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Investigation of the Attenuation and Release of Cu^{2+} Ions by Polymer-Treated Tailings

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Abstract: This study investigated the attenuation and release behaviour of copper ions using a standard kaolin-silt slurry as the synthetic tailings in a high solids/high salinity application before and after inline flocculation. A homogenous, synthetic tailings slurry was prepared in a 0.6 M NaCl solution and treated in a low-shear mixer by adding Magnafloc® 336 flocculant. Following the evaluation of morphological properties of both the untreated (UT) and polymer-treated tailings (PT), identical equilibrium tests were performed via the bottle-point method constant concentration technique. The maximum copper ions uptake capacity of polymer-treated tailings was 25% more than the untreated slurry at the equilibrium state in a chemisorption process in which the ions had the capability of binding onto one location on the sorbent, which could be influencing other binding sites on the same sorbent. Polymer treatment resulted in a highly porous structure that exhibited an increased capacity to adsorb and retain copper ions compared to the UT materials. This behaviour indicates the strong binding between the copper ions and active site of the treated tailings particles with greater capability of this material for preserving heavy metal ions within their structure across a wide pH range (2–10) compared to the UT materials. The results advance the fundamental understanding of how inline flocculation can considerably improve the sorption capacity of high solids/high salinity tailings favouring potential long-term rehabilitation purposes at mine closure and the role of sorption and desorption of heavy metal ions' behaviour play to achieve this goal.

Keywords: inline flocculation; heavy metal; sorption; desorption; high solid tailings; copper ions

1. Introduction

Heavy metal ions released during mining activities are major potential contaminants of soil, water, and vegetation [1,2]. Poorly controlled mine residues are easily dispersed into the environment by surface drainage, wind, and groundwater [3,4]. In particular, mineral processing tailings can have high heavy metal concentrations and consequently are often sources of heavy metal pollution, and owing to the serious toxic effects, it is imperative to prevent and/or mitigate heavy metal pollutions. In line with recommendations and government guidelines, the current inclination is to expand and apply in situ techniques where possible to minimise disturbance of contaminated lands. Therefore, tailings dewatering by an effective technique which would also provide the opportunity for in situ remediation is desirable.

Generally, tailings are comprised of water and a range of materials remaining from the mineral processing including finely sized clay minerals which are the most problematic components in tailings dewatering [5,6]. Among several available techniques for treating

fine-particle tailings, polymer-bridging flocculation is an effective approach which achieves solid–liquid separation by increasing the settling rate of individual particles by forming larger aggregated structures [7–9]. In this regard, one of the industrially trialled methods is inline flocculation, where a polymer is added at high dosages to the thickener underflows, resulting in additional aggregation and water release on deposition compared to conventional low-solids thickening alone [10,11]. These highly flocculated materials have potential properties and structure that may be beneficial for removing hazardous metal ions.

Copper (II) is known to be one of the heavy metals widely used in many industries [12], which spreads into the environment through soils and water streams and accumulates along the food chain, resulting in a high risk to human health [13]. Most of the mine tailings, especially the copper sulphide ores tailings, contain copper ions which are generated through the oxidation of sulphide and dissolution/weathering of tailings or the acid mine drainage processes [12]. As copper (II) does not degrade biologically, the control of Cu (II) pollution has special importance for both organisms that live in waters and those that benefit from waters.

Clay minerals have shown a range of sorption capabilities for different heavy metal ions. For example, kaolinite clay was used to remove Cu (II), Pb (II), Zn (II), and Ni (II) in aqueous medium and has been investigated through the process of sorption under a set of varied conditions [14,15]. The removal of metal ions using kaolinite clay is based on ion exchange and sorption mechanism even though kaolinite exhibits the least exchangeability among clay minerals sorption [16,17].

