

1 **Acid mine drainage treatment with novel high-capacity bio-based anion** 2 **exchanger**

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8 **Abstract**

9 Aminated peat (termed PG-Peat) produced using polyethylenimine and glycidyltrimethylammonium
10 chloride was used for the removal of sulphate from real acid mine drainage (AMD) in batch and
11 column mode sorption studies. In the batch tests, the highest sulphate removal capacity achieved was
12 125.7 mg/g. PG-Peat was efficient and rapid in sulphate removal from AMD even at low temperatures
13 (2-5 °C), achieving equilibrium within a contact time of 30 min. The PG-Peat column treating real
14 AMD showed even higher sulphate uptake capacity (154.2 mg SO₄²⁻/g) than the batch sorption
15 studies. The regenerative and practical applicability of PG-Peat was also tested in column set-ups
16 using synthetic sulphate solutions (at pH 5.8 and pH 2.0). The sulphate uptake capacity obtained was
17 higher in column mode when the solutions were treated at acidic pH (2.0) compared to pH 5.8. This
18 could be attributed to the presence of cationized amine groups on PG-Peat under acidic pH conditions.
19 Almost complete sulphate desorption was achieved with NaCl in the column that treated synthetic
20 sulphate solution at pH 5.8, while the lowest desorption rates were observed in the column that treated
21 acidic synthetic sulphate solution (pH 2).

22 **Keywords** Sulphate removal, Biosorbent, Aminated peat, Regeneration, Practical application

23

24 **1 Introduction**

25 Acid mine drainage (AMD) is generated through combined physico-chemical and biological
26 processes in mine water, and is characterized by low pH and high metal concentrations (Sánchez-
27 Andrea et al., 2014). AMD also contains elevated levels of sulphate, which is generated by the
28 geochemical weathering of acid-labile minerals and from the chemical oxidation of pyrite and other
29 sulphidic minerals when exposed to air and water; the processes are accelerated by bacterial action
30 (Chockalingam and Subramanian, 2006; Vera et al., 2013; Wills and Finch, 2016). In addition, the
31 chemicals (for example, sulphuric acid) used in mining operations also contribute to the high sulphate
32 concentrations present in AMD (Mamelkina et al., 2019; Runtti et al., 2018). High sulphate levels in
33 freshwater bodies cause salinization, which leads to a decrease in dissolved oxygen and can have
34 lethal effects on aquatic species as a result of osmoregulatory stress (Cañedo-Argüelles et al., 2013;
35 Soucek and Kennedy, 2005).

36 Global sulphate discharge limits vary considerably. Regarding sulphate discharge limits from mine
37 drainage and industrial wastewater, many environmental agencies have set limits between 250 and
38 1000 mg/L (Liang, 2014; Runtti et al., 2018; Silva et al., 2012), whereas countries like Finland have
39 set a sulphate concentration range of 1000-4000 mg/L as the discharge limits from mining effluents
40 (AVI, 2017, 2016, 2015, 2013). The sulphate level recommended in drinking water is 250 mg/L
41 (Decree of the Ministry of Social Affairs and Health, 2017; WHO, 2011).

42 There are several conventional methods for sulphate treatment. Wastewaters with high sulphate
43 concentrations are generally treated using gypsum precipitation, which is able to reduce sulphate
44 levels down to 1500-2000 mg/L, thus requiring supplemental treatment methods to achieve an even
45 lower residual sulphate concentration (Decree of the Ministry of Social Affairs and Health, 2017;
46 Kinnunen et al., 2018; Mamelkina et al., 2019; Tian et al., 2019). Biological sulphate treatment from
47 industrial effluents and mine water is another widely suggested method, which utilizes sulphate-

48 reducing bacteria to reduce sulphate to sulphide, which then forms metal precipitates. However, under
49 anoxic or anaerobic conditions hydrogen sulphide may form, which raises safety issues for operating
50 personnel and also presents corrosion problems (Barton and Hamilton, 2007; Kinnunen et al., 2018;
51 Muyzer and Stams, 2008). Sulphate-reducing bacteria can also accelerate the conversion of mercury
52 to its methylated form (Andrews et al., 2004). Additionally, apart from high operational costs, this
53 method of sulphate removal is extremely sensitive to the environmental conditions around it as a
54 consequence of rigid microbial growth conditions (Muyzer and Stams, 2008; Silva et al., 2012).
55 Membrane technologies such as electrodialysis, nanofiltration and reverse osmosis exhibit high
56 sulphate removal efficiency, but require the pre-treatment of AMD in order to prevent setbacks such
57 as membrane fouling, which in turn leads to increased operational costs and lower water recovery
58 (Soucek and Kennedy, 2005).

59 Adsorption is a simple, low-cost and effective treatment method for sulphate removal (Gogoi et al.,
60 2019; Katal et al., 2012; Sang et al., 2013). Although several commercial anion exchange resins are
61 available for anionic pollutant adsorption, their application on industrial scale is quite expensive (Xu
62 et al., 2016). Additionally, there is a shortage of commercial sorbents which are specifically capable
63 of removing sulphate from mine water (Soucek and Kennedy, 2005). Sorption using bio-based anion
64 exchangers is a green and sustainable alternative for sulphate removal as biomass-based raw materials
65 are cheap, abundantly available and environment-friendly (Cao et al., 2011). It should be noted that
66 cationic functional groups, which may bind anionic pollutants, need to be introduced onto the biomass
67 surface through chemical modification (Gogoi et al., 2019; Hong et al., 2017). Cellulose and
68 hemicellulose, the two main polysaccharides present in biomass, contain reactive hydroxyl groups in
69 the constituent anhydroglucose units, which are responsible for interacting with introductory
70 chemicals and hence produce functional polymers (Orlando et al., 2002).

