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# Sulphate removal over barium-modified blast-furnace-slag geopolymer

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## Abstract

Blast-furnace slag and metakaolin were geopolymerised, modified with barium or treated with a combination of these methods in order to obtain an efficient  $\text{SO}_4^{2-}$  sorbent for mine water treatment. Of prepared materials, barium-modified blast-furnace slag geopolymer (Ba-BFS-GP) exhibited the highest  $\text{SO}_4^{2-}$  maximum sorption capacity (up to **119**  $\text{mg g}^{-1}$ ) and it compared also favourably to materials reported in the literature. Therefore, Ba-BFS-GP was selected for further studies and the factors affecting to the sorption efficiency were assessed. Several isotherms were applied to describe the experimental results of Ba-BFS-GP and the Sips model showed the best fit. Kinetic studies showed that the sorption process follows the pseudo-second-order kinetics. In the **dynamic** removal experiments with columns, total  $\text{SO}_4^{2-}$  removal was observed initially when treating mine effluent. The novel modification method of geopolymer material proved to be technically suitable in achieving extremely low concentrations of  $\text{SO}_4^{2-}$  ( $< 2 \text{ mg L}^{-1}$ ) in mine effluents.

Keywords: blast-furnace slag, metakaolin, geopolymer, adsorption, sulphate

# 1 Introduction

Sulphate ( $\text{SO}_4^{2-}$ ) is a common anion in both natural water and industrial wastewater, such as acid mine drainage. Natural sources of  $\text{SO}_4^{2-}$  include the chemical weathering of sulphur-containing minerals and the oxidation of sulphides and sulphur [1–3].  $\text{SO}_4^{2-}$  is non-toxic, and sulphur is a necessary mineral for several organisms. However, high concentrations of  $\text{SO}_4^{2-}$  in aqueous environments can cause the mineralisation of water, corrosion of reinforced steel, scaling of equipment and damage to mammals as well as endangering human health [1–4]. Under anaerobic conditions,  $\text{SO}_4^{2-}$  can be reduced to hydrogen sulphide ( $\text{H}_2\text{S}$ ) by sulphate-reducing bacteria.  $\text{H}_2\text{S}$  is dangerous to environmental ecosystems due to its reactivity, toxicity and corrosivity [1, 4].

In Finland, the  $\text{SO}_4^{2-}$  limit in drinking water is set at  $250 \text{ mg L}^{-1}$ . However, the recommended maximum concentration is even lower ( $150 \text{ mg L}^{-1}$ ) to ensure that water pipes are not damaged [5]. Environmental agencies in many countries have set the maximum  $\text{SO}_4^{2-}$  concentration between 250 and  $500 \text{ mg L}^{-1}$  for both mine drainage and industrial effluents [2, 6]. When there is no established limit for  $\text{SO}_4^{2-}$ , limits for total dissolved solids (TDS) are usually defined, which means that  $\text{SO}_4^{2-}$  concentrations must comply with the TDS values [7]. In many countries, increasingly strict legislation has been introduced to control water pollution, so there is a need for effective  $\text{SO}_4^{2-}$  removal technologies.

The processes for  $\text{SO}_4^{2-}$  removal from wastewater include biological treatment with sulphate-reducing bacteria, membrane filtration (e.g. reverse osmosis), adsorption and/or ion exchange and chemical precipitation as gypsum, barium sulphate or ettringite. However, these methods suffer from limitations. For example, precipitation produces a large amount of potentially toxic sludge. Low concentrations (approx.  $1200$  to  $2000 \text{ mg L}^{-1}$ ) cannot be removed by lime precipitation because of the solubility of the  $\text{CaSO}_4$  that is produced [2, 8, 9]. In addition, biological treatment and ion exchange are costly [2, 3, 10, 11]. An adsorption system has the potential to be used in a so-called hybrid-system with precipitation, in which the remaining sulphate concentrations after the precipitation process could be removed via adsorption.

Adsorption may be preferred for  $\text{SO}_4^{2-}$  removal due to its simplicity, effectiveness and low cost [11, 12]. Suggested sorbents have included, for example, activated carbon [13], fly ash [14], limestone

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4 1 [2, 15], minerals [3, 16–19], modified coir pith [6], modified rice straw [1], modified zeolites [20, 21],  
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6 2 nano-alumina [22], soils [23–25] and waste materials [15].

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8 3 Geopolymers are amorphous or partly crystalline inorganic polymers with a three-dimensional  
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10 4 negatively charged framework structure, which is similar to zeolite [26–31]. They can be prepared at  
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12 5 ambient or slightly elevated temperatures by the hydrothermal conversion of a solid aluminosilicate  
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14 6 material, e.g. metakaolin [30, 32, 33], blast-furnace slag [34] or fly ash [29, 35–38] with an alkali  
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16 7 hydroxide and/or silicate solution. In this study, blast-furnace slag (BFS) and metakaolin (MK) were  
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18 8 used as a raw material for geopolymerisation. BFS is a residue product of smelting iron ore in a blast  
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20 9 furnace and MK is a dehydroxylated form of the naturally occurring clay mineral kaolinite. BFS and MK  
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22 10 are good raw material candidates for preparing geopolymers due to their abundance and easy  
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24 11 availability [33, 34, 39, 40].

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26 12 The series of geochemical reactions that comprise this process are not exactly known, but it has  
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28 13 been suggested that they include mineral dissolution, aluminosilicate polycondensation and structural  
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30 14 re-organisation [28, 29, 41–43]. Geopolymers possess permanent negative charges on Al on their  
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32 15 structure that are balanced by exchangeable cations (e.g. Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Ba<sup>2+</sup>) [43]. They have a high  
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34 16 cation exchange capacity, which has been applied for the removal of metal(loid)s [32, 33, 35, 38, 44,  
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36 17 45], dyes [29] and ammonium [46], but there are no studies on SO<sub>4</sub><sup>2-</sup> removal to our knowledge.  
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38 18 Because geopolymers have a low affinity for anions, a chemical modification is needed to apply a  
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40 19 sorbent for anionic SO<sub>4</sub><sup>2-</sup> removal. In literature, it has been reported that the chemical modification  
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42 20 with inorganic salts such as NaCl, CaCl<sub>2</sub>, BaCl<sub>2</sub> or FeCl<sub>3</sub> improves properties of zeolites and increase its  
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44 21 efficiency in water treatment [47–49]. In the present study, a similar approach was applied for  
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46 22 geopolymer modification. In the case of anion removal, the modification has been reported to for  
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48 23 example create an oxi-hydroxide adsorption layer on the surface and change the surface charge (from  
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50 24 negative to positive) [49, 50]. These changes allow to form stable complexes with anions in solution.  
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52 25 In the present study, the BaCl<sub>2</sub> modification was expected to impregnate Ba in the framework  
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54 26 structure of geopolymers and subsequently enable the surface precipitation or complexation of  
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56 27 sulphate.

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58 28 In this study, the effects of geopolymerisation, barium modification and a combined treatment  
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60 29 on metakaolin (MK) and blast-furnace slag (BFS) were studied in order to develop an efficient SO<sub>4</sub><sup>2-</sup>

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4 1 sorbent for mine effluent. Comparative experiments were first performed for synthetic water (model  
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6 2 solution). The influence of initial pH, initial  $\text{SO}_4^{2-}$  concentration, sorbent dosage, contact time and  
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8 3 temperature was studied. In addition, adsorption isotherms, kinetics and thermodynamic parameters  
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10 4 were studied. Column studies were also performed for the most promising sorbent material: barium-  
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12 5 modified BFS geopolymer (Ba-BFS-GP).  
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## 16 6 **2 Experimental**

### 17 7 18 7 19 20 8 **2.1 Materials**

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23 10 **BFS and** MK were obtained from Finnish suppliers. Technical grade sodium hydroxide (VWR  
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25 11 International) and sodium silicate (VWR International,  $\text{SiO}_2:\text{Na}_2\text{O} = 3.1\text{--}3.4$ ) were used for the  
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27 12 synthesis of geopolymers. NaCl and  $\text{BaCl}_2$  were used in chemical modifications. A stock solution of  
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29 13  $\text{SO}_4^{2-}$  was prepared by dissolving  $\text{Na}_2\text{SO}_4$  (VWR 99,9%) in ultrapure water and further diluted to  
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31 14 concentrations required for the experiments. The pH of the solution was adjusted through the  
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33 15 addition of HCl and/or NaOH (FF-Chemicals).  
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35 16 A mine effluent (settled drainage water treated with ferric sulphate) sample was obtained from  
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37 17 an underground gold mine and it was characterized earlier [44].  
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### 41 19 **2.2 Geopolymerisation**

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44 21 An alkaline solution containing 10 M NaOH and sodium silicate ( $\text{SiO}_2:\text{Na}_2\text{O} = 3.1\text{--}3.4$ ) in a weight ratio  
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46 22 of 1:1 was prepared 24 h before use. BFS or MK was mixed with the alkaline solution in a weight ratio  
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48 23 of 3:2 or 1.3:1, respectively. The mixtures were mixed for 15 minutes, vibrated for 2 minutes and  
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50 24 allowed to consolidate for 3 days at room temperature. The resulting solid material was crushed to a  
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52 25 particle size of 63–125  $\mu\text{m}$  or 0.5–1 mm for batch (**equilibrium**) and **dynamic (non-equilibrium)**  
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54 26 experiments, respectively. Materials were washed with ultrapure water, dried at 105 °C and stored in  
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56 27 a desiccator.  
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### 2.3 Chemical modification

The materials (5 g) were mixed with 1 M NaCl solution (50 mL) for 24 h, filtered, rinsed with deionised water and dried at 105 °C to ensure that all the ion exchange sites were in the Na form. Barium modification was conducted by mixing the material (5 g) in a 1 M BaCl<sub>2</sub> solution (100 mL) for 16 h, filtering, rinsing with deionised water and drying at 105 °C. The materials were ground and stored in a desiccator before use.

### 2.4 Characterisation of the sorbent

The specific surface area, total pore volume and average pore size were determined from nitrogen adsorption–desorption isotherms at the temperature of liquid nitrogen (-196 °C) using a Micromeritics ASAP 2020 instrument. The X-ray diffraction (XRD) patterns of materials were obtained using a PanAnalytical Xpert Pro diffractometer, and chemical compositions were determined using a PanAnalytical Minipal 4 X-ray fluorescence (XRF) spectrometer. Fourier Transform Infrared Spectroscopy (FTIR) spectra of the sorbent were collected using a Perkin Elmer Spectrum One spectrometer.