To study the equilibrium sorption of metal ions, it is important to understand the fundamental differences between sorption and ion exchange isotherms. For sorption studies, the isotherm is applicable for a particular system if the temperature remains constant. Though, in the case of ion exchange, the system is not only at a constant temperature but also of constant solution normality and as concluded in a study by Limousin et al. [18], if constant solution normality is not satisfied, then the uniqueness of the isotherm is not acceptable. In this regard, Millar et al. [19] assessed the influence of the bottle-point technique to generate equilibrium ion exchange isotherms. It was found that the constant-mass method in which the concentration of the metal ions was diverse while the sorbent mass was preserved constant seemed to be unreliable in determining the maximum loading of ions on the sorbent surface. Alternatively, the constant-concentration methodology with a solution of constant normality and different sorbent masses, was observed as a more reliable method and emphasised that the ion exchange phenomenon was required to be studied not only at isothermal but also isonormal conditions [20]. In this regard, there are several isotherm statements described in the literature for the fitting of equilibrium data [18] such as Langmuir, Freundlich, Hill models, etc., which apply to the experimental equilibrium data to discover the important scientific observations.

To the best of our knowledge, no previous research has investigated the potential capacity of polymer-treated tailing at high solids in removing heavy metal ions from tailings pore water. Therefore, this study aims to examine the efficiency of polymer-treated tailings for Cu^{2+} sorption/desorption from the aquatic environment and to compare these data with those of untreated materials. The hypothesis was that the porous, non-homogenous structure of polymer-treated materials could allow more Cu^{2+} ions removal and retention. In this regard, Figure 1 presents the tailings profile after flocculation and deposition at the tailings storage facility (TSF) with the potential aggregates for removing the heavy metal ions. Research questions that were addressed include: (1) what are the maximum Cu^{2+} ion exchange capacities of polymer treated and untreated tailings? (2) What equilibrium and kinetic model fits the experimental data more optimally? (3) How does pH impact the sorption and desorption behaviour of materials? (4) Do the polymer-treated sorbents have an acceptable breakthrough time? The investigation comprised three stages. In the first stage, the morphological structure of the polymer-treated and untreated tailings were investigated using the Cryo-SEM imaging and BET analysis. Then the bottle-point method constant concentration method was applied for both the sorption and desorption

experiments and studying the impact of pH. The third stage consisted in determining the capacity of materials in removing the copper ions through the column leaching tests and the behaviour of the materials over time in removing the copper ions.
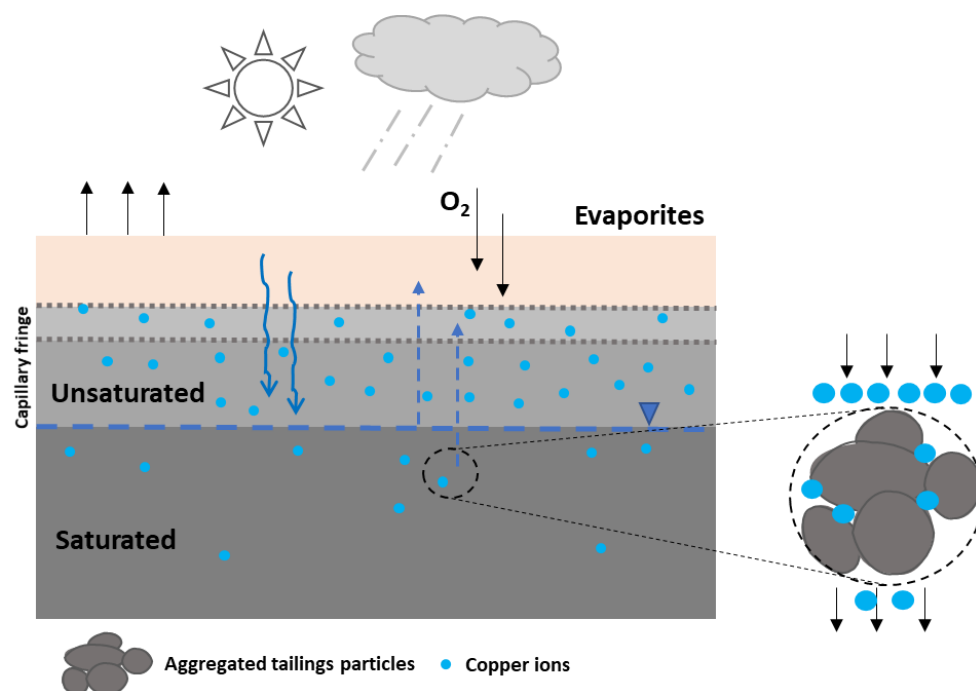

Figure 1. Tailings profile after dewatering and deposition on TSF.