71 A novel bio-based anion exchanger (PG-Peat) was developed in the previous work reported by Gogoi
72 et al., (2019) wherein a unique combination of chemicals (polyethylenimine and

glycidyltrimethylammonium) was applied. Characterization studies like Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) proved the successful grafting of both amine and quaternary ammonium groups onto the surface of modified peat. The novel product exhibited a sulphate uptake capacity of 189.5 ± 2.7 mg/g in acidic synthetic sulphate solution. As there is limited information available on how biosorbents (including PG-Peat) would work on actual industrial effluents, the main focus and novelty of the present study is to evaluate PG-Peat in batch and column mode for sulphate removal from real AMD. Additionally, bearing in mind that winter is the predominant season in Nordic countries as well as in many other cold climate regions, this study investigates the performance of aminated peat for treating acid mine drainage under cold conditions. As the regenerative capability of aminated peat has already been confirmed through batch studies (Gogoi et al., 2019), the current research focuses on regeneration studies performed in the column mode using both synthetic sulphate solutions and real AMD.

2 Materials and methods

2.1 Chemicals and materials used and water analysis

All the chemicals used in the study were of analytical grade. The chemicals used for biomass modification were polyethylenimine ($\geq 99\%$ purity, M_w 25,000 by LS, branched, Sigma-Aldrich) (PEI) and glycidyltrimethylammonium chloride ($\geq 90\%$ purity, Sigma-Aldrich) (GTMAC). Sodium sulphate (99% purity, Baker) was used for preparing synthetic sulphate solutions. Concentrated HCl (37%, Merck) was diluted using Milli-Q water (Merck Millipore) to prepare 0.1 M and 2 M HCl solutions, which were used for pH adjustment of sulphate solutions and for analysing sulphate concentrations (in the case of the turbidimetric method). Sodium chloride (Merck) was dissolved in Milli-Q water to prepare 1 M NaCl solutions. Barium chloride (99.9% purity, VWR) and ethylene glycol (99%, Merck) were used in the sulphate analysis using a UV-Vis spectrophotometer.

96 Raw peat was acquired from Stora Enso Veitsiluoto, a pulp mill located in Kemi (Finland) which
97 burns peat for energy production. The properties of the raw peat used has been reported in the study
98 by Leiviskä et al., (2018). Peat was sieved to a size fraction of 90-250 μm in order to ensure uniformity
99 throughout the study. Acid mine drainage (AMD) was obtained from a Finnish mine site. The
100 characteristics of the sampled AMD can be found in the supplementary material (Table S1).

101 The pH of the samples was measured using a VWR Phenomenal pH 1000L meter. For the batch
102 sorption tests and column experiments involving AMD, the initial and residual SO_4^{2-} concentrations
103 were analysed using Hach Lange cuvette tests (LCK 153 for 40-150 mg/L and LCK 353 for 150-900
104 mg/L) and a Hach Lange spectrophotometer. For analysis of sulphate concentrations between 40-150
105 mg/L, a sample of 5 mL in volume was pipetted into the test cuvette (LCK 153), following which a
106 spoonful of barium chloride (BaCl_2) was added and then the cuvette was shaken for 2 min. Samples
107 having sulphate concentrations in the range of 150-900 mg/L were prepared by adding 2 mL of sample
108 volume into the test cuvette (LCK 353), adding a pinch of the barium chloride provided by the test
109 kit, then shaking the cuvette for 1 min and letting it rest for 30 sec. The prepared cuvettes were
110 inserted into the cuvette slot provided in the spectrophotometer equipment to measure the residual
111 sulphate levels. For analysis of sulphate concentrations from samples collected from the column
112 studies using synthetic sulphate solutions, the turbidimetric method (APHA, 1992) was used. This
113 method involved adding 5 mL of prepared samples (diluted accordingly) to 10 mL test tubes, to which
114 1 mL of 2 M HCl, 0.2 mL of ethylene glycol, 3 mL of Milli-Q water and 0.8 mL of 5% BaCl_2 were
115 then added. The samples were shaken and allowed to stand for 30 min, during which white colloidal
116 BaSO_4 was formed. The samples were measured using the UV-Vis spectrophotometer (480 nm
117 wavelength).

118 Analysis of real acid mine drainage was performed as follows: SO_4^{2-} , Cl^- and F^- were analysed using
119 ion chromatography (SFS-EN ISO 10304-1:2009), while a continuous flow analyser (SFS-EN ISO
120 13395:1997, SFS-EN ISO 11732:2005, SFS-EN ISO 15681-2:2005) was used to analyse $\text{NO}_2\text{-N}$,

121 NO₃-N, NH₄-N and PO₄-P. The concentration of elements in the AMD (see supplementary material,
122 Table S1) was analysed using inductively coupled plasma mass spectrometry (ICP-MS) (SFS-EN
123 ISO 17294-2:2016). The water quality data of AMD was analysed using MineQL+ software.

124 **2.2 Production of aminated peat (PG-Peat)**

125 Aminated peat was prepared using a two-step procedure that was developed by Gogoi et al., (2019).
126 Briefly, 2 g of raw peat was reacted with PEI (dosage 0.26 mmol/g biomass) for 6 h in a round-bottom
127 flask in a water bath. After the reaction with PEI, the material was washed with Milli-Q water two or
128 three times to remove the excess unreacted chemical. The second reaction step involved mixing the
129 PEI-modified peat with GTMAC (dosage 0.0447 mol/g biomass) for 12 h. A constant reaction
130 temperature (60 °C) was maintained for both the reactions involving PEI and GTMAC for peat
131 modification. The PEI+GTMAC-modified peat (referred to as PG-Peat) was washed carefully several
132 times with deionized water to remove excess chemicals and then dried at 60 °C for 1-2 days. Once
133 the modification method was confirmed to be effective for sulphate removal, a larger batch (40 g) of
134 the modified biosorbent (PG-Peat) was prepared and used for all the sorption experiments performed
135 in this study. The bulk density of the PG-Peat was measured to be 0.805 g/cm³.