### 2.5 Batch sorption experiments

In the batch sorption experiments the system was allowed to reach the sorption equilibrium. The screening of potential sorbents Ba-modified metakaolin (Ba-MK), Ba-modified metakaolin geopolymer (Ba-MK-GP), Ba-modified blast-furnace slag (Ba-BFS) and Ba-modified blast-furnace-slag geopolymer (Ba-BFS-GP) was performed at different initial pH values in mine effluent. Initial pH was adjusted by using HCl and/or NaOH. Ba-BFS-GP was selected for further experiments: the effects of initial SO<sub>4</sub><sup>2-</sup> concentration, sorbent dosage, temperature and contact time were studied. The studied parameters are shown in Table 1. Samples were filtrated through 0.45 µm filter paper (Sartorius Stedim Biotech) or separated using a centrifuge. SO<sub>4</sub><sup>2-</sup> concentration was determined in the filtrate solution via ion

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4 1 chromatography (Metrohm 761 Compact IC) or a flow injection analysis system (Foss-Tecator Fiastar  
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8 3 All experiments were run as duplicates, except experiments with mine effluent. The sorption  
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10 4 experiments were performed in acid-washed vessels to minimise contamination.  
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12 5  
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14 6 **Table 1.** Parameters for testing the effects of initial pH, initial  $\text{SO}_4^{2-}$  concentration, sorbent dosage,  
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16 7 contact time and temperature on  $\text{SO}_4^{2-}$  removal efficiency.  
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Parameter	Initial pH of solution	Initial $\text{SO}_4^{2-}$ concentration [ $\text{mg L}^{-1}$ ]	Sorbent dosage [ $\text{g L}^{-1}$ ]	Contact time	Temperature [ $^{\circ}\text{C}$ ]	Sorbent	Water matrix
Effect of initial pH	4,6,8,10	850–870	5	24 h	22	Ba-MK, Ba-BFS, Ba-MK-GP, Ba-BFS-GP	Mine effluent*
Effect of initial $\text{SO}_4^{2-}$ concentration	7–8	50–1000	5	24 h	22	Ba-BFS-GP	Synthetic
Effect of sorbent dosage	7–8	1200	0.5–15	3 h	10, 22, 40	Ba-BFS-GP	Synthetic
	7–8	865	0.5–25	24 h	22	Ba-BFS-GP	Mine effluent*
Effect of contact time	7–8	1100	5	1 min – 24 h	22	Ba-BFS-GP	Synthetic
	7–8	853	5	1 min – 24 h	22	Ba-BFS-GP	Mine effluent*

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34 8 \*There was a minor variation ( $850\text{--}870 \text{ mg L}^{-1}$ ) between the concentrations of different water samples.  
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## 38 11 2.6 Dynamic sorption experiments

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40 12 In the dynamic experiments, the sorption was performed in the non-equilibrium state. The  
41 13 experiments were performed using a plastic column (diameter 44.0 mm, height 98.8 mm, volume  
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43 14 0.15 L), which was loaded with 30.45 g of Ba-BFS-GP with a particle size of 0.5–1 mm. The sorbent bed  
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45 15 height was 2.0 cm with a bed volume of  $30.41 \text{ cm}^3$ . Mine effluent with  $820 \text{ mg L}^{-1} \text{ SO}_4^{2-}$  was pumped  
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47 16 through the column by a peristaltic pump. The flow of effluent was adjusted to 0.24 or  $0.85 \text{ L h}^{-1}$ ,  
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49 17 corresponding to 7.60 and 2.15 min empty bed contact time, respectively. Samples were taken from  
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51 18 the outlet of the column at different time intervals.  
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## 2.7 Barium leaching test

To evaluate the stability of impregnated barium in Ba-BFS-GP, 0.125 g of material was added to 25 mL mine effluent and shaken 24 h. Barium leaching experiments were also performed with distilled water by weighing 0.005 or 0.125 g of Ba-BFS-GP to 10 mL or 25 mL of distilled water, respectively. Samples were filtered through 0.45 µm filter paper, and the barium concentration was analysed using inductively coupled plasma emission spectrometers (Thermo Electron IRIS Intrepid II XDL Duo or PerkinElmer Optima 5300 DV ICP-OES instrument) according to the SFS-EN ISO 11885 standard.

## 2.8 Adsorption isotherms

Bi-Langmuir [51], Sips [52], Redlich–Peterson (R–P) [53] and Toth [54] isotherms are presented in Equations 1–4, respectively. Isotherm parameters were obtained using nonlinear regression with the Microsoft Excel solver tool (GRG nonlinear).

$$q_e = \frac{q_{m1} b_{L1} C_e}{1 + b_{L1} C_e} + \frac{q_{m2} b_{L2} C_e}{1 + b_{L2} C_e}, \quad (1)$$

where  $q_{m1}$  and  $q_{m2}$  are the maximum adsorption capacities ( $\text{mg g}^{-1}$ ) of two different adsorption sites. Similarly,  $b_{L1}$  and  $b_{L2}$  represent the energies ( $\text{mg g}^{-1}$ ) of adsorption at these sites.

$$q_e = \frac{q_m (b_S C_e)^{n_S}}{1 + (b_S C_e)^{n_S}}, \quad (2)$$

where  $b_S$  ( $\text{L mg}^{-1}$ ) is a constant related to the adsorption energy and  $n_S$  is a dimensionless constant characterising the heterogeneity of the system.

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}, \quad (3)$$



where  $K_R$  ( $\text{dm}^3 \text{g}^{-1}$ ) and  $a_R$  ( $\text{dm}^3 \text{mg}^{-1}$ ) are R-P isotherm constants and  $\beta$  is an exponent, the value of which lies between 0 and 1.

$$q_e = \frac{q_{Th} K_{Th} C_e}{[1 + (K_{Th} C_e)^{Th}]^{1/Th}}, \quad (4)$$

where  $q_m$  ( $\text{mg g}^{-1}$ ) is the monolayer adsorptive uptake,  $K_{Th}$  ( $\text{L mg}^{-1}$ ) is the Toth isotherm constant and  $Th$  is the dimensionless Toth isotherm exponent, which characterises the heterogeneity of the system.

The residual root mean square error (RMSE) and chi-square test ( $\chi^2$ ) were used to assess the error:

$$\text{RMSE} = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (q_{e(\text{exp})} - q_{e(\text{calc})})^2}, \quad (5)$$

$$\chi^2 = \sum_{n=1}^n \frac{(q_{e(\text{exp})} - q_{e(\text{calc})})^2}{q_{e(\text{calc})}}, \quad (6)$$

where  $n$  is the number of experimental data,  $p$  is the number of parameters whilst  $q_{e(\text{exp})}$  and  $q_{e(\text{calc})}$  are experimental and calculated values of adsorption capacity in equilibrium.

## 2.9 Kinetic modelling

The kinetics of the adsorption processes were studied using the pseudo-first-order [55], the pseudo-second-order [56] and the Elovich [57] kinetic models:

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t, \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t, \quad (8)$$

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$$q = \frac{1}{\beta} \ln \left( u_0 \beta + \frac{1}{\beta} \ln t \right), \tag{9}$$

where  $q_e$  and  $q_t$  are the amounts of  $\text{SO}_4^{2-}$  sorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$  (min), respectively.  $k_f$  ( $\text{min}^{-1}$ ),  $k_s$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) and  $u_0$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ) are the pseudo-first-order, pseudo-second-order and Elovich rate constants, respectively. The Elovich parameter  $\beta$  ( $\text{g mg}^{-1}$ ) is related to the extent of surface coverage and activation energy for chemisorption.

The diffusion mechanism was analysed using the intraparticle diffusion model [58]:

$$q_t = k_{id} t^{1/2} + C, \tag{10}$$

where  $k_{id}$  ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) is the intraparticle diffusion on the rate determining step and C is the intercept related to the thickness of the boundary layer.

### 2.10 Sorption thermodynamics

The change in free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) were determined to describe the sorption of  $\text{SO}_4^{2-}$ :

$$\Delta G = -RT \ln(K_c), \tag{11}$$

$$K_c = \frac{q}{C_e}, \tag{12}$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \tag{13}$$

where,  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature (K), and  $K_c$  is the equilibrium constant.

### 3 Results and discussion

#### 3.1 Sorbent characterisation

Specific surface area, average pore size and volumes (Table 2) of MK increase as a result of geopolymerisation. However, with BFS, the surface area and pore volumes increase whereas pore size decreases during geopolymerisation. Barium modification has no significant effect on surface area, pore sizes and volumes of geopolymerised BFS.

**Table 2.** Specific surface areas, pore sizes and volumes of sorbents.

Sorbent	Specific surface area [m <sup>2</sup> g <sup>-1</sup> ]	Average pore size[nm]	V <sub>macro+meso</sub> [cm <sup>3</sup> g <sup>-1</sup> ]	V <sub>micro</sub> [cm <sup>3</sup> g <sup>-1</sup> ]
MK	11.5	18.2	0.047	0.005
MK-GP	22.4	31.0	0.165	0.008
BFS	2.79	12.7	0.008	0.001
BFS-GP	64.5	5.93	0.070	0.025
BFS-GP-Ba	63.1	6.32	0.070	0.030

Macropore:  $d_0 > 50$  nm, Mesopore:  $2 \text{ nm} \leq d_0 \leq 50$  nm, Micropore:  $d_0 \leq 2$  nm.

Table 3 shows the chemical composition of BFS, BFS-GP and Ba-BFS-GP. The main components of BFS are calcium, silicon, magnesium, aluminium and sulphur. In addition, sorbents included some other impurities. Aluminium and silicon contents decrease while Na content increases after geopolymerisation. In addition, the loss on ignition (L.O.I.) increases due to the increased water content. The decrease of CaO as BFS is converted into BFS-GP is possibly due to the dissolution of gehlenite and other phases [27]. In Ba-BFS-GP, Na ions are completely replaced by Ba, as signified by corresponding concentrations.

**Table 3.** Main chemical constituents as determined by XRF.

Composition	BFS [w/w%]	BFS-GP [w/w%]	Ba-BFS-GP [w/w%]
CaO	38.5	29.9	26.3
SiO <sub>2</sub>	27.2	25.8	26.8
MgO	9.4	6.4	7.1
Al <sub>2</sub> O <sub>3</sub>	8.4	5.9	6.7
SO <sub>3</sub>	3.8	2.7	0.7

Na <sub>2</sub> O	0.3	8.0	0.0
Ba	0.0	0.0	17.3
Other*	2.9	2.4	0.0
L.O.I.	0.5	12.9	14.5
Sum	90.9	93.9	99.4

\*Including Ti, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Mn.

The XRD patterns (Fig. 1) of BFS, BFS-GP, and Ba-BFS-GP indicate initially a completely X-ray amorphous structure, formation of hydrotalcite (Mg<sub>6</sub>Al<sub>2</sub>CO<sub>3</sub>(OH)<sub>16</sub>·4(H<sub>2</sub>O)) and haturite (Ca<sub>3</sub>SiO<sub>5</sub>) after geopolymerisation and further formation of witherite (BaCO<sub>3</sub>) after Ba-modification.

**Figure 1.** XRD patterns of blast-furnace slag (BFS), blast-furnace-slag geopolymer (BFS-GP) and barium-modified blast-furnace-slag geopolymer (Ba-BFS-GP) samples. HT = hydrotalcite, HAT = haturite, W = witherite.

FTIR spectra for BFS, BFS-GP and Ba-BFS-GP are shown in Fig. 2. The peak in the spectra of Ba-BFS-GP at 856 cm<sup>-1</sup> is related to the witherite (BaCO<sub>3</sub>) vibration. The bands in the spectra of BFS, Ba-BFS and Ba-BFS-GP appearing at 960, 942, 894 cm<sup>-1</sup>, respectively, belong to Si-O stretching vibrations [59]. The bands at 1471 and 1391 cm<sup>-1</sup> are associated with carbonate vibration in the structure of Ba-BFS-GP and Ba-BFS [26]. Carbon dioxide shows a strong band in the area of 2350 cm<sup>-1</sup>, and thus the band in Ba-BFS-GP could be related to adsorbed carbon dioxide [60, 61].

**Figure 2.** The FTIR spectra of blast-furnace slag (BFS), barium-modified blast-furnace-slag (Ba-BFS) and barium-modified blast-furnace-slag geopolymer (Ba-BFS-GP).