2. Materials and Methods

2.1. Materials

Kaolinite-NY prestige, silica 200 G silt, and silica fine sand were purchased from Sibelco Company, Australia, to prepare the initial slurry. All three slurry components are produced from chemically treated and water-washed high purity materials and the milling process ensures minimal contamination, resulting in high purity products. Table 1 depicts the dominant minerals for each slurry ingredient in this study. Magnafloc® 336 was selected because it gave higher water recovery (more than 60%) with reasonable final solid properties after specific time in preliminary testing under saline conditions. BASF's Magnafloc® products are all acrylamide/acrylate copolymers with their general behaviour considered representative of nominally equivalent products available from other flocculant suppliers. Magnafloc® 336 is a very high molecular weight anionic polyacrylamide flocculant supplied as a free-flowing granular powder. The intrinsic viscosity (IV) of the flocculant, as specified by the supplier, was 24 dL/g, providing a relative indication of its solution dimensions. Higher molecular weight (MW) polymers typically offer a larger hydrodynamic size of chains in solution, with increasing MW producing loops and, more importantly, long extended tails that can form bridges with other particles to create aggregates [21]. At higher ionic strength, which was applied in this study, the polymer chains are expected to be more mobile and flexible on the colloidal surface, which allows the restructuring of aggregated clusters to proceed unhindered [22]. Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) purchased from Sigma Aldrich was used to prepare the copper ions solution for either the batch or the continuous sorption experiments.

Table 1. Synthetic slurry mineralogy.

|	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	TiO$_2$ (%)
Kaolinite-NY prestige	49.2	35	0.94	0.96
Silica 200 G	99.6	0.17	0.02	0.03
Silica fine sand	98.5	0.1	0.3	0.9

2.2. Slurry and Polymer Preparation

A synthetic homogenous tailings slurry was prepared in 0.6 M NaCl solution to avoid the natural variability that exists with real tailings samples and to enable the preparation of large batches for testing. Slurry was prepared at 50 wt% solids from a combination of 25% kaolin, 45% silica 200 G (93% finer than 53 μm), and 30% silica fine sand (99% finer than 0.3 mm), as described elsewhere [23]. The specific gravity of the slurry solid particles was 2.64. Conditioning of the slurries was conducted at 1200 rpm for five days in a baffled 200 L tank to ensure a stable, reproducible size for the duration of testing which was confirmed by laser diffraction measurements.

Working polymer solutions (0.4 wt%) were prepared in the same saline solution used for slurry make-up. The weighed polymer was added slowly to the vortex produced in salted water under vigorous mixing to fully disperse the powder. Initial strong agitation with a 3-bladed axial flow impeller with blade dimension of each 7 cm × 2.2 cm (Lightnin A310) at 250 rpm for 30 min was followed by gentle agitation (80–100 rpm) for 16 h to produce clear, homogenous solutions. Flocculant solutions were aged for 3 days in a cool room (4 °C) to ensure optimal activity before adding to the slurry and producing polymer amended tailings [24].