136 **2.3 Batch sorption tests**

137 The efficiency of PG-Peat in removing sulphate from AMD was studied through batch sorption
138 experiments. A specific amount of PG-Peat was weighed into 50 mL tubes, followed by the addition
139 of 50 mL of AMD. The samples were shaken in a horizontally rotating shaker for a specific period of
140 time at a specific temperature. The treated AMD was separated from the sorbent by centrifugation
141 (Jouan C4.12, 2500 rpm, 10 min). The sulphate cuvette test method (mentioned in section 2.1) was
142 used to analyse the residual sulphate concentration. The samples were measured for their initial and
143 final pH values. The following equation was used to measure the sulphate removal capacity of PG-
144 Peat from AMD:

$$q = \frac{(C_o - C_e)V}{m} \quad (1)$$

where C_o and C_e 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. All the batch experiments were performed in duplicate and the error values were calculated as the deviation of two repetitions.

2.3.1 Effect of dosage

The effect of dosage on the capacity of PG-Peat to remove sulphate from AMD was studied at varying dosages (4, 12, 16 and 20 g/L) of PG-Peat and 50 mL of AMD. The samples were shaken for 24 h at room temperature. The residual sulphate concentration and final pH of the solutions were measured. The optimum dosage was then chosen for the subsequent batch sorption experiments.

2.3.2 Effect of temperature and contact time

The effect of temperature (2, 5, 10 and 22 ± 2 °C) was studied at varying contact times (5 min, 30 min, 1 h, 2 h, 4 h, 8 h and 24 h) using a dosage of 12 g/L PG-Peat and 50 mL of AMD. The residual sulphate concentration and final pH of the treated solutions were measured. The experimental data was fitted to pseudo-first order (PFO) (Lagergren, 1898), pseudo-second order (PSO) (Blanchard et al., 1984) and Elovich (Roginsky and Zeldovich, 1934) models in order to study the sorption kinetics. The equations are given in the supplementary material and the nonlinear optimization technique was applied.

2.4 Column tests

PG-Peat was tested in column sorption set-ups for its capacity to remove sulphate from synthetic sulphate solutions as well as from real AMD. The regeneration efficiency of PG-Peat was tested using synthetic sulphate solutions (1050-1180 mg/L SO_4^{2-}) using three sorption-desorption cycles. In the first column, the synthetic sulphate solutions were fed into the inlet pipe at their original pH (5.8),

168 whereas the pH of the synthetic sulphate solutions fed into the second column was adjusted to 2. A
169 third column was used to study the sulphate sorption capacity of PG-Peat from real acid mine drainage
170 ($1950 \text{ mg/L SO}_4^{2-}$) using one sorption-desorption cycle. Between each sorption-desorption cycle, the
171 column was rinsed with 100 mL of Milli-Q water and the sulphate concentration was analysed and
172 taken into account in the mass balance calculations.

173 For the column set-up used for sulphate treatment of synthetic solutions, 5 g of sorbent was mixed
174 with 70 g of quartz sand (0.5-1 mm) to create a sorbent-quartz mixture so as to facilitate the upward
175 flow of inlet solution throughout the column length. The concept of having a mixed column of sorbent
176 and quartz sand to maintain a high flow rate was obtained from the study by Shabtai and Misheal
177 (2018). Mixing the sorbent with quartz sand also prevented clogging of the column, as the sorbent in
178 itself was in powder form and the quartz sand (having a fixed fraction size) facilitated a stable flow
179 of solution through the column. It was confirmed with batch tests that quartz sand did not sorb
180 sulphate. In comparison, the column used for real AMD contained 10 g of PG-Peat mixed with 90 g
181 of quartz sand (0.5-1 mm). All columns were 29 cm long and had an inner diameter of 1 cm. Bed
182 volumes were 72.2 cm^3 in the columns used for synthetic sulphate solutions and 81.6 cm^3 in the
183 columns used for AMD. The upper and lower parts of the column (3 cm height at each end for the
184 columns treating synthetic sulphate solutions and 1.5 cm height at each end for the columns treating
185 AMD) were filled with quartz sand (0.7-12 mm particle size); the column ends were sealed with glass
186 wool to prevent leakage. A flow rate of 8.4 mL/min was used in the sorption-desorption cycles in all
187 the columns studied. Empty bed contact times were 8.6 min in the columns used for synthetic sulphate
188 solutions and 9.7 min in the columns used for AMD.

189 PG-Peat was regenerated in the desorption cycles using 1 M NaCl solution. The effluent solutions
190 were collected in fractions of 100 mL: (a) for the sorption cycles, the number of fractions collected
191 depended on the biosorbent reaching its saturation capacity and (b) in the case of desorption, the
192 fractions were collected until all the sulphate ions that had sorbed during the preceding sorption cycle

193 were desorbed as effluents from the column. All the fractions collected from the first two columns
194 were tested for their residual sulphate concentration using the turbidimetric method. The fractions
195 which were collected from the columns treating acid mine drainage were analysed using the cuvette
196 test method. The saturation capacity q_s (mg/g) of PG-Peat for each of the columns tests was calculated
197 using the following formula:

$$198 \quad q_s = \frac{c_0 V_0 - \sum c_n V_n}{m} \quad (2)$$

199 where c_0 is the initial sulphate concentration (mg/L), V_0 is the input volume of the sulphate solution
200 (L), c_n is the final sulphate concentration in fraction n (mg/L), V_n is the volume of fraction n (L) and
201 m is the mass of the sorbent (g).