### 3.2 Effect of initial pH and screening of sorbents

The effect of initial pH on the removal of SO<sub>4</sub><sup>2-</sup> from mine effluent over BFS-GP, Ba-BFS-GP, Ba-MK and Ba-MK-GP is shown in Fig. 3. Sorption efficiency decreases slightly as the initial pH increases from 4 to 10. This may be due to the competition for the sorption sites by OH<sup>-</sup> ions at high pH [22, 62]. Ba-BFS-

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4 1 GP is the most effective sorbent material and it was selected for further study. Sorption efficiency is  
5  
6 2 c.a. 50% at pH range 4–10.  
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10 4 **Figure 3.** Total  $\text{SO}_4^{2-}$  removal percent (left, solid lines) and total adsorbed amount (right, dashed lines)  
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12 5 versus initial pH on the sorption of  $\text{SO}_4^{2-}$  from mine effluent. Sorbent dosage:  $5 \text{ g L}^{-1}$ , contact time: 24  
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14 6 h, temperature:  $22\text{--}23 \text{ }^\circ\text{C}$ , adsorbate: mine effluent ( $C_0$ ,  $\text{SO}_4^{2-}$ :  $\sim 850\text{--}870 \text{ mg L}^{-1}$ ).  
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### 19 8 **3.3 Effect of initial $\text{SO}_4^{2-}$ concentration**

20 9  
21 10 The effect of initial  $\text{SO}_4^{2-}$  concentration was investigated with model solutions in the range of  $100\text{--}$   
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23 11  $1800 \text{ mg L}^{-1}$ . The results are presented in Fig. 4. The  $\text{SO}_4^{2-}$  sorption capacity of Ba-BFS-GP increases as  
24  
25 12 the  $\text{SO}_4^{2-}$  concentration is increased and reaches a maximum value ( $90 \text{ mg g}^{-1}$ ) at about  $1200 \text{ mg L}^{-1}$ .  
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27 13 The initial sharp rise of sorption capacity in Fig. 4 indicates that sorption sites are readily available and  
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29 14 the surface becomes saturated as the curve levels off [22, 62].  
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33 16 **Figure 4.** Effect of the initial concentration on the sorption of  $\text{SO}_4^{2-}$  on Ba-BFS-GP from model solution.  
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35 17 Initial pH:  $7\text{--}8$ , sorbent dosage:  $5 \text{ g L}^{-1}$ , contact time: 24 h, temperature:  $22\text{--}23 \text{ }^\circ\text{C}$ .  
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### 39 19 **3.4 Effect of sorbent dosage and temperature**

40 20  
41 21 The effect of Ba-BFS-GP dosage on the removal of  $\text{SO}_4^{2-}$  from model solution and mine effluent are  
42  
43 22 shown in Fig. 5. In both cases the percentage of  $\text{SO}_4^{2-}$  removal increases with the increasing sorbent  
44  
45 23 dosage and reaches a saturation level at high doses. This phenomenon could be explained by the  
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47 24 increase in surface area and the available sorption sites with an increase in the sorbent dosage  
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49 25 [63–65]. The sorbent reached maximum removal of  $\text{SO}_4^{2-}$  at dose  $10 \text{ g L}^{-1}$  of sorbent, probably due to  
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51 26 the of mass transfer resistance of  $\text{SO}_4^{2-}$  from bulk liquid to the surface of the solid, which becomes  
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53 27 important at high sorbent loading. In addition, at  $40 \text{ }^\circ\text{C}$  the percentage of  $\text{SO}_4^{2-}$  removal was  
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55 28 decreased slightly with the higher dosage ( $> 10 \text{ g L}^{-1}$ ). The higher sorbent dosage results in  
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57 29 interference or repulsive forces between binding sites and formation of particle aggregates,  
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4 1 decreasing the interaction of  $\text{SO}_4^{2-}$  with the sorbent and reducing the total surface area of the sorbent  
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6 2 [10, 22, 63–66]. Maximum removal efficiencies with model solution and sorbent dosage  $10 \text{ g L}^{-1}$  were  
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8 3 68% ( $51.98 \text{ mg g}^{-1}$ ), 60% ( $59.67 \text{ mg g}^{-1}$ ) and 55% ( $51.98 \text{ mg g}^{-1}$ ) at 10, 23 and  $40 \text{ }^\circ\text{C}$ , respectively. In the  
9  
10 4 case of mine effluent, maximum sorption efficiency was 100% ( $85.69 \text{ mg g}^{-1}$ ) at  $23 \text{ }^\circ\text{C}$ . The better  
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12 5 removal efficiency of  $\text{SO}_4^{2-}$  in mine effluent compared to model solution could be explained by  
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14 6 different initial concentrations and partially by the presence of sodium: sodium hinders  $\text{SO}_4^{2-}$  removal  
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16 7 via the formation of aqueous sodium sulphate complex. The effect of sodium was calculated by  
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18 8 MineQL software [67] to account for approximately 10% of the lower removal efficiency.

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20 9 The sorption capacity ( $q$ ,  $\text{mg g}^{-1}$ ) increases as temperature is increased (Fig. 5). This indicates that  
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22 10 the sorption is an endothermic process in nature. An increase in temperature from  $10 \text{ }^\circ\text{C}$  to  $23 \text{ }^\circ\text{C}$  has  
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24 11 a larger effect on sorption capacity than a further increase from  $23 \text{ }^\circ\text{C}$  to  $40 \text{ }^\circ\text{C}$ .

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28 13 **Figure 5.** Effect of Ba-BFS-GP dosage on  $\text{SO}_4^{2-}$  removal. a) Model solution:  $C_0(\text{SO}_4^{2-})$ :  $\sim 1200 \text{ mg L}^{-1}$ ,  
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30 14 contact time: 3 h. b) Mine effluent:  $C_0(\text{SO}_4^{2-})$ :  $865 \text{ mg L}^{-1}$ , contact time: 24 h. In both cases initial pH  
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32 15 was 7–8.

### 35 36 17 **3.5 Adsorption isotherms**

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38 18 Bi-Langmuir, Sips, R–P and Toth isotherm models were applied for the experimental results of Ba-BFS-  
39 19 GP (Fig. 6 and Table 4). Comparison of the results for the errors (RMSE,  $X^2$ ) and correlation  
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41 20 coefficients ( $R^2$ ) indicated that the  $\text{SO}_4^{2-}$  sorption onto Ba-BFS-GP from model solution can be best  
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43 21 represented by the Sips isotherm. Maximum experimental ( $q_{m,exp}$ ) and theoretical ( $q_{m,calc}$ ) sorption  
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45 22 capacities are quite similar. In the case of mine effluent, all studied isotherm models gave practically  
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47 23 similar correlation coefficient values ( $R^2$ : 0.920–0.930) and errors.

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53 26 **Figure 6.** Bi-Langmuir, Sips, Redlich-Peterson and Toth isotherms of  $\text{SO}_4^{2-}$  sorption on Ba-BFS-GP. a)  
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55 27 Model solution:  $C_0(\text{SO}_4^{2-})$ :  $100\text{--}1800 \text{ mg L}^{-1}$ , sorbent dose:  $5 \text{ g L}^{-1}$ . b) Mine effluent:  $C_0(\text{SO}_4^{2-})$ :  $865 \text{ mg}$   
56  
57 28  $\text{L}^{-1}$ , sorbent dose:  $1.3\text{--}15 \text{ g L}^{-1}$ . Initial pH was 7–8, contact time 24 h and temperature  $22\text{--}23 \text{ }^\circ\text{C}$ .

**Table 4.** Isotherm parameters and errors for the sorption of  $\text{SO}_4^{2-}$  removal on Ba-BFS-GP.

	Constant (unit)	Model solution <sup>a)</sup>	Mine effluent <sup>b)</sup>
<b>Isotherm</b>			
Experimental	$q_m$ ( $\text{mg g}^{-1}$ )	<b>91.1</b>	<b>119.0</b>
Bi-Langmuir	$q_{m1}$ ( $\text{mg g}^{-1}$ )	42.109	55.290
	$b_{L1}$ ( $\text{L mg}^{-1}$ )	0.463	0.400
	$q_{m2}$ ( $\text{mg g}^{-1}$ )	42.109	55.290
	$b_{L2}$ ( $\text{L mg}^{-1}$ )	0.463	0.400
	$R^2$	0.926	0.920
	RMSE	<b>8.737</b>	<b>10.452</b>
	$\chi^2$	3.810	7.501
Sips	$q_{sm}$ ( $\text{mg g}^{-1}$ )	83.691	110.580
	$b_s$ ( $\text{L mg}^{-1}$ )	0.482	0.400
	$n_s$	2.102	1.000
	$R^2$	0.951	0.920
	RMSE	<b>6.174</b>	<b>9.541</b>
	$\chi^2$	1.822	7.501
Redlich-Peterson (R-P)	$K_R$ ( $\text{dm}^3 \text{g}^{-1}$ )	48.978	57.107
	$a_R$ ( $\text{dm}^3 \text{mg}^{-1}$ )	0.734	0.650
	$\beta$	0.964	0.963
	$R^2$	0.931	0.929
	RMSE	<b>7.318</b>	<b>8.945</b>
	$\chi^2$	3.990	7.714
Toth	$q_{Th}$ ( $\text{mg g}^{-1}$ )	64.937	85.863
	$K_{Th}$ ( $\text{mg dm}^{-3} \text{Th}$ )	1.391	1.593
	Th	1.042	1.043
	$R^2$	0.932	0.930
	RMSE	7.257	8.870
	$\chi^2$	3.943	7.071

a) Model solution: Initial pH: 7–8,  $C_0(\text{SO}_4^{2-})$ : 100–1800  $\text{mg L}^{-1}$ ,  $m(\text{Ba-BFS-GP})$ : 5  $\text{g L}^{-1}$ .

b) Mine effluent: Initial pH: 7–8,  $C_0(\text{SO}_4^{2-})$ : 865  $\text{mg L}^{-1}$ ,  $m(\text{Ba-BFS-GP})$ : 1.3–15  $\text{g L}^{-1}$ .

Contact time: 24 h and temperature 22–23 °C.

The sorbents produced were compared with other materials (Table 5). The Ba-BFS-GP shows a higher or comparable sorption capacity to other similar anion sorbents.

**Table 5.** Comparison of adsorption capacity  $q_m$  (mg g<sup>-1</sup>) of various sorbents for the removal of SO<sub>4</sub><sup>2-</sup> from aqueous phase.

Sorbent	Capacity $q$ (mg g <sup>-1</sup> )	pH	Concentration (mg L <sup>-1</sup> )	Reference
Coir pith carbon	0.06 <sup>a</sup>	4.0	20–80	[68]
Iron sand	1.15 <sup>b</sup> (12 mmol g <sup>-1</sup> )	-	20–2000	[15]
Feldspar	0.275 <sup>a</sup>	5.5	1–5	[5]
Pulp and paper waste	2.786 <sup>b</sup> (29 mmol g <sup>-1</sup> )	-	20–2000	[15]
Surfactant-modified palygorskite	3.24 <sup>b</sup>	4.0	20–130	[4]
ZnCl <sub>2</sub> activated coir pith carbon	4.9 <sup>a</sup>	4.0	20–80	[68]
Surfactant-modified clinoptilolite	~ 7.0 <sup>a</sup>	-	96–500	[20]
γ-Al <sub>2</sub> O <sub>3</sub>	7.7 <sup>a</sup>	5.7	20–40	[69]
Surfactant modified coir pith	8.76 <sup>a</sup>	2	10–50	[7]
Raw rice straw	11.68 <sup>a</sup>	6.4	50–500	[1]
Flotation fines	21.23 <sup>b</sup> (221 mmol g <sup>-1</sup> )	-	20–2000	[15]
Limestone	23.7 <sup>a</sup>	9.6–9.8	588–1100	[2]
Filter sand	25.07 <sup>b</sup> (261 mmol g <sup>-1</sup> )	-	20–2000	[15]
Alkali-treated fly ash	43.0 <sup>a</sup>	-	200	[36]
Ba-modified zeolite	64.10 <sup>a</sup> (1.33 meq g <sup>-1</sup> )	6.0	<1000	[21]
Epichlorohydrin and trimethylamine modified rice straw	74.76 <sup>a</sup>	6.4	50–500	[1]
poly( <i>m</i> -phenylenediamine)	108.5 <sup>a</sup>	1.75–3	50–4000	[11]
Ba-modified blast-furnace-slag geopolymers	119.0 <sup>b</sup>	7–8	865	This study
Chitin-based shrimp shells	156.0 <sup>a</sup>	4.5	2350	[70]

<sup>a</sup>Langmuir maximum sorption capacity,  $q_{m,cal}$ , <sup>b</sup>Experimental maximum sorption capacity

### 3.6 Effect of contact time

The effect of contact time on the removal of SO<sub>4</sub><sup>2-</sup> by Ba-BFS-GP at room temperature is presented in Fig. 7. It can be seen from the curves that the sorption is rapid in the first 10 min while sorption equilibrium is attained at approximately 3 h. The rate of SO<sub>4</sub><sup>2-</sup> removal was higher at the beginning of the sorption experiment due to a larger number of available adsorption sites [71]. Maximum SO<sub>4</sub><sup>2-</sup> sorption capacities of Ba-BFS-GP were 159.1 mg g<sup>-1</sup> (74.5% removal) and 99.0 mg g<sup>-1</sup> (58.0% removal) in model SO<sub>4</sub><sup>2-</sup> solution and mine effluent, respectively.