2.3. Inline Polymer Addition

Figure 2 shows the lab-scale experimental setup used to simulate the inline flocculation process. To control the polymer dosage (1000 g/t), polymer solution (45 mL/min) and slurry (0.25 L/min) were pumped to the inlet of the pre-conditioning coil (1 m length, 7.7 mm I.D.) before entering a low-shear chaotic mixer for continued mild mixing. The final products were collected from the discharge point for further testing [25].
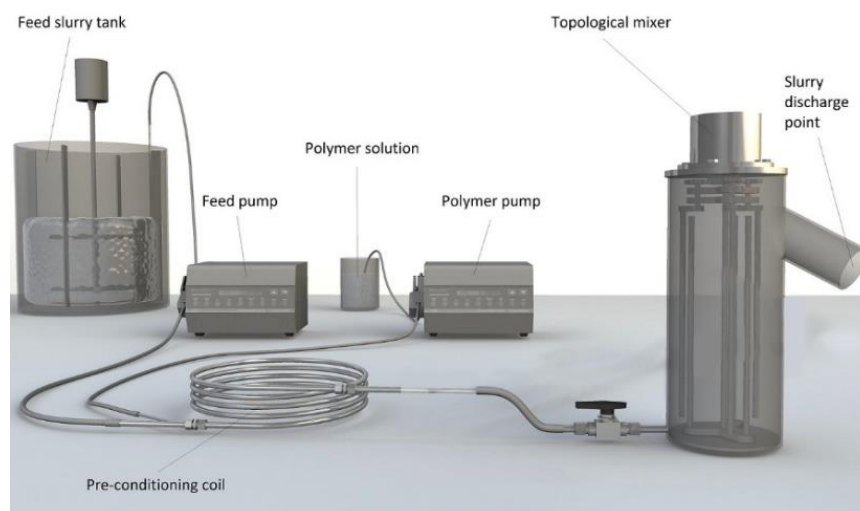
Figure 2. Tapered shear setup for polymer addition to high-solids suspensions [26].

2.4. Cryo-SEM

Morphological properties of the aggregated tailings were investigated using Cryo-SEM. An EM HPM 100 High-Pressure Freezer (HPF) technique was applied to prevent ice crystal formation or soluble aggregation that could provide poor vitrification. Samples were

quickly frozen by a jet of high pressure after placing into the HPF and then was fractured with a knife in the cold preparation-chamber to be ready for coating with iridium at 10 mA for 120 s at around 5–10 nm thickness [27]. Scanning electron microscopy (JEOL JSM 7001F FESEM, JEOL, Tokyo, Japan) was operated at different voltages and magnifications to compare the treated and untreated tailings.

2.5. BET

Specific surface area and pore size distribution were defined using Brunauer–Emmett–Teller (BET) and Barrette–Joynere–Halenda (BJH) measurements on a Micromeritics TriStar 3020 analyser (TriStar II Plus, Micromeritics Instrument Corp, Norcross, GA, USA) after degassing under vacuum on a Micromeritics VacPrep061. Multi-point BET and BJH sorption isotherms models were employed to calculate the specific surface areas [15,28].

2.6. Cation Exchange Capacity (CEC) on ICP-OES

For CEC analysis, the collected water samples after each experiment were mixed with silver thiourea (AgTU+) for 24 h. Then, to determine the exchangeable base concentrations, the centrifuged and filtered extracts using a Varian Vista Pro ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) (, Varian, Inc, Santa Clara, CA, USA) apparatus were analysed, and CEC was determined by calculating the total of silver ions that were exchanged. ICP-OES analysis was performed using the standard high-concentration wavelengths for each element. 328.0 nm for Ag, 38.215 nm for Al, 317.933 nm for Ca, 766.491 nm for K, 279.553 nm for Mg and 588.995 nm for Na, though other wavelengths can be used if matrix effects make these lines unsuitable [29].

2.7. Methodology for Bottle-Point Method Constant Concentration

For the copper isotherm test, duplicate equilibrium tests were performed by adding an accurately weighed mass of sorbent (1–50 g), i.e., polymer-treated (PT) and untreated materials (UT), into a set of 200 mL Nalgene flasks including copper ions solution with the constant concentration of 200 mg/L. This concentration was chosen to show the equilibrium at the end with attention to the selected range of mass of sorbent after some preliminary works similar to what was shown in previous research investigating the equilibrium sorption of metal ions [13,17,30]. Stock solutions were prepared by dissolving $CuSO_4 \cdot 5H_2O$ in Millipore water. The equilibrium time was previously obtained from dynamic tests and shown to be less than 24 h (details are mentioned in the kinetic study section). The samples were stirred at a low speed (25 rpm) for 24 h at room temperature. Both the untreated and polymer-treated material had a constant pH in the range of 6.5–7.5 [25], while the 200 mg/L copper solution pH was 5.2. Eventually, pH was recorded after the experiment and found to be in the range of 5.5–6.5 for all samples, then the liquid and solid phase were separated by centrifuging (5 min with 2500 rcf), and the liquid phase was syringe filtered. The concentration of Cu^{2+} ion remaining in the solutions after equilibrium, Ce (mg/L), was measured using ICP-OES and the equilibrium loading of copper ions on the UT/PT phase (q_e (mg/g)) deduced from below equation.

$$q_e = V/m \times (C_0 - C_e) \tag{1}$$

where V is the solution volume (L), m is the mass of sorbent (g), and C_o is the initial concentration of the copper ion (mg/L).