202 **3 Results and discussion**

203 **3.1 Water quality analysis**

204 The AMD had a pH of 4.3 and contained 1950 mg/L of sulphate and 1.8 mg/L of nitrate (Table S1).
205 The elements present in the AMD in the highest concentrations were calcium (249 mg/L), sodium
206 (229 mg/L), magnesium (143 mg/L), aluminium (55.2 mg/L), potassium (23 mg/L), silicon (14.3
207 mg/L) and zinc (11.7 mg/L). The sulphate concentration in the AMD (pH 4.3) used in this study was
208 significantly lower than that of the AMDs reported in the literature. For example, AMD samples
209 collected from a mine in Ireland in the study by Gray (1996) contained 10579 mg/L SO_4^{2-} (pH 2.7).
210 On the other hand, Luptáková et al. (2016) reported sulphate concentrations of 1800-3200 mg/L in
211 the AMD discharge (pH 3.5-3.9) between the period 2006-2015 in the abandoned Smolnik sulphide
212 deposit in the Slovak Republic. When the pH of acid mine drainage is increased, the extent of sulphate
213 removal by precipitation and the type of precipitates formed are greatly affected by the chemical
214 characteristics of the AMD (Madzivire et al., 2014, 2011). It should be noted that gypsum
215 precipitation is capable of reducing the residual sulphate concentration down to only 1500-2000 mg/L

(Kinnunen et al., 2018). Since the sulphate concentration in the AMD used in this study was within this range (1950 mg/L), further additional treatment (apart from gypsum precipitation) would be required to lower the residual sulphate concentration further.

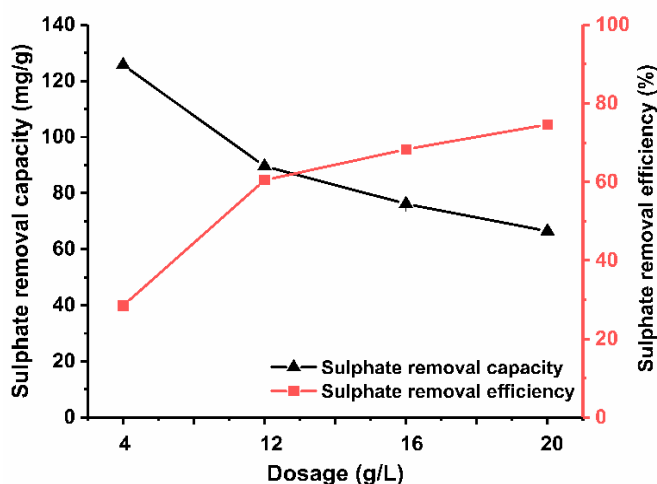
Chemical speciation calculations made with MineQL+ software (Schecher and McAvoy, 1992) estimated that 51% of the sulphate (mol. %) was present as the SO_4^{2-} ion in the AMD (pH 4.3), while about 0.25% could be present as HSO_4^- . A large portion of the sulphate in the AMD solution was assumed to be strongly associated with Ca^{2+} , Mg^{2+} and Na^+ ions (21.5% CaSO_4 (aq), 18.9% MgSO_4 (aq), 2.6% NaSO_4^-). Additionally, the calculations also indicated that the vast majority of the nitrate (99.4%) in the AMD was present in the NO_3^- ion form. The speciation of components present in AMD is listed in supplementary material (Table S2).

3.2 Batch sorption results

3.2.1 Effect of dosage

The effect of dosage on sulphate removal from acid mine drainage was studied using different dosages of PG-Peat (4-20 g/L) for 24 h contact time at room temperature (22 ± 2 °C). As can be seen from Fig. 1, the sulphate removal capacity of PG-Peat was the highest (125.7 mg SO_4^{2-} /g) at the initial dosage of 4 g/L and decreased gradually with the increase in sorbent dosage. The final pH of the AMD after 24 h sorption varied between 5.3 and 6.3, depending on the sorbent dosage used (a slight increase in final pH was observed as the dosage was increased). The increase in the final pH of AMD after the sorption tests is most likely related to the transfer of protons onto the biosorbent, as was also stated in the research by Awual and Jyo (2011). In terms of removal efficiency (%), PG-Peat performed better with increasing dosages due to the presence of an increased number of active sorption sites (Gogoi et al., 2018). However, in terms of capacity, the results were the opposite because the sorption capacity of the sorbent at higher sorbent dosages was not completely utilized in comparison to a lower dosage of PG-Peat.