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4 **Figure 7.** Effect of contact time on the removal efficiency of  $\text{SO}_4^{2-}$  onto Ba-BFS-GP. o: Model  $\text{SO}_4^{2-}$   
5 solution ( $C_0$ ,  $\text{SO}_4^{2-}$ : 1100 mg L<sup>-1</sup>), □: Mine effluent ( $C_0$ ,  $\text{SO}_4^{2-}$ : 853 mg L<sup>-1</sup>). Initial pH: 7–8, sorbent  
6 2 dosage: 5 g L<sup>-1</sup>, temperature: 22–23 °C.  
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### 10 4 11 12 13 5 **3.7 Kinetic modelling**

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15 7 The pseudo-first-order, pseudo-second-order and Elovich kinetic models were used to evaluate the  
16 7 experimental data. The results are shown in Fig. 8, and the corresponding kinetic parameters are  
17 8 listed in Table 6. The best fit was observed with the pseudo-second-order kinetic model. Theoretical  
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19 9  $q_{e,cal}$  values of the pseudo-second-order kinetic model agree well with the experimental uptake  
20 9 values.  
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27 13 **Figure 8.** a) Pseudo-first-order kinetic, b) pseudo-second-order kinetic and c) Elovich model plots of  
28 14  $\text{SO}_4^{2-}$  sorption on Ba-BFS-GP. o: Model  $\text{SO}_4^{2-}$  solution ( $C_0$ ,  $\text{SO}_4^{2-}$ : 1100 mg L<sup>-1</sup>), □: Mine effluent ( $C_0$ ,  
29 14  $\text{SO}_4^{2-}$ : 853 mg L<sup>-1</sup>). Initial pH: 7–8, sorbent dosage: 5 g L<sup>-1</sup>, contact time: 24 h, temperature: 22–23 °C.  
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**Table 6.** Pseudo-first-order, pseudo-second-order and Elovich model parameters for Ba-BFS-GP in  $\text{SO}_4^{2-}$  removal.

Pseudo-first-order model				
$C_0$ ( $\text{mg L}^{-1}$ )	$q_{e,\text{exp}}$ ( $\text{mg g}^{-1}$ )	$q_{e,\text{calc}}$ ( $\text{mg g}^{-1}$ )	$k_1$ ( $\text{min}^{-1}$ )	$R^2$
1100	159.08	40.51	0.0108	0.9776
853	99.0	56.65	0.0085	0.9643
Pseudo-second-order				
$C_0$ ( $\text{mg L}^{-1}$ )	$q_{e,\text{exp}}$ ( $\text{mg g}^{-1}$ )	$q_{\text{calc}}$ ( $\text{mg g}^{-1}$ )	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$R^2$
1100	159.08	158.73	2.217E-03	1
853	99.0	100	7.6E-04	0.9994
Elovich model				
$C_0$ ( $\text{mg L}^{-1}$ )	$q_{e,\text{exp}}$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{g L}^{-1}$ )	$u_0$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	$R^2$
1100	159.08	0.1633	1E+09	0.9214
853	99.0	0.1037	224.175	0.8826

### 3.8 Weber and Morris intraparticle diffusion model

The Weber and Morris intraparticle diffusion model was applied to the kinetic data of Ba-BFS-GP against the  $\text{SO}_4^{2-}$  (Fig. 9). If a plot of  $q_t$  versus  $t^{1/2}$  presents a straight line from the origin, the rate-limiting step in the sorption mechanism is diffusion from the outer surface into the pores of the material. The data of  $\text{SO}_4^{2-}$  sorption on Ba-BFS-GP shows two plots, which do not pass through the origin. This indicates that intraparticle diffusion is not the rate-limiting step. The first stage can be attributed to the instantaneous or external surface sorption while the second stage is the low diffusion of adsorbate from the surface to the inner pore [62].

**Figure 9.** Weber and Morris intraparticle diffusion model plot of  $\text{SO}_4^{2-}$  sorption on Ba-BFS-GP.  $\circ$ : Model  $\text{SO}_4^{2-}$  solution ( $C_0$ ,  $\text{SO}_4^{2-}$ : 1100  $\text{mg L}^{-1}$ ),  $\square$ : Mine effluent ( $C_0$ ,  $\text{SO}_4^{2-}$ : 853  $\text{mg L}^{-1}$ ). Initial pH: 7–8, sorbent dosage: 5  $\text{g L}^{-1}$ , contact time: 24 h, temperature: 22–23 °C.

### 3.9 Thermodynamic parameters

Standard enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) were obtained from the slope and intercept of the plot of  $\ln K_c$  vs.  $1/T$ , as shown in Fig. 10 and listed in Table 7. The negative value of  $\Delta G$  indicated that the sorption process is spontaneous in nature. Affinity of the Ba-BFS-GP for  $\text{SO}_4^{2-}$  is represented by the positive value of  $\Delta S$ , which indicated that the sorption process increased the entropy at the solid/solution interface during the sorption process. The positive value of  $\Delta H$  suggested that the interaction of  $\text{SO}_4^{2-}$  and Ba-BFS-GP is endothermic in nature. The  $\Delta H$  obtained from thermodynamic calculations ( $\leq 40 \text{ kJ mol}^{-1}$ ) suggests a physisorption process involving weak interactions. [10, 62, 66, 72–74]

**Figure 10.** Van't Hoff plot for adsorption of  $\text{SO}_4^{2-}$  removal. Initial pH: 7–8, adsorbent dosage:  $5 \text{ g L}^{-1}$ ,  $C_0(\text{SO}_4^{2-})$ :  $1200 \text{ mg L}^{-1}$ .

**Table 7.** Thermodynamics parameters for the sorption of  $\text{SO}_4^{2-}$  on Ba-BFS-GP at different temperatures.

Temperature ( $^{\circ}\text{C}$ )	$\Delta G(\text{kJ mol}^{-1})$	$\Delta S(\text{J mol}^{-1} \text{ K}^{-1})$	$\Delta H(\text{kJ mol}^{-1})$
10	-10.354		
22	-11.389	56.598	5.556
40	-12.059		

### 3.10 Column studies

Column studies (Fig. 11) have been carried out for Ba-BFS-GP as a sorbent in order to study its sorption capacity in dynamic conditions. Flow rates of  $0.24$  and  $0.85 \text{ L h}^{-1}$  were used for the breakthrough simulation. Initially, total  $\text{SO}_4^{2-}$  removal was observed with a lower flow rate. However, the removal of  $\text{SO}_4^{2-}$  starts to linearly decrease after 40 min (corresponding to 0.16 L of treated effluent) and drops below 50% after 140 min (corresponding to 0.56 L of treated effluent). Therefore, it could be estimated that  $18.7 \text{ m}^3$  of mine effluent with a similar composition could be treated with 1 t of Ba-

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4 1 BFS-GP with over 50%  $\text{SO}_4^{2-}$  removal. After use, Ba-BFS-GP could be further utilised in selective radium  
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6 2 adsorption from contaminated waters due to accumulation of  $\text{BaSO}_4$  as indicated by Kunze et al. [75]  
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10 4 **Figure 11.** Breakthrough curves of  $\text{SO}_4^{2-}$  by Ba-BFS-GP packed column for two different flow rates.  
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### 15 6 **3.11 Barium leaching**

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18 8 The leaching of Ba from Ba-BFS-GP was studied in mine effluent and distilled water at initial pH values  
19 8 of 2 and 8. The results indicate that dissolved  $\text{Ba}^{2+}$  concentrations from Ba-BFS-GP were 600 and 32  
20 9  $\text{mg L}^{-1}$  at initial pH values 2 and 8 in distilled water. However, in the case of mine effluent ( $C_0(\text{SO}_4^{2-})$ :  
21 9 850–870  $\text{mg L}^{-1}$ ), the dissolved  $\text{Ba}^{2+}$  concentrations were 0.175 and 0.375  $\text{mg L}^{-1}$  at initial pH values 2  
22 10 and 8, respectively. Clearly lower concentrations of dissolved Ba in mine effluent are due to the  
23 10 instantaneous precipitation of low solubility  $\text{BaSO}_4$ . The limit for Ba content in domestic water is 0.7  
24 11  $\text{mg L}^{-1}$  [76], so it would be safe to utilise Ba-BFS-GP for treating industrial wastewater containing  $\text{SO}_4^{2-}$ .  
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### 32 15 **3.12 Sorption mechanism**

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36 17 The sorption mechanism of geopolymers in the removal of cations from aqueous solutions has been  
37 17 suggested to be cation exchange [31, 44, 77]. However, geopolymers have low affinity towards  
38 18 sorption of anions due to negative zeta potential [46]. In the present work, geopolymers were  
39 19 converted into Ba-form by a cation-exchange process and further applied for  $\text{SO}_4^{2-}$  removal. The  
40 19 probable removal mechanism of  $\text{SO}_4^{2-}$  is based on the surface complexation or precipitation of  
41 20 extremely low solubility  $\text{BaSO}_4$  ( $K_{sp} = 1.08 * 10^{-10}$  at 25°C, solubility 0.0031  $\text{g L}^{-1}$ , 20°C) [50, 78]. Due to  
42 21 the low solubility,  $\text{BaSO}_4$  is considered non-toxic. However, the removal of sulphate with the direct  
43 22 precipitation as  $\text{BaSO}_4$  is not recommended due to generation of secondary waste in the form of  
44 23 sludge [14]. The presence of  $\text{BaSO}_4$  was confirmed with XRD from a used sorbent material.  
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## 4 Conclusions

Ba-modified blast-furnace-slag and Ba-modified metakaolin with and without a geopolymerisation step were studied for  $\text{SO}_4^{2-}$  removal. Ba-modified geopolymerised materials exhibit higher  $\text{SO}_4^{2-}$  ion removal capacity than Ba-modified materials without a geopolymerisation step. This is explained by the cation exchange process ( $\text{Na}^+$  is replaced by  $\text{Ba}^{2+}$ ) taking place in the geopolymer framework structure during Ba-modification. The best sorbent material for  $\text{SO}_4^{2-}$  removal was Ba-BFS-GP. The optimum pH required for maximum sorption was found to be 7–8. The maximum experimental sorption capacities were 91.1 and 119.0  $\text{mg g}^{-1}$  for synthetic model solution and mine effluent, respectively. Sorption capacities found in this study were among the highest of reported in the literature. The Sips isotherm model described the sorption well. Sorption kinetics followed the pseudo-second-order kinetic model, and the Weber and Morris intraparticle diffusion model showed that the sorption mechanism included two different steps. The positive enthalpy value indicates that the adsorption process was endothermic in nature. The results from the present study indicate that Ba-BFS-GP could be a technically feasible  $\text{SO}_4^{2-}$  sorbent for wastewater treatment (e.g. in the mining industry) especially for applications in which very low  $\text{SO}_4^{2-}$  levels are desired.