2.8. Sorption Isotherm Models

Based on the published studies, between the non-linear least squares (NLLS) and linear least squares (LLS) approaches for fitting isotherm data in both sorption and ion exchange isotherms, the NLLS method is preferable based on the way of estimating the parameters and the error functions [31,32]. Fitting using non-linearised versions of equations was applied to calculate the R^2 values plus the error functions to assess the different models and find the best fit on experimental data by using the Microsoft Solver add-on in Excel.

The mechanism of the sorption can be evaluated based on the theoretical isotherm models and the corelated paraments of each model can describe the properties of the sorbent in the presence of the used metal ions in the solution during the sorption [21]. For example, the Langmuir model which follows the equation 2 estimates that the metal ions sorption take place on a monolayer homogenous surface without any interaction between adsorbed ions.

$$q_e = C_e/(1/bq_0 + C_e/q_0) \tag{2}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the metal ions (mg/L), and q_0 (mg/g) and b (L/mg) are Langmuir constants.

Another common isotherm model is the Freundlich model that takes the Equation (3) which is an empirical equation based on sorption on a heterogeneous surface. Freundlich model is not restricted to the monolayer formation in which its application to the multilayer sorption is possible and defines the heterogeneity of the surface as well as the exponential distribution of the active sites and the active sites energies [33]. It proved that the stronger binding sites will be taken and then an exponential decrease in the sorption force will happen upon completing the sorption process.

$$q_e = K_f C_e^{1/n} \tag{3}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the metal ions (mg/L), and K_f ($mg^{1-1/n} \, L^{1/n} \, g^{-1}$) and n (g/L) are the Freundlich constants and specify the sorption capacity and the sorption strength, respectively [14].

Finally, the Hill isotherm model that supports different species' binding onto homogeneous surfaces, is also a common isotherm model with sorption occurring as a cooperative phenomenon in which the ions have the capability of binding into one location on the sorbent, which could be influencing other binding sites on the same sorbent. Originally, the equation of this sorption isotherm model was developed from the non-ideal competitive sorption isotherm [34]. The non-linear form of this isotherm model is expressed as follows:

$$q_e = (q_{max} C^{\alpha})/(K^{\alpha} + C_e^{\alpha}) \tag{4}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the metal ions (mg/L), q_{max} (mg/g), and K and α are Hill model constants. Likewise, in this model, if $\alpha = 1$ it indicates that binding is hyperbolic or non-cooperative, if $\alpha > 1$, binding has positive cooperativity, while negative cooperativity happens when $\alpha < 1$ [35].

2.9. Kinetic Studies

The kinetic tests were performed using an initial concentration of 200 mg/L copper with a volume of 50 mL and UT/PT mass of 5 g, at room temperature. Thirty similar bottles in the same condition were placed on a shaker with a speed of 25 rpm for untreated and treated samples. At different time intervals, a bottle was taken, and the supernatant was decanted for transferring to the centrifuge and then analysing by ICP for the residual copper. To understand the dynamic interactions of ions with solid phases and to predict their fate with time, the copper ions sorption constants were calculated using the non-linear form of the pseudo-first-order and pseudo-second-order equations (Equations (5) and (6), respectively).

$$dq_t/dt = k_1(q_e - q_t) \tag{5}$$

$$dq_t/dt = k_2(q_e - q_t)_2 \tag{6}$$

where q_t is copper ions loading at a time (t), q_e is copper ions loading at equilibrium, t represents time, k_1 and k_2 are the pseudo-first-order and pseudo-second-order rate constants. As mentioned earlier, to ensure the accuracy of the results, analysis by NLLS is crucial which requires the use of error functions and the SNE (sum of normalised errors) term should

be calculated to introduce the appropriate error function that was studied in detail in a study by Foo and Hameed [36]. Thus, here in this study, based on the calculated data with different error function using Solver function in Microsoft Excel, the suitable fitted model and its parameters were presented.