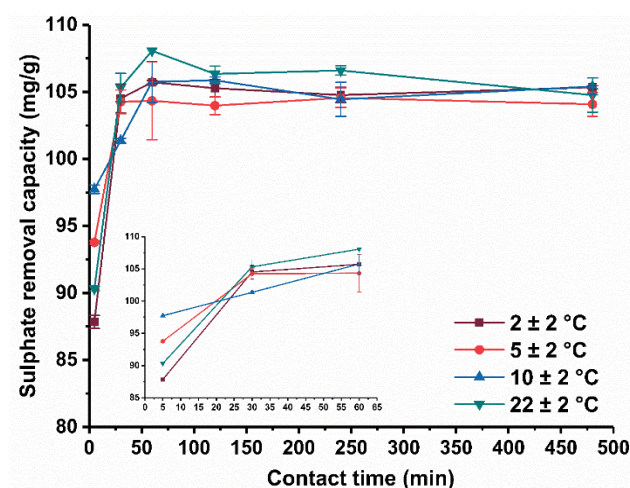
240 The sulphate removal capacity achieved by PG-Peat with AMD was lower than the sorption capacity
241 achieved earlier for synthetic solutions at pH 2 (189.5 mg SO₄²⁻/g) (Gogoi et al., 2019). This could
242 be due to the slightly higher pH (4.3) of AMD and the presence of competing ions contained in it (for
243 example chloride, fluoride, nitrite and nitrate). The higher sorption capacity at PG-Peat at lower pH
244 is due to the presence of cationized amine groups which become protonated under acidic conditions,
245 in addition to the quaternary ammonium groups which are cationized throughout the pH range (Gogoi
246 et al., 2019). It was previously found that the presence of co-existing anions such as nitrate had a
247 slight effect on the sulphate removal capacity of PG-Peat (Gogoi et al., 2019). Nevertheless, the
248 sorbent still maintained a very high sulphate sorption capacity (>100 mg SO₄²⁻/g) with real AMD,
249 especially when compared to other studies previously reported. For example, Cao et al. (2011)
250 reported a sulphate sorption capacity of 74.8 mg/g using modified rice straw from aqueous sulphate
251 solutions, while the organo-nanoclay-based sorbent produced by Chen and Liu (2014) showed a
252 maximum sulphate sorption capacity of 38.0 mg/g. Runtti et al. (2016) developed a barium-modified
253 analcime that exhibited a sulphate sorption capacity of 119 mg/g from mine water (pH 7-8), whereas
254 Hong et al. (2014) reported a capacity of 41 mg/g with AMD (pH 8 after lime treatment) using
255 polypyrrole-grafted granular activated carbon. Additionally, Zheng et al. (2019) achieved a sulphate
256 removal capacity of 123.9 mg/g from AMD (pH 2) using unmodified Malan loess (a sediment formed
257 by the accumulation of windblown dust, consisting of calcium and carbonate) as a sorbent. It is also
258 worth noting that the sulphate sorption capacity of PG-Peat (i.e. 125.7 mg/g = 2.62 meq/g obtained
259 at 4 g/L PG-Peat in batch tests with AMD) is quite close to the total exchange capacity given for the
260 commercial strong anion exchange resins, Purolite A300 (3.5-3.7 meq/g of dry resin) (Purolite) and
261 Purolite A520E (2.8 meq/g of dry resin) (Nur et al., 2012). Considering the effect of PG-Peat dosage
262 on both the sulphate removal capacity and removal efficiency, the decision was made to use 12 g/L
263 PG-Peat dosage for further batch sorption studies involving the AMD samples.



264 **Fig.1** Effect of dosage on sulphate removal from acid mine drainage using PG-Peat. Initial sulphate
 265 concentration 1950 mg/L; $\text{pH}_{\text{initial}}$ 4.3, pH_{final} 5.3-6.3; temperature 22 ± 2 °C. Contact time 24 h. Error
 266 bars represent the deviation of two repetitions (however, error bars are smaller than the data point
 267 symbols).

268 3.2.2 Effect of temperature and contact time

269 PG-Peat was tested at different temperatures using a range of contact times with the aim of checking
 270 whether the biosorbent's sorption efficiency was affected by the variation in temperature and whether
 271 PG-Peat could be used for the treatment of cold acid mine drainage. The sorption of sulphate from
 272 AMD at temperatures of 2-22 °C exhibited similar performance for longer contact times (2 h – 24 h;
 273 24 h data not shown) with >100 mg SO_4^{2-} /g being removed. It should be noted that the effect of
 274 temperature varied with a short contact time (5 min). The sorption performance was highest (97.7
 275 mg/g sulphate removal capacity) at 10 ± 2 °C, thus indicating the efficiency of the sorption mechanism
 276 even at low temperature ranges. At all of the temperatures studied, sorption equilibrium was achieved
 277 at 30 min contact time (104.5-105.3 mg/g sulphate removal capacity) (Fig. 2). It can be inferred that
 278 the overall sorption performance of PG-Peat for sulphate removal from acid mine drainage remained
 279 higher than 100 mg/g even at low temperatures and that the sorption mechanism maintained its rapid
 280 uptake. The fast sorption is due to the ion exchange mechanism, which is considered to be the main
 281 sorption mechanism with PG-Peat (Gogoi et al., 2019).



282 **Fig. 2** Effect of temperature and contact time on sulphate removal capacity from acid mine drainage
 283 using PG-Peat. PG-Peat dosage 12 g/L; initial sulphate concentration 1950 mg/L; $\text{pH}_{\text{initial}}$ 4.3, pH_{final}
 284 5.3-6.4. Error bars represent the deviation of two repetitions.

285 The affinity between the sorbent and the sorbate play an important role in understanding the kinetics
 286 of the sorption process (Tran et al., 2017). The experimental data from the contact time sorption tests
 287 studied at different temperatures was fitted to pseudo-first-order (PFO), pseudo-second-order (PSO)
 288 and Elovich models in order to study the sorption kinetics (Fig. 3); the parameters of the three kinetic
 289 models are shown in Table S3 (supplementary material). The experimental sorption capacity at
 290 equilibrium is similar to the theoretical values provided by the PFO and PSO kinetic models. With
 291 the exception of the contact time experiments performed at 10 ± 2 °C, close-to-unity values (0.96-0.99)
 292 of the correlation coefficients (R^2) were provided by the PFO model, thus implying that the sorption
 293 of sulphate on PG-Peat follows the PFO model the best. The negligible values of the error analysis
 294 (χ^2) for the PFO model further support this inference. The poor values of R^2 and χ^2 provided by the
 295 Elovich model suggested that the sorption phenomena was not a heterogeneous diffusion process
 296 (Tran et al., 2017). The isotherm modelling by Gogoi et al. (2019) had earlier reported that the
 297 isotherm data followed the Langmuir isotherm.