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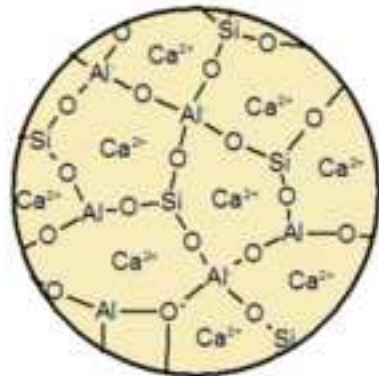
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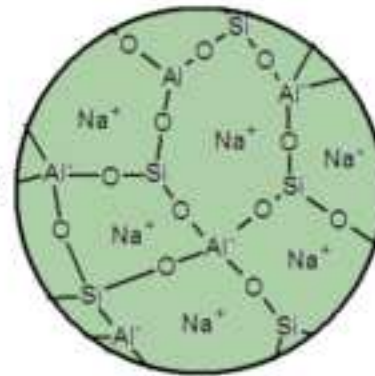
### Blast furnace slag (gehlenite)



Sulphate removal capacity  
 $q \approx 0 \text{ mg/g SO}_4^{2-}$

Alkali treatment /  
geopolymerisation

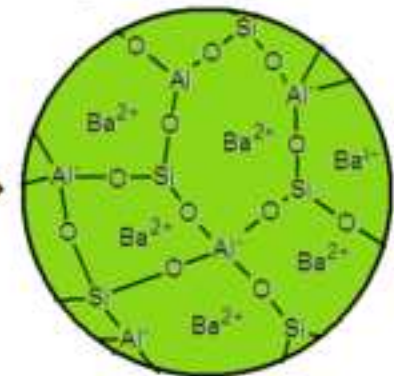
### Blast-furnace-slag geopolymer



Sulphate removal capacity  
 $q \approx 0 \text{ mg/g SO}_4^{2-}$

Ion-exchange

### Barium-modified blast-furnace-slag geopolymer



Sulphate removal capacity  
 $q \approx 119 \text{ mg/g SO}_4^{2-}$

Figure 1  
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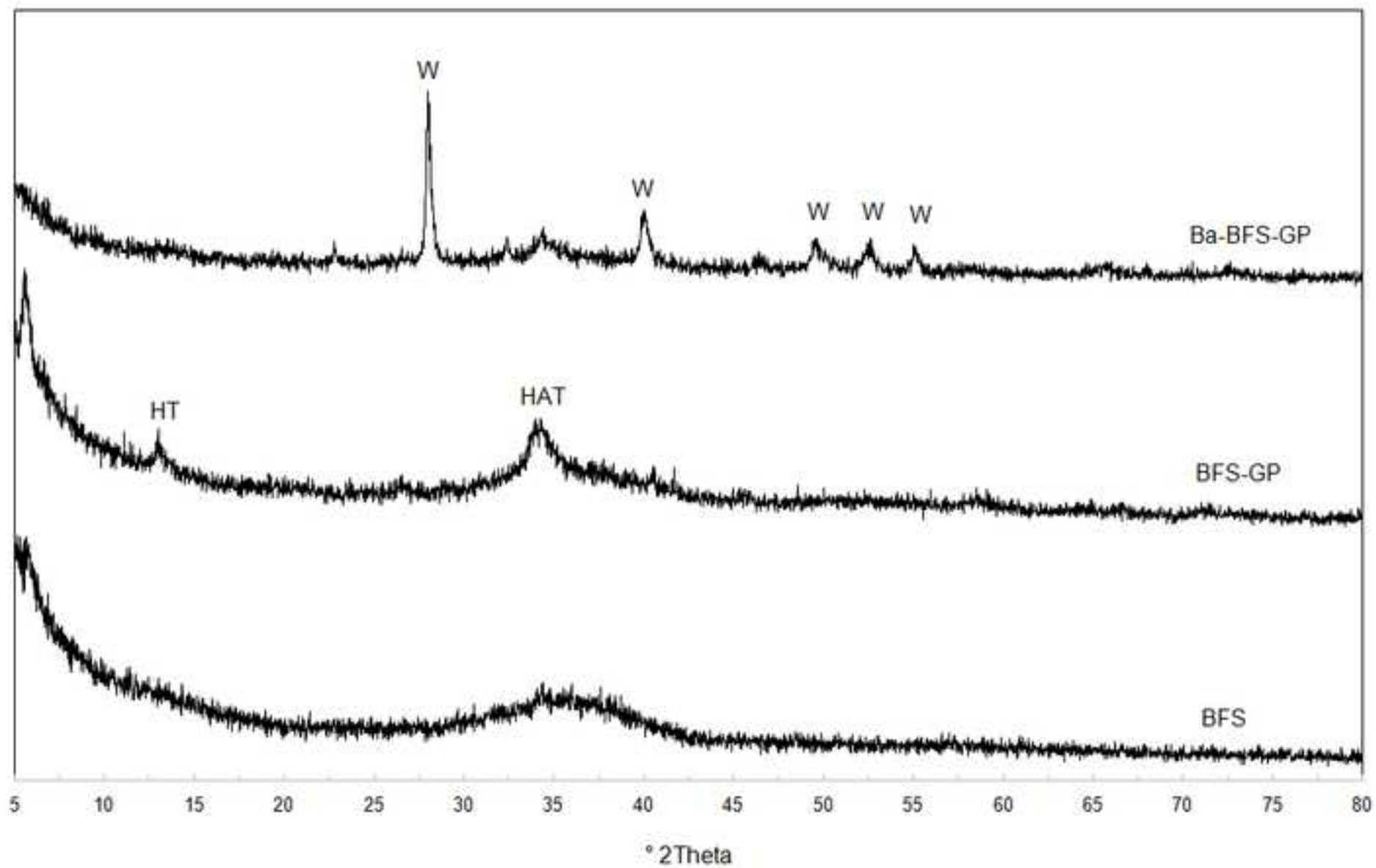


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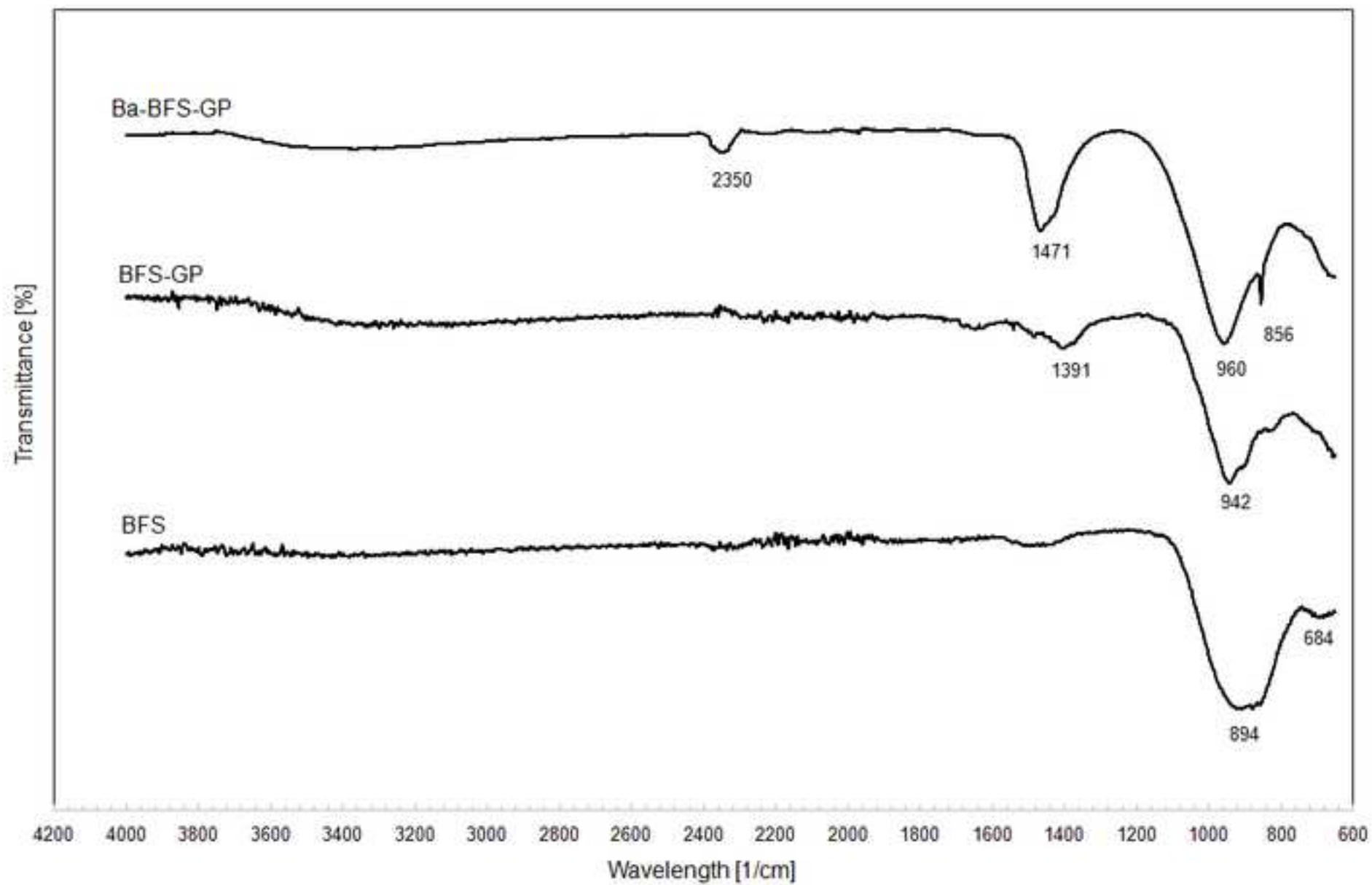


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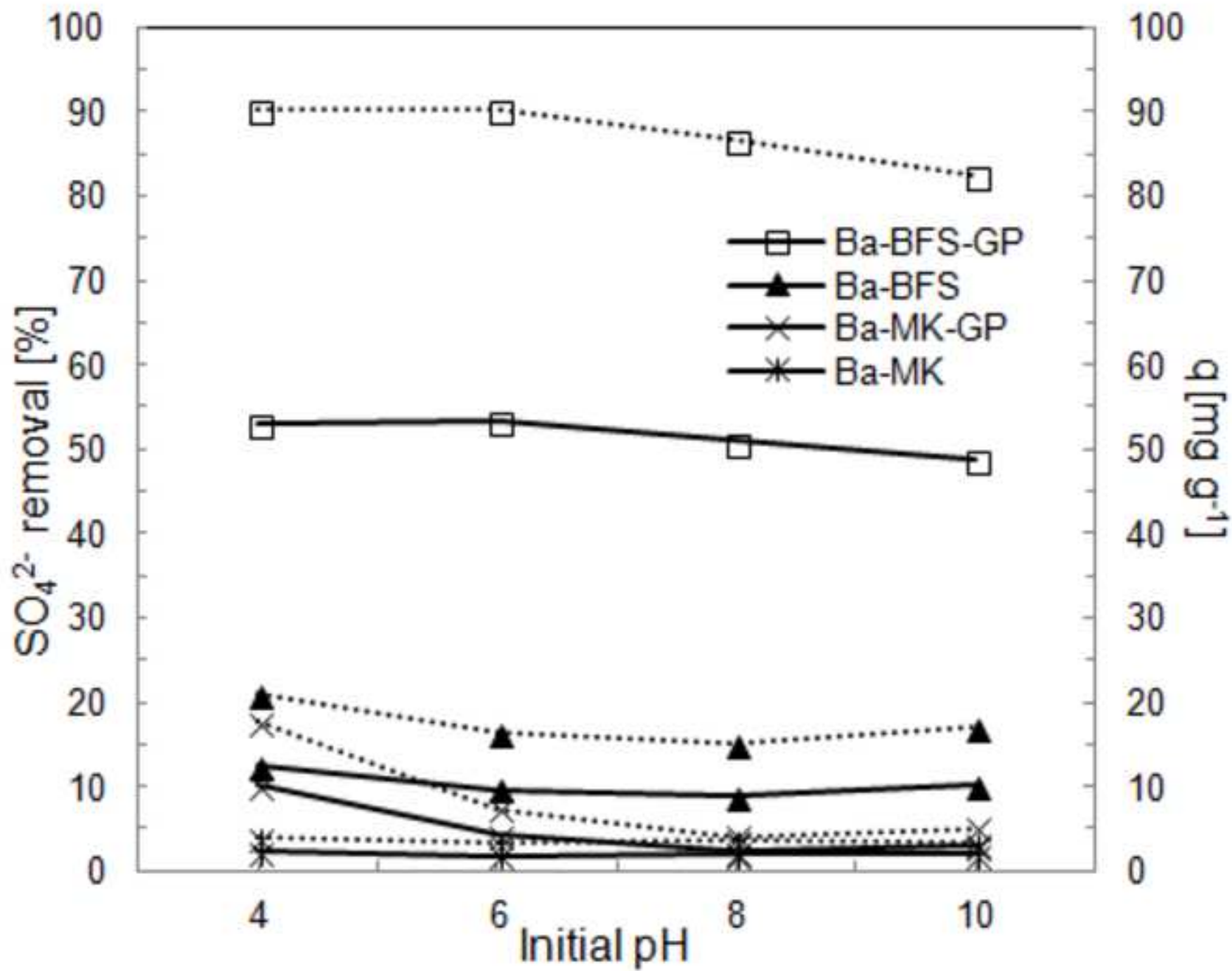