2.10. Desorption Studies

The same samples that were used and loaded with copper ions during the sorption experiments in different masses of UT/PT samples were used for the desorption tests after decanting their supernatant and replacing it with the constant volume of DI water. Samples were placed on the shaker for 24 h and then analysed for determining the released copper ions to solution.

2.11. Effect of pH on Sorption and Desorption

To investigate the impact of pH on sorption and desorption of copper ions, initially the pH of the solutions was adjusted by using HCl and NaOH for six different points. Then, sorption tests were conducted on 50 mL bottles of 200 mg/L copper concentration containing 5 g of sorbent mass for each test in 24 h shaking conditions. For desorption experiments, 5 g of previously loaded masses of UT/PT samples were transferred to the newly prepared bottles of 50 mL DI water at different pH and were placed on the shaker for 24 h. All the solutions were analysed using ICP for calculating the concentration of copper.

2.12. Column Leaching Experiments

Column tests were performed to investigate the Cu^{2+} removal using untreated and polymer-treated tailings. The Cu^{2+} initial concentrations were 200 ppm, with initial pH values of 6. All experiments were conducted at ambient temperature (25 °C). The fixed bed studies were performed in a 115 mm long acrylic column of 75 mm internal diameter (Figure 3). Untreated and polymer-treated materials were used in the column, which gave a packed bed with a pore volume of 211.2 mL and 261.6 mL, respectively. The copper solution was introduced at a constant volumetric flow rate (Q) of 10 mL/min using a peristaltic pump from the bottom of the column to ensure maximum contacting of the solution with the tailing particles and remove the gravity impact on conducting the copper solution through the porous media. The effluent stream was sampled for ICP analysis after each pore volume. By plotting the exit metal concentration versus time (or pore volume PV), the breakthrough curves were obtained.
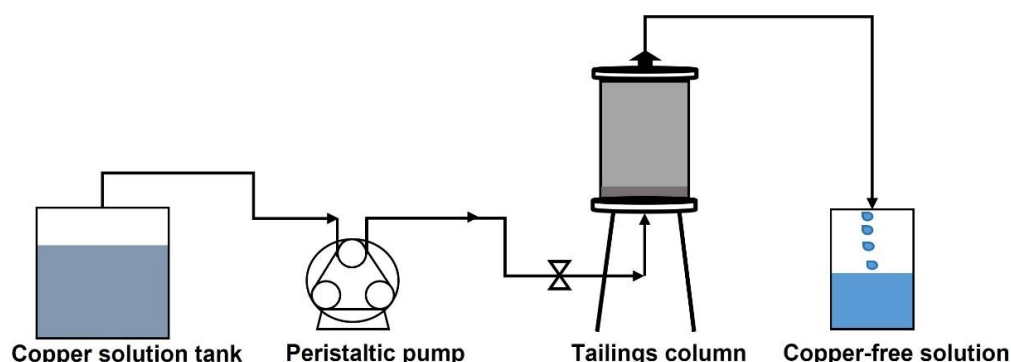

Figure 3. Column leaching sorption experimental setup.

3. Results

3.1. Morphological Structure Characterisations

Cryo-SEM imaging was used to study the effect of polymer addition on the morphological structure of the tailings' particles. Figure 4 compares the morphological structure of untreated and polymer-treated materials in different magnifications through inline flocculation. After adding the polymer, the raw slurry particles were agglomerated and compacted on a configuration that potentially makes the sample with greater porosity as