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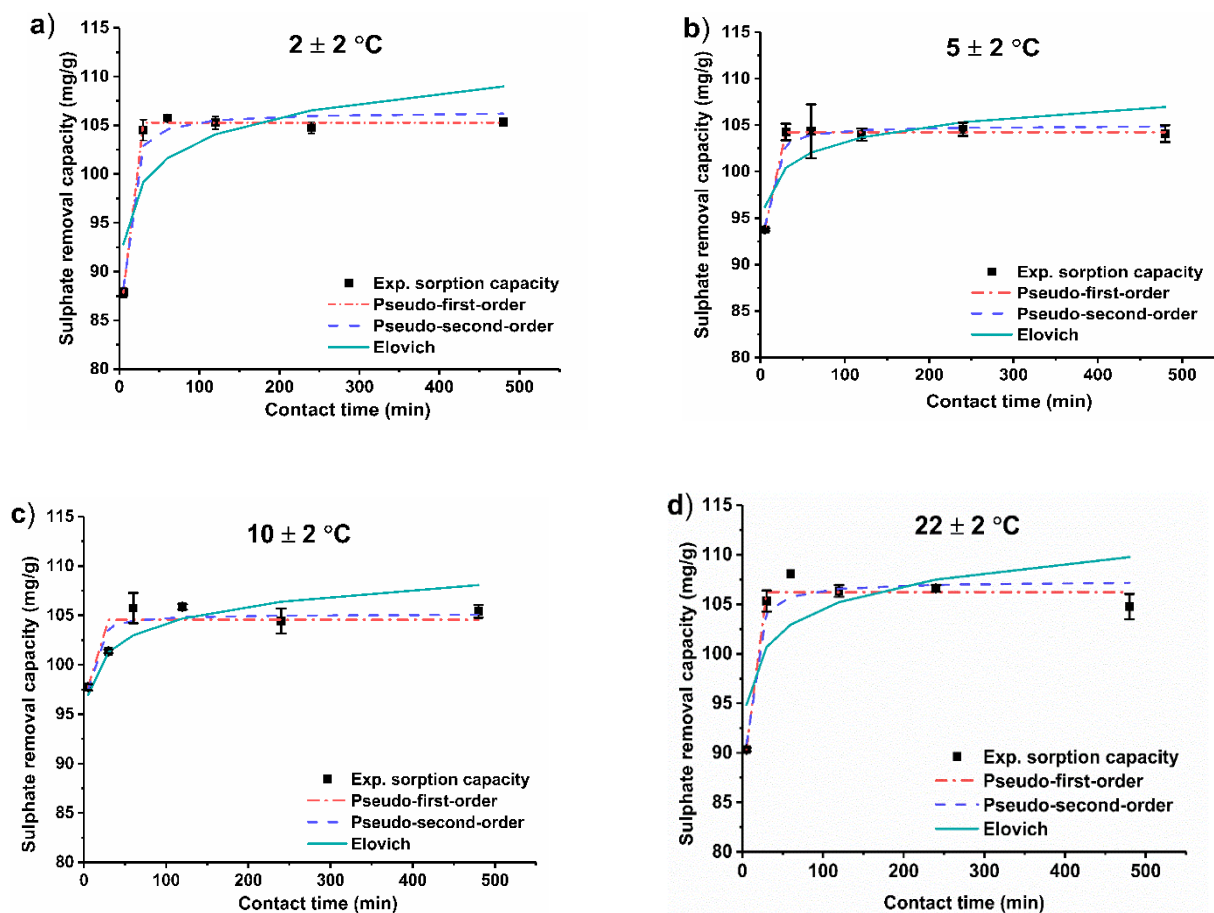


Fig. 3 Pseudo-first-order, pseudo-second-order and Elovich kinetics and experimental kinetics for the sorption of sulphate from AMD on PG-Peat at different temperatures. PG-Peat dosage 12 g/L; initial sulphate concentration 1950 mg/L; $\text{pH}_{\text{initial}}$ 4.3, pH_{final} 5.3-6.4. Error bars represent the deviation of two repetitions.

3.3 Column studies

3.3.1 Regeneration studies with synthetic sulphate solutions

The regenerative performance of PG-Peat was studied in columns by using synthetic sulphate solutions (at pH 2 and 5.8) through three cycles of sorption-desorption. These studies were performed as the re-usability of the biobased anion exchanger is crucial for applying the sorbent on an industrial scale. Since the main sorption mechanism for sulphate removal by PG-Peat is ion exchange (Gogoi

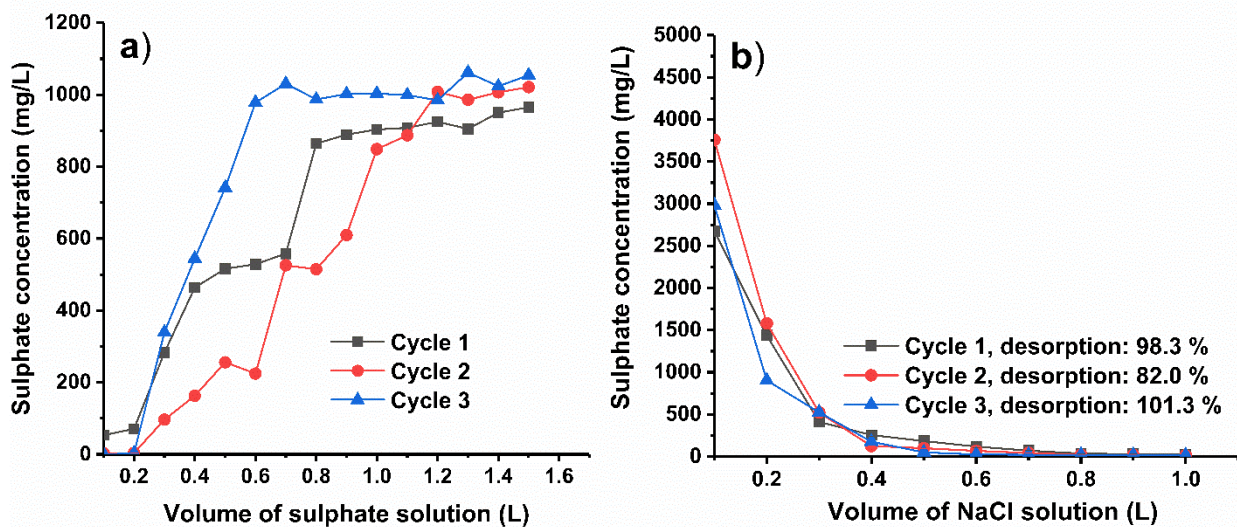
et al., 2019), the desorption procedure was performed using NaCl solutions as Cl^- ions are able to elute SO_4^{2-} ions from PG-Peat's active binding sites.