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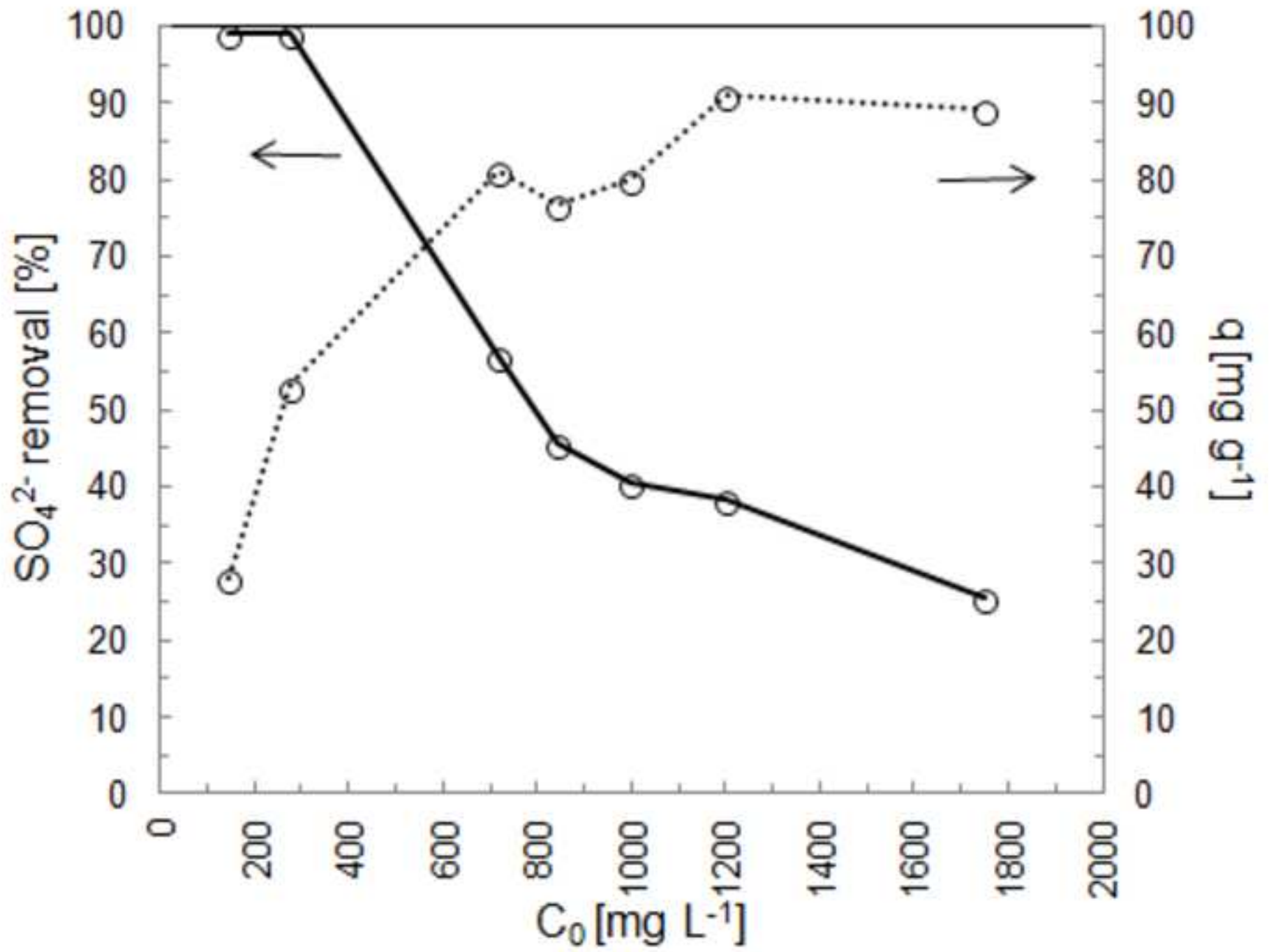


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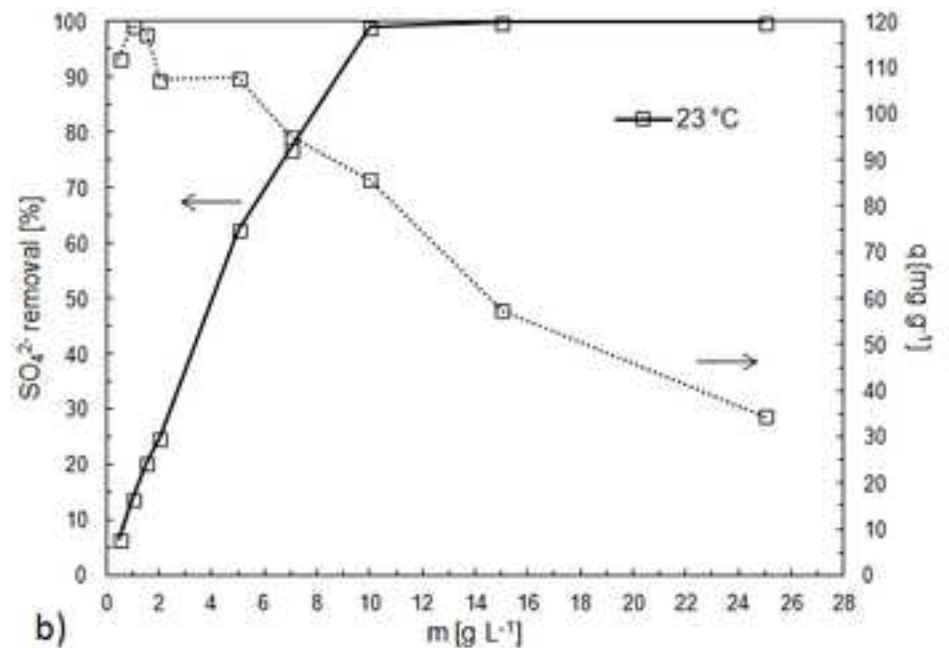
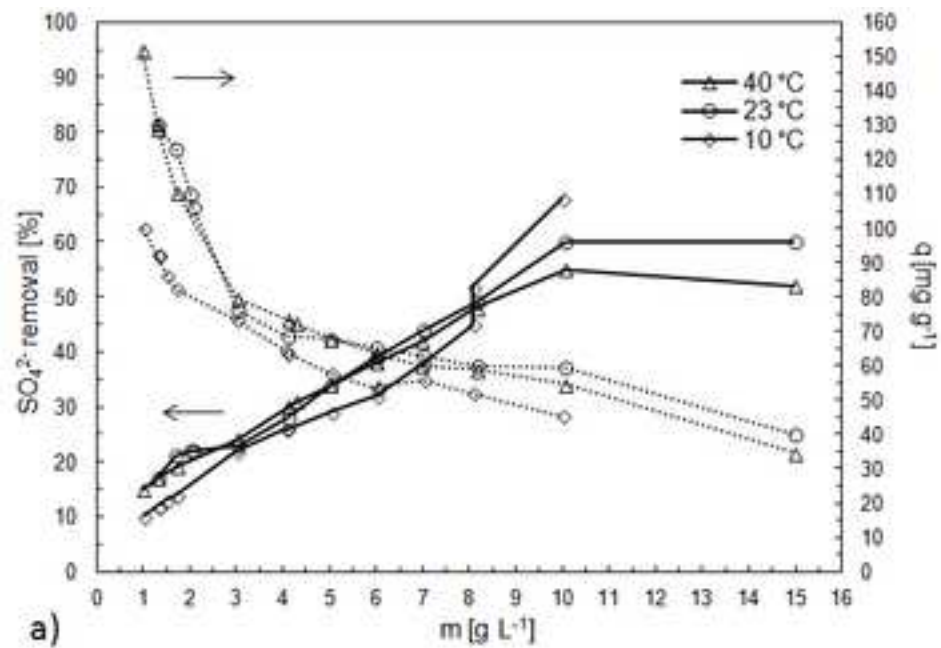


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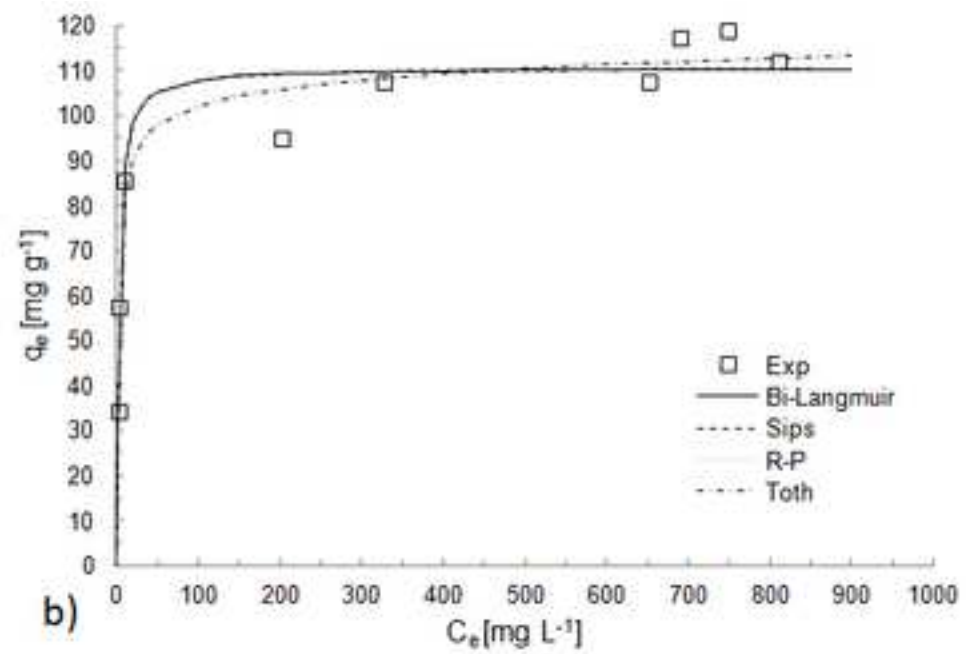
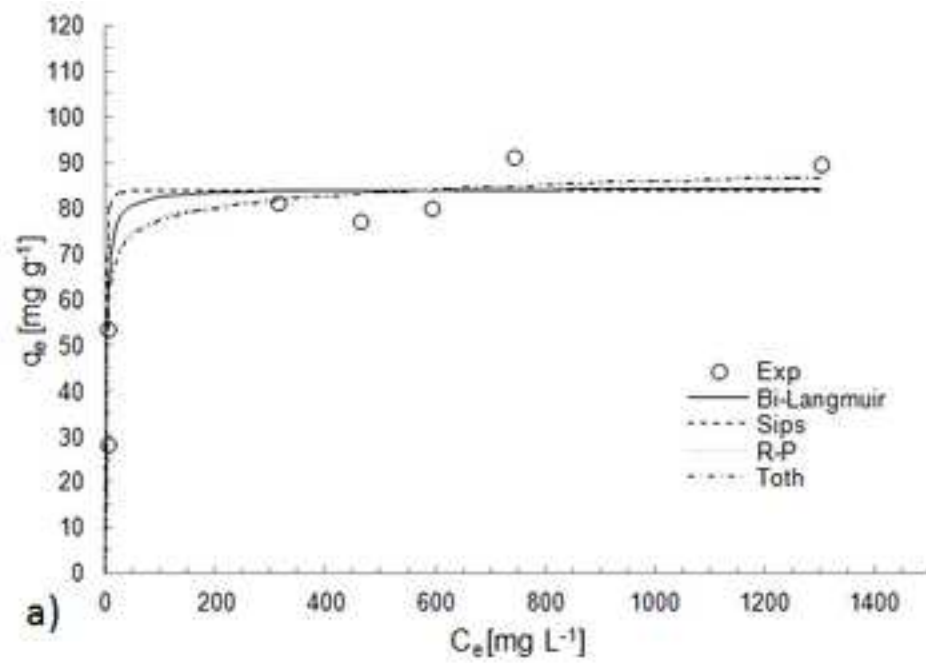