presented in our previous study that showed polymer addition increased the void ratio, and consequently the saturated hydraulic conductivity, of the materials due to producing a porous structure [37]. The pH of the pore solution during flocculation was in the range of 6.5–7.5 which caused the kaolinite particle edges to be positively charged and particle faces to be negatively charged as shown in previous studies [38]. In this configuration, more positively charged sorption sites would be available for the negatively charged polymers and in the presence of a high concentration of NaCl, the van der Waals forces prevailed in drawing particles towards each other. This, together with hydrogen bonding, allowed more contact opportunities for kaolinite edge and face surfaces to form a combination of edge-to-edge (E-E) and edge-to-face (E-F) forms aggregates in high-salinity water [28].
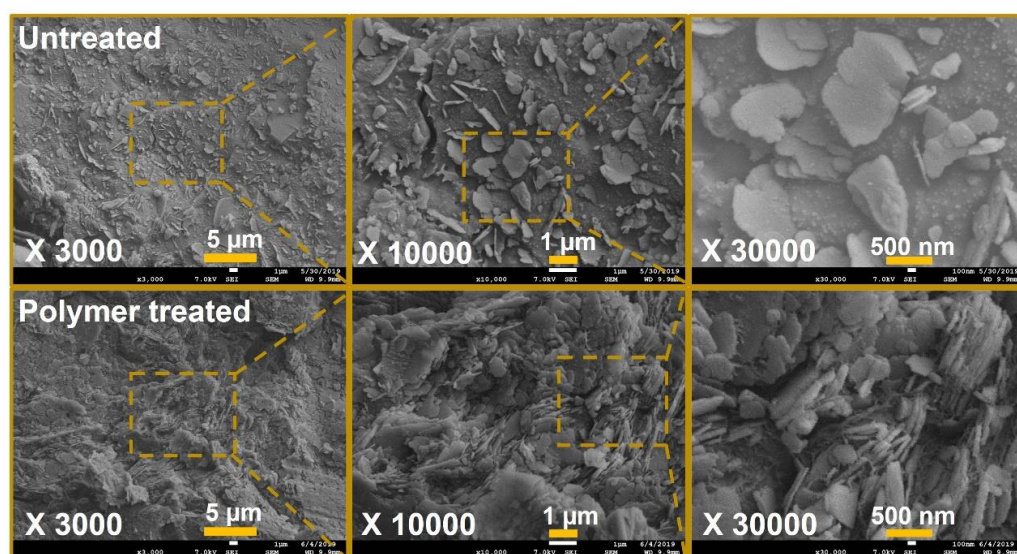

Figure 4. Cryo-SEM imaging of untreated and polymer-treated materials in three different magnifications.

To better understand the morphological structure of untreated and polymer-treated samples, the BET isotherm plots were employed to calculate the specific surface area of tailings before and after polymer addition (Figure 5A,C) [39]. According to the corresponding Barrett–Joyner–Halenda (BJH) pore size distribution curves in Figure 5B,D, the vertical axis (dV/dD) representing the rate of change of pore volume with pore diameter increased with the increasing pore diameter which tended to be flat when the pore diameter approached 450 A°. It seems a significant proportion of the pore areas with diameter less than 50 A° in the untreated sample converted to the larger pores after the polymer addition with the maximum peak around 100–150 A°. It is worth mentioning that the BET testing was done in the same conditions for the UT and PT samples to highlight their differences in structure and pore size distribution and the absolute values do not matter. The calculated sorption percentages for each sample during the designed sorption process are independent of the reported specific surface area measurement of each sample and the interaction of ions with the active sites of the sorbents depends on the applied conditions [40,41].
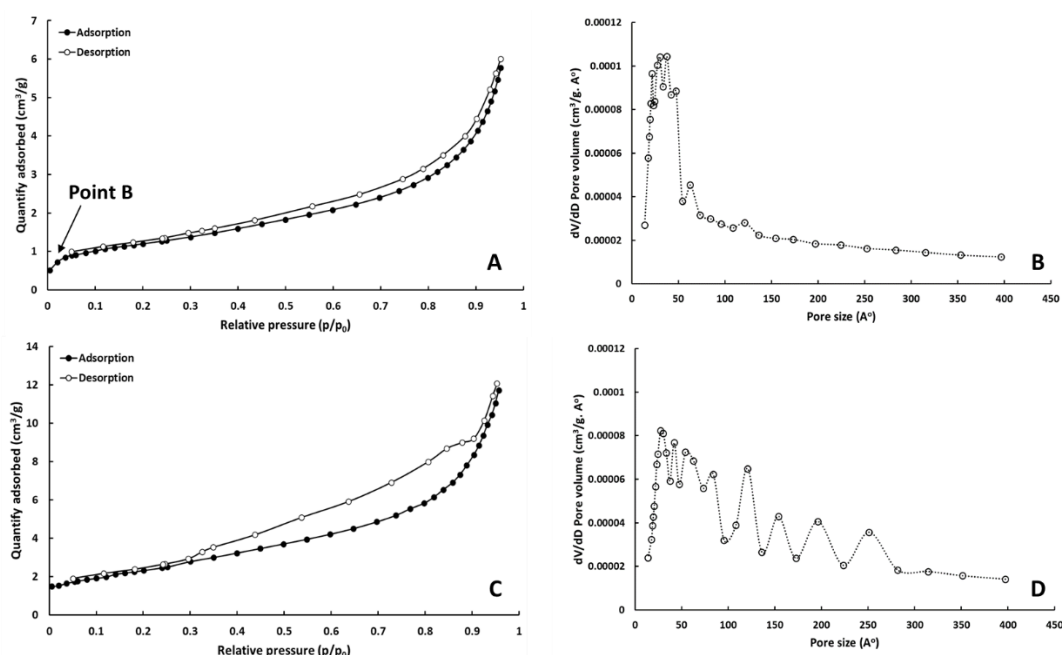
Figure 5. The N_2 gas sorption/desorption isotherm loop for (**A**) untreated and (**C**) polymer-treated tailings plus a histogram of the pore size distribution of (**B**) untreated and (**D**) polymer-treated tailings.