The results of the sorption and regeneration studies with synthetic solutions are presented in Fig. 4 and Fig. 5. For an ideal S-shaped sorption curve at the beginning of the sorption process, nil or a minimal amount of sulphate should be detected in the initial fractions, which would symbolize a rapid and effective sorption by the sorbent during the initial phase. In this study, the first column (pH 5.8) achieved breakthrough at the very beginning of the sorption cycles, indicating that the contact time was too short (Fig. 4 a). Following the breakthrough points, there was a rapid increase in the sulphate concentration of the effluent solutions. After this period, the sulphate sorption subsequently decreased as the sorbent approached saturation. The sorbent reached its saturation point quite early during the first and final sorption cycle, whereas the second sorption cycle exhibited an irregular pattern to achieve its saturation point. For column 2, through which acidic sulphate solution (pH 2) was passed, the breakthrough point of the first cycle was achieved much later compared to the second and third sorption cycles (Fig. 5 a). However, all the sorption cycles exhibited a similar trend when approaching their saturation point after about 1000 mL of acidic sulphate solution had passed through the column.

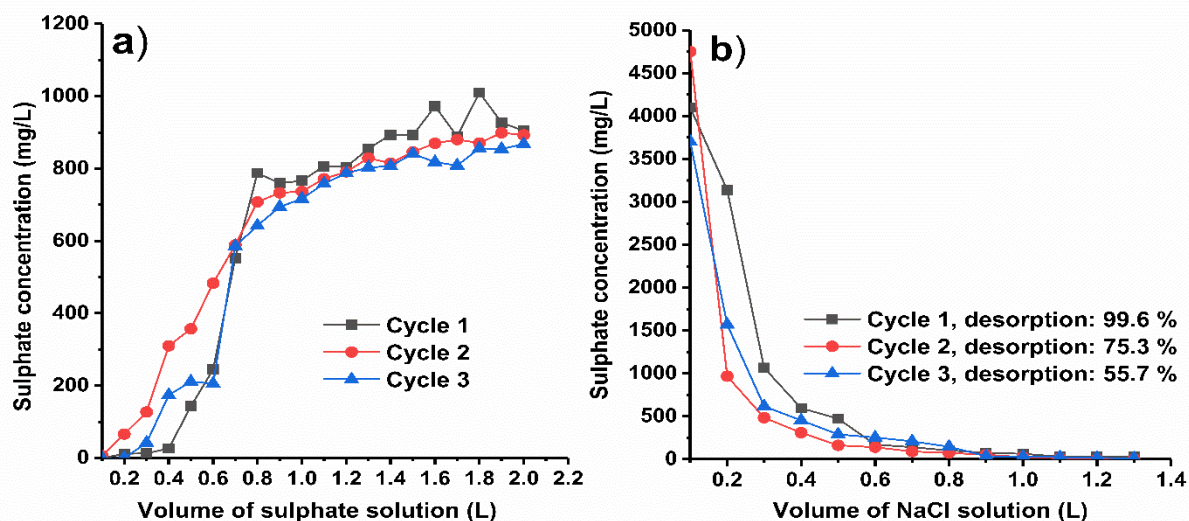
Table 1 presents the obtained saturated sorption capacities of PG-Peat in column mode. In the case of column 1, the sorption capacity was very high (122.7 and 151.9 mg/g) during the first two cycles, although the slightly lower removal capacity during the first cycle (122.7 mg/g) could be attributed to the early breakthrough point compared to the second cycle. The third sorption cycle exhibited the lowest sorption saturation capacity (79.9 mg/g), which could be attributed to the saturation of the sorbent after the multiple sorption-desorption cycles as a consequence of blocking or loss of active binding sites on the PG-Peat. Interestingly, in the second column, which studied the sorptive performance of PG-Peat from acidic sulphate solutions, the sorbent exhibited much higher saturation capacities throughout the sorption cycles ($> 220 \text{ mg SO}_4^{2-}/\text{g}$). This could be attributed to the presence of protonated amine groups on the sorbent under acidic conditions in addition to the quaternary

334 ammonium groups (cationic throughout the pH range). The saturation capacities of the first two
335 sorption cycles were close to one another, while there was a slight increase in the saturation capacity
336 during the third cycle (Table 1), thus proving that the sorbent maintained its high efficiency in treating
337 acidic sulphate solutions throughout all the cycles studied.

338 The results of desorption cycles for both the columns studied are shown in Fig. 4 (b) and 5 (b). For
339 column 1 (pH 5.8), the desorption efficiency varied between 82 and 101% for the three cycles studied.
340 The desorption curve showed a very high sulphate concentration in the first fractions followed by a
341 sharp decrease in the subsequent fractions (Fig. 4 b). When a rinsing step was used (with Milli-Q
342 water) after each desorption cycle, almost no sulphate was found in the rinsing water fractions. In the
343 case of column 2 (pH 2), the desorption cycles generated a high sulphate concentration in the first
344 fraction collected followed by a steep decline as more salt solutions were passed through (Fig. 5 b).
345 The first desorption cycle exhibited a high regeneration efficiency of 99.6%, followed by a decrease
346 in efficiency during the subsequent cycles (55.7% in the final cycle). The lower desorption efficiency
347 witnessed in column 2 (operated under acidic conditions) could be attributed to the stronger bond
348 between the sulphate ions and the protonated amine groups under the acidic conditions.