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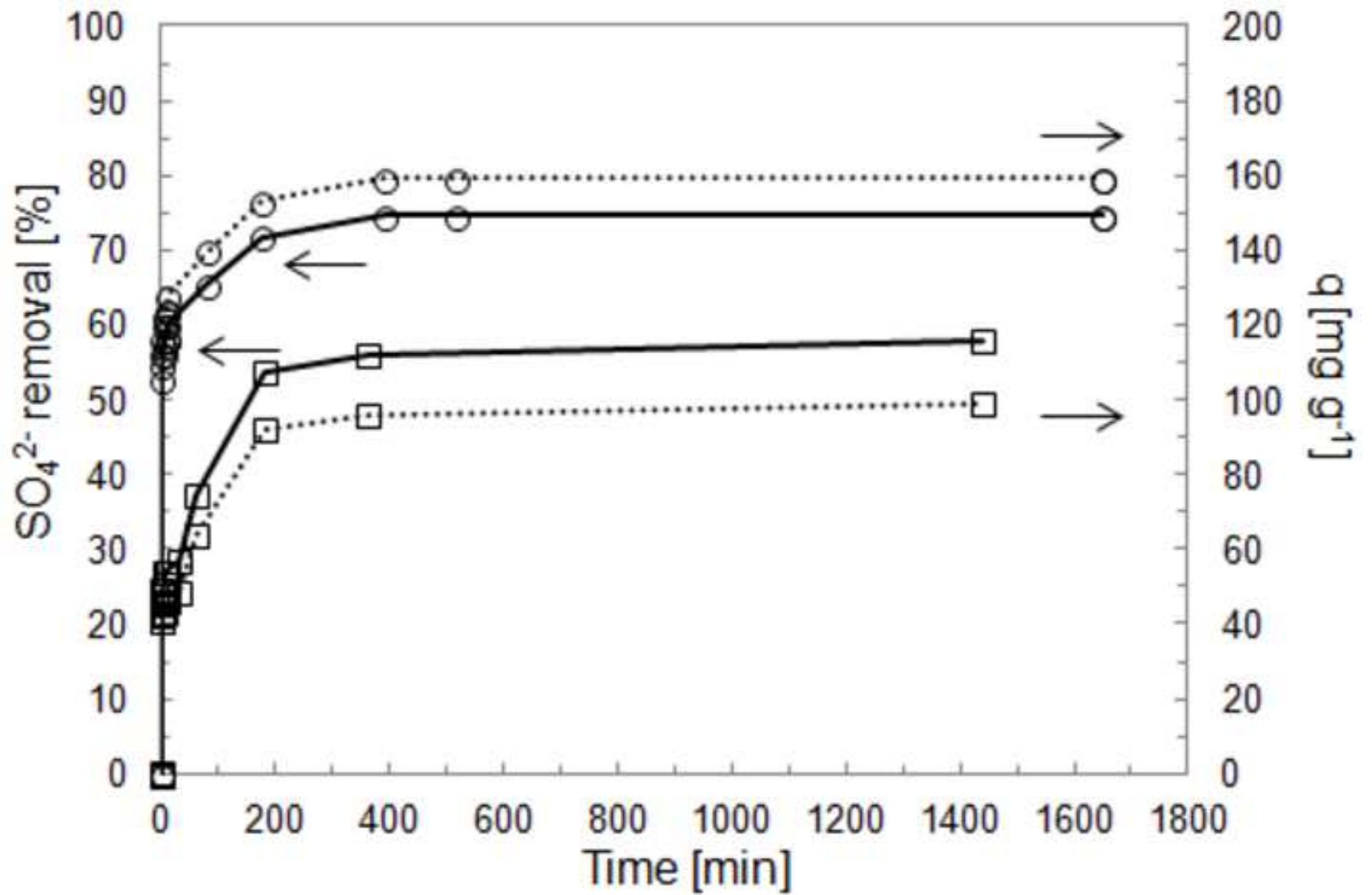


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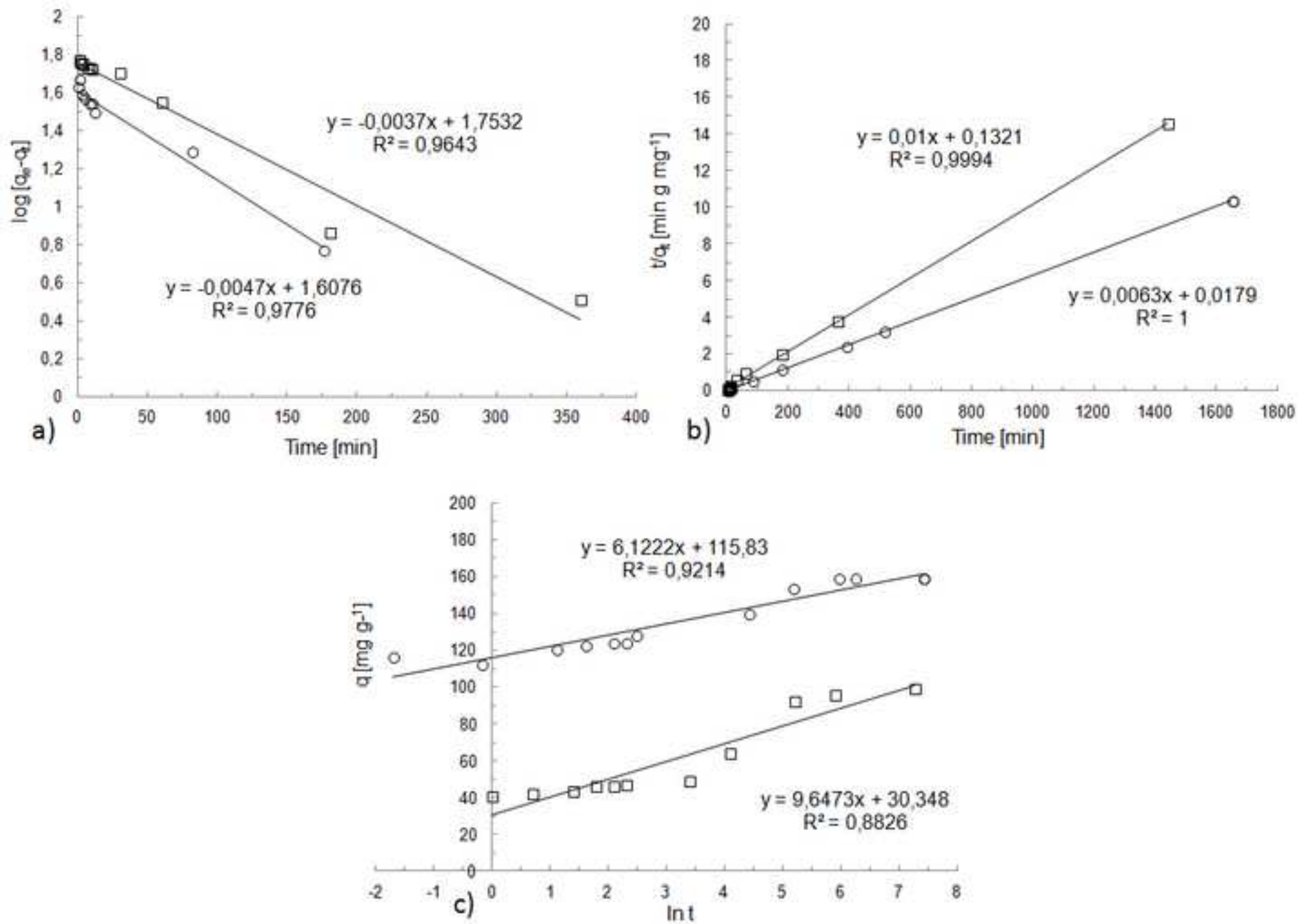


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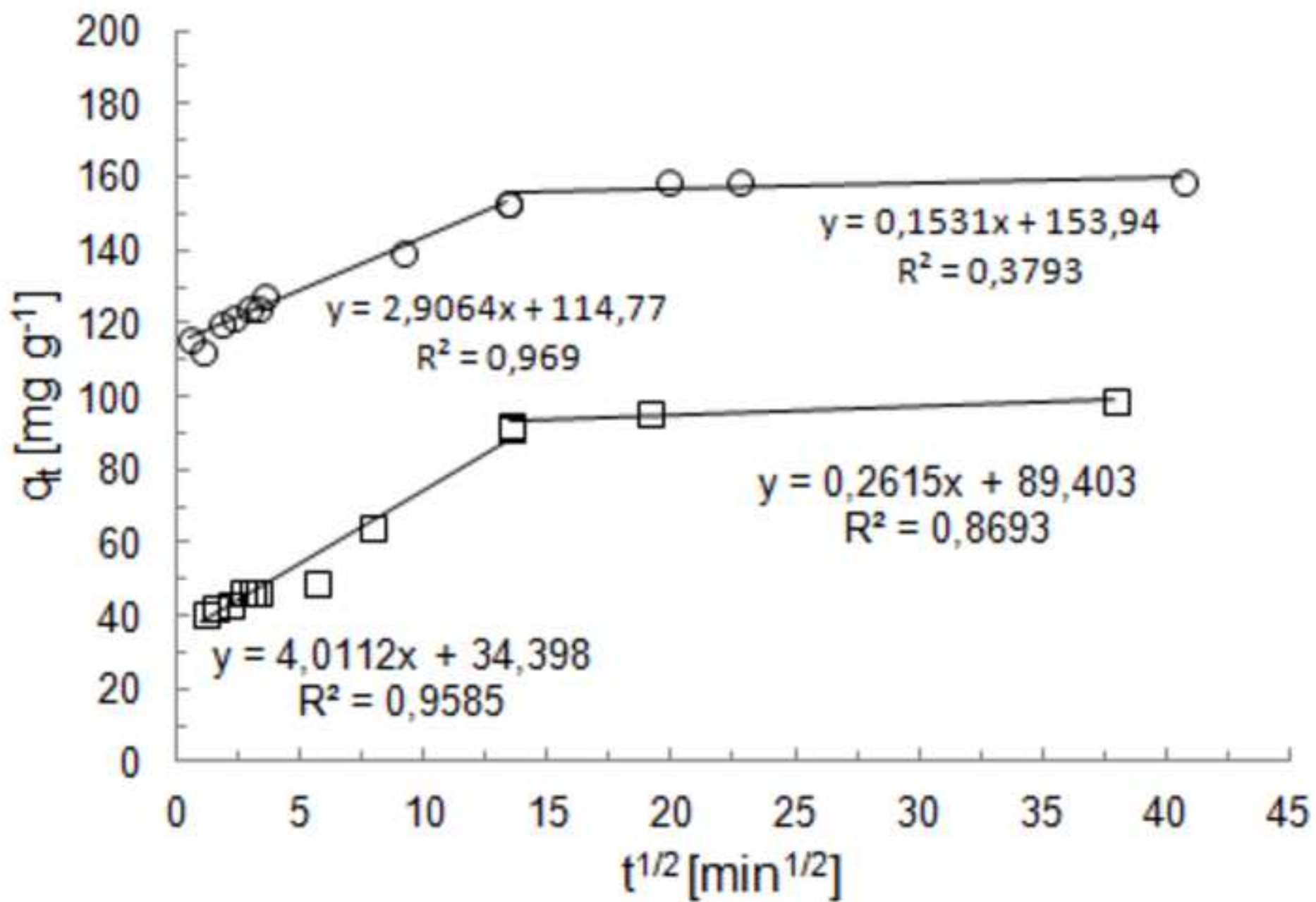


