence of quaternary ammonium and N-H groups, indicating the successful grafting of polymers onto the surface. Sulphate sorption on PG-peat was rapid and more efficient at lower pH values. The sulphate uptake capacity of the bio-based anion exchanger was not affected by the presence of chloride ions and only slightly affected by the presence of nitrate ions in the solution. Sorption-desorption studies revealed that PG-peat has high regeneration capacity, further highlighting the cost-effectiveness of the product. Preliminary tests with real mine water demonstrated the superior effectiveness of PG-peat under acidic conditions, indicating its suitability for treating acid mine water. Future studies will be focused on identifying the optimal sorption conditions for sulphate removal from real mine water.

Declaration of interest

None.

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Appendix A. Supplementary data

Supplementary data to this chapter can be found online at https://doi.org/10.1016/j.envres.2019.05.022.

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