349 **Fig. 4** Sorption and regeneration studies in column mode: a) sorption and b) desorption with synthetic
 350 sulphate solution ($\text{pH}_{\text{initial}} 5.8$) using PG-Peat. PG-Peat amount 5 g; initial sulphate concentration
 351 1050 mg/L; NaCl concentration 1 M.



352 **Fig. 5** Sorption and regeneration studies in column mode: a) sorption and b) desorption with synthetic
 353 sulphate solution ($\text{pH}_{\text{initial}} 2.0$) using PG-Peat. PG-Peat amount 5 g; initial sulphate concentration
 354 1180 mg/L; NaCl concentration 1 M.

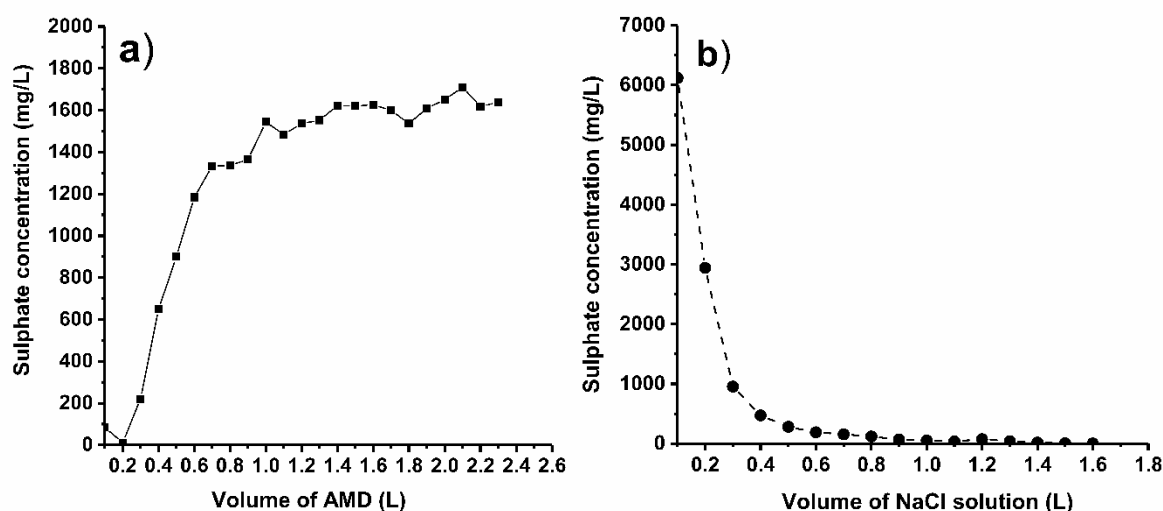
355 **Table 1.** Saturation capacity q_s (mg/g) of column sorption studies using PG-Peat from synthetic
 356 sulphate solutions (at pH 5.8 and at pH adjusted to 2) and AMD (pH 4.3).

Cycles	Saturation capacity q_s (mg/g)		
	Synthetic	Synthetic	AMD
	(pH 5.8)	(pH 2.0)	(pH 4.3)
1	122.7	226.8	154.2
2	151.9	220.4	-
3	79.9	242.6	-

357

358 3.3.2 Column sorption tests with acid mine drainage

359 The sorption performance of PG-Peat was also tested in column mode using acid mine drainage (only
360 one cycle). As can be seen in Fig. 6 (a), the breakthrough point was achieved already after 200 mL
361 of AMD had passed through the column. However, the saturation sorption capacity of the biosorbent
362 was 154.2 mg SO_4^{2-} /g (Table 1), which is even higher than that obtained in batch mode (section 3.2.1).
363 The sorption-desorption curves (Fig. 6) showed a similar shape to those of the columns with synthetic
364 sulphate solutions. The initial desorption fraction consisted of a very high amount of sulphate (6118
365 mg/L), and rapidly released sulphate in exchange for chloride ions as desorption progressed. The
366 desorption efficiency was 74.8%. About 0.8 L of salt solution (9.8 bed volumes) was required to
367 desorb most of the sulphate from the sorption column. When considering the concentration factor and
368 the practical application of PG-Peat for sulphate removal from AMD, a few conditions would still
369 need to be optimized. Firstly, in both the sorption and desorption stages, the contact time should be
370 increased. Secondly, the desorption process could be made more efficient by increasing the salt
371 concentration in the regenerant solution. These optimization steps could thereby increase the
372 desorptive performance of the sorbent and hence make it more viable for practical application. The
373 regenerant solution used, containing a high concentration of sulphate, is waste and needs to be
374 disposed of appropriately. Upon the exhaustion of PG-Peat after several regeneration cycles, the peat-
375 based product could be burnt and energy could be recovered.



376 **Fig. 6** a) Sorption and b) desorption studies with acid mine drainage using PG-Peat in column mode.
 377 PG-Peat amount 10 g; initial sulphate concentration 1950 mg/L; NaCl concentration 1 M; $pH_{initial}$ 4.3.

378 4 Conclusion

379 The research was conducted to study the removal of sulphate from real acid mine drainage using PG-
 380 Peat, a novel bio-based anion exchanger. Batch sorption studies conducted at different temperatures
 381 and at different contact times revealed that the sorbent was efficient in treating AMD even under cold
 382 conditions and that the sorption process maintained its rapidity. Column sorption experiments
 383 involving synthetic sulphate solutions revealed that PG-Peat performed much better in sulphate
 384 sorption under very acidic conditions, while it maintained a better regenerative efficiency for the
 385 treatment of sulphate solutions at its original pH. Overall, the sulphate uptake capacity of PG-peat
 386 from AMD was higher in column mode compared to batch sorption mode. Studies conducted using
 387 real AMD in column mode indicated the potential applicability of the sorbent for sulphate removal
 388 from AMD. The optimization of process parameters would be the next step. Treated AMD can be
 389 released into nearby water bodies as long as the effluent quality complies with the permissible limits
 390 established by the authorities concerned.

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