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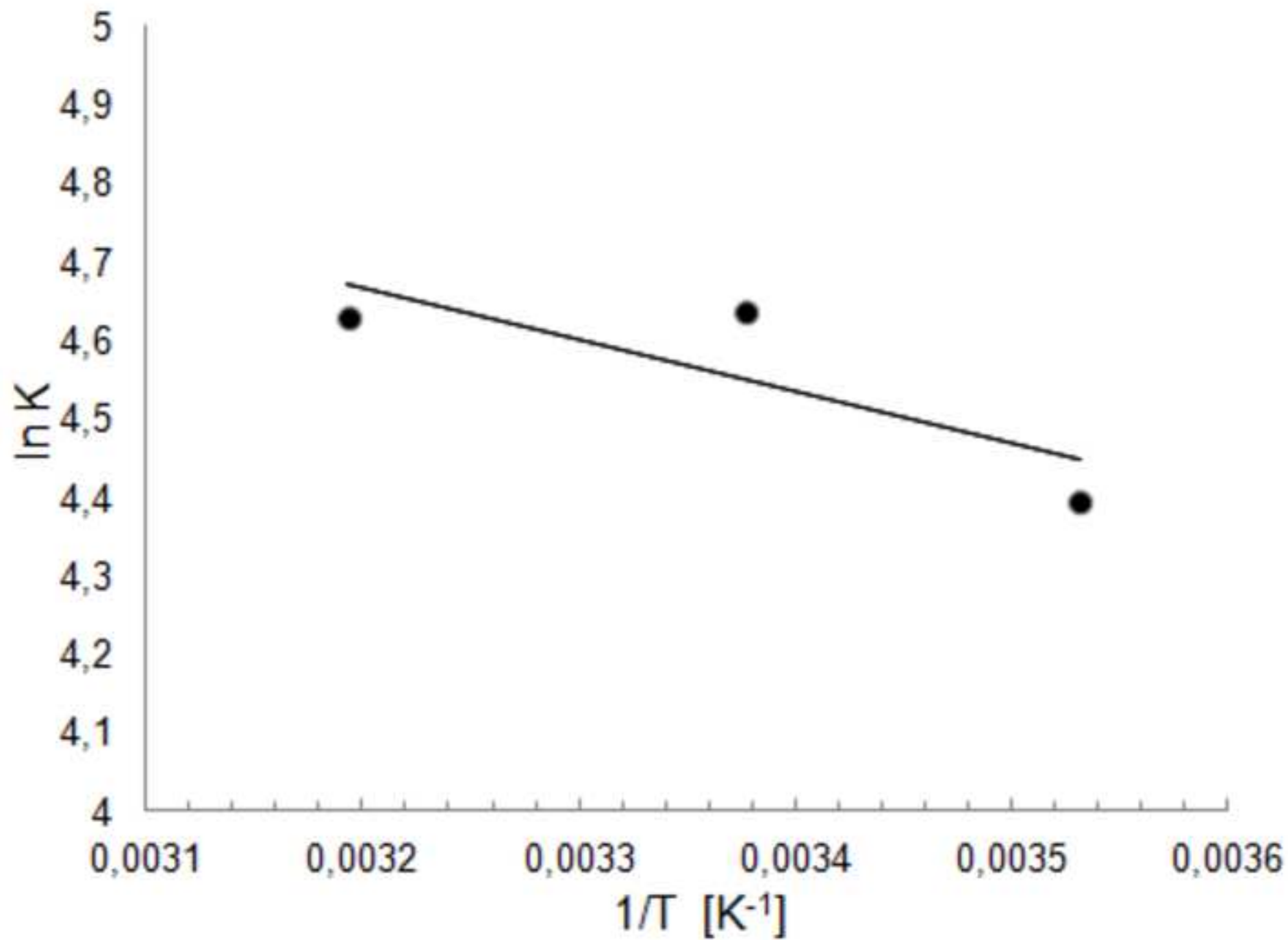
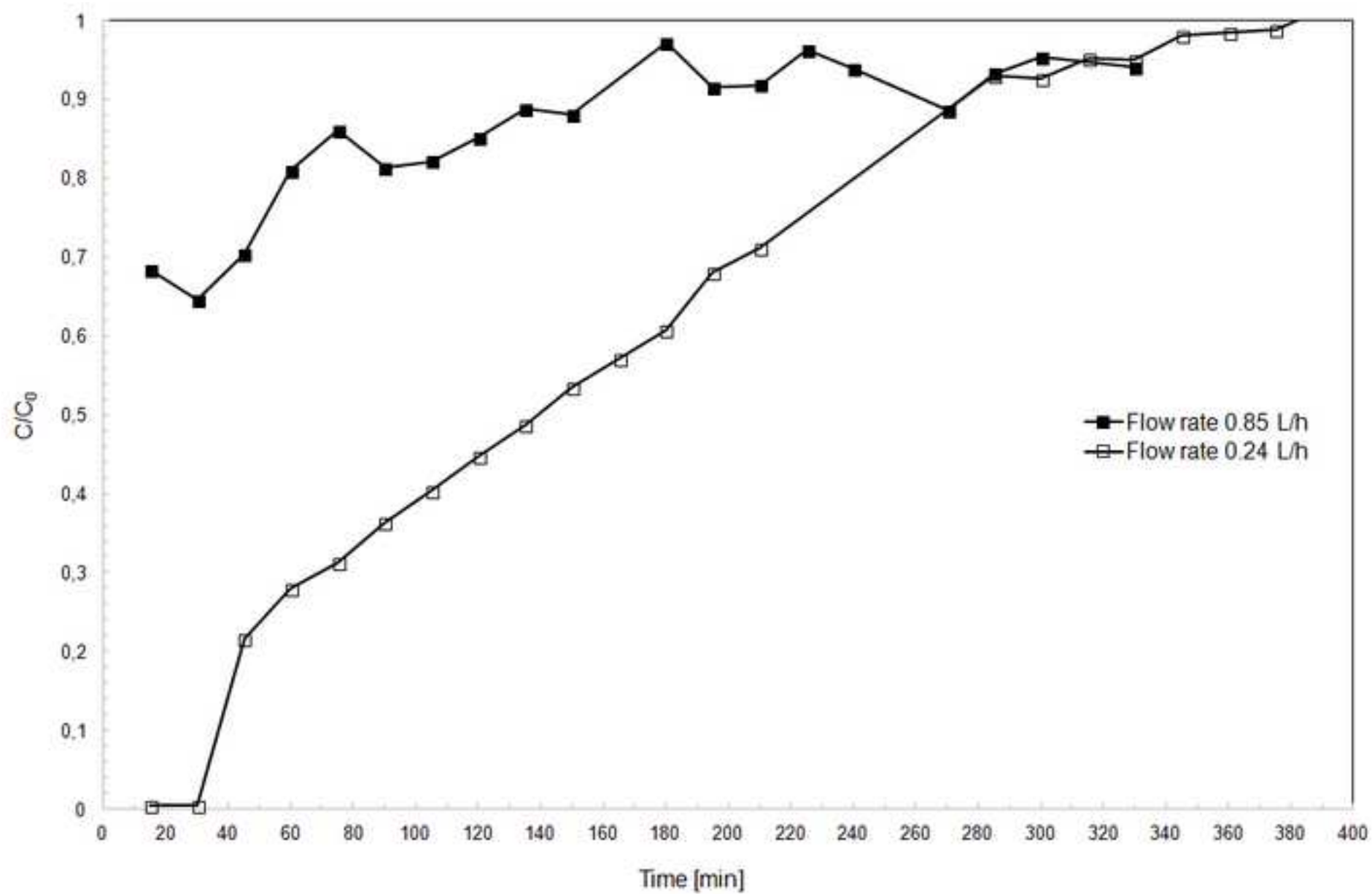


Figure 11  
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**Figure 1.** XRD patterns of blast-furnace slag (BFS), blast-furnace-slag geopolymer (BFS-GP) and barium-modified blast-furnace-slag geopolymer (Ba-BFS-GP) samples. HT = hydrotalcite, HAT = haturite, W = witherite.

**Figure 2.** The FTIR spectra of blast-furnace slag (BFS), barium-modified blast-furnace-slag (Ba-BFS) and barium-modified blast-furnace-slag geopolymer (Ba-BFS-GP).

**Figure 3.** Total  $\text{SO}_4^{2-}$  removal per cent (left, solid lines) and total adsorbed amount (right, dashed lines) versus initial pH on the sorption of  $\text{SO}_4^{2-}$  from mine effluent. Sorbent dosage:  $5 \text{ g L}^{-1}$ , contact time: 24 h, temperature: 22–23 °C, adsorbate: mine effluent ( $C_0, \text{SO}_4^{2-}$ :  $\sim 850\text{--}870 \text{ mg L}^{-1}$ ).

**Figure 4.** Effect of the initial concentration on the sorption of  $\text{SO}_4^{2-}$  on Ba-BFS-GP from model solution. Initial pH: 7–8, sorbent dosage:  $5 \text{ g L}^{-1}$ , contact time: 24 h, temperature: 22–23 °C.

**Figure 5.** Effect of Ba-BFS-GP dosage on  $\text{SO}_4^{2-}$  removal. a) Model solution:  $C_0(\text{SO}_4^{2-})$ :  $\sim 1200 \text{ mg L}^{-1}$ , contact time: 3 h. b) Mine effluent:  $C_0(\text{SO}_4^{2-})$ :  $865 \text{ mg L}^{-1}$ , contact time: 24 h. In both cases initial pH was 7–8.

**Figure 6.** Bi-Langmuir, Sips, Redlich-Peterson and Toth isotherms of  $\text{SO}_4^{2-}$  sorption on Ba-BFS-GP. a) Model solution:  $C_0(\text{SO}_4^{2-})$ :  $100\text{--}1800 \text{ mg L}^{-1}$ , sorbent dose:  $5 \text{ g L}^{-1}$ . b) Mine effluent:  $C_0(\text{SO}_4^{2-})$ :  $865 \text{ mg L}^{-1}$ , sorbent dose:  $1.3\text{--}15 \text{ g L}^{-1}$ . Initial pH was 7–8, contact time 24 h and temperature 22–23 °C.

**Figure 7.** Effect of contact time on the removal efficiency of  $\text{SO}_4^{2-}$  onto Ba-BFS-GP. o: Model  $\text{SO}_4^{2-}$  solution ( $C_0, \text{SO}_4^{2-}$ :  $1100 \text{ mg L}^{-1}$ ), □: Mine effluent ( $C_0, \text{SO}_4^{2-}$ :  $853 \text{ mg L}^{-1}$ ). Initial pH: 7–8, sorbent dosage:  $5 \text{ g L}^{-1}$ , temperature: 22–23 °C.

**Figure 8.** a) Pseudo-first-order kinetic, b) pseudo-second-order kinetic and c) Elovich model plots of  $\text{SO}_4^{2-}$  sorption on Ba-BFS-GP. o: Model  $\text{SO}_4^{2-}$  solution ( $C_0, \text{SO}_4^{2-}$ :  $1100 \text{ mg L}^{-1}$ ), □: Mine effluent ( $C_0, \text{SO}_4^{2-}$ :  $853 \text{ mg L}^{-1}$ ). Initial pH: 7–8, sorbent dosage:  $5 \text{ g L}^{-1}$ , contact time: 24 h, temperature: 22–23 °C.

**Figure 9.** Weber and Morris intraparticle diffusion model plot of  $\text{SO}_4^{2-}$  sorption on Ba-BFS-GP.  $\circ$ : Model  $\text{SO}_4^{2-}$  solution ( $C_0, \text{SO}_4^{2-}$ :  $1100 \text{ mg L}^{-1}$ ),  $\square$ : Mine effluent ( $C_0, \text{SO}_4^{2-}$ :  $853 \text{ mg L}^{-1}$ ). Initial pH: 7–8, sorbent dosage:  $5 \text{ g L}^{-1}$ , contact time: 24 h, temperature: 22–23 °C.

**Figure 10.** Van't Hoff plot for adsorption of  $\text{SO}_4^{2-}$  removal. Initial pH: 7–8, adsorbent dosage  $5 \text{ g L}^{-1}$ ,  $C_0(\text{SO}_4^{2-})$ :  $1200 \text{ mg L}^{-1}$ .

**Figure 11.** Breakthrough curves of  $\text{SO}_4^{2-}$  by Ba-BFS-GP packed column for two different flow rates.

Blast-furnace slag and metakaolin were geopolymerised, modified with barium or treated with a combination of these methods in order to obtain an efficient  $\text{SO}_4^{2-}$  sorbent for mine water treatment. Of prepared materials, barium-modified blast-furnace slag geopolymer (Ba-BFS-GP) exhibited the highest  $\text{SO}_4^{2-}$  maximum sorption capacity (up to 119  $\text{mg g}^{-1}$ ) and it compared also favourably to materials reported in the literature. Therefore, Ba-BFS-GP was selected for further studies and the factors affecting to the sorption efficiency were assessed. Several isotherms were applied to describe the experimental results of Ba-BFS-GP and the Sips model showed the best fit. Kinetic studies showed that the sorption process follows the pseudo-second-order kinetics. In the **dynamic** removal experiments with columns, total  $\text{SO}_4^{2-}$  removal was observed initially when treating mine effluent. The novel modification method of geopolymer material proved to be technically suitable in achieving extremely low concentrations of  $\text{SO}_4^{2-}$  ( $< 2 \text{ mg L}^{-1}$ ) in mine effluents.