3.2. Sorption Kinetics and Isotherms of Copper Ions

In this study, the pseudo-first-order and pseudo-second-order models were studied to understand the kinetic behaviour of copper ions sorption by UT and PT materials. Figure 6 shows the Cu^{2+} sorption against time for both the untreated and polymer-treated samples with similar trends but a different rate of copper loading on the materials.
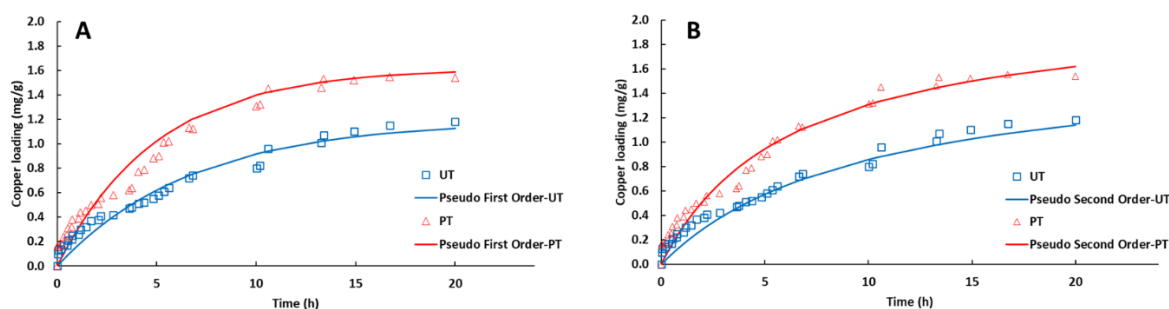

Figure 6. (**A**) Pseudo-first-order and (**B**) pseudo-second-order kinetic models for sorption of copper ions on UT and PT materials.

The copper ions sorption was relatively faster for the polymer-treated sample with over 60% removal during the first 5 h contacting the copper solution with the materials. Similar fast removal of copper ions was also reported in the study of removing heavy metal ions using only kaolinite [42]. The higher sorption degree of both samples at the beginning of the sorption process is because of the higher initial copper concentration, which results in a higher driving force for sorption.

Kinetic constants were verified using NLLS fits of pseudo-first and second-order equations (Equations (5) and (6)) and the calculated constants derived from these models are given in Table 2. From a statistical point-of-view and regression coefficient (R^2) values, the pseudo-first-order fitted the experimental data more accurately for the untreated materials while the pseudo-second-order showed the better fitting on the polymer-treated tailings data.

Table 2. Kinetic constants for the copper ions sorption of untreated and polymer-treated tailings.

Sample	q_{exp} (mg/g)	Pseudo-First-Order				Pseudo-Second-Order			
		q_e (mg/g)	K_1	SNE	R^2	q_e (mg/g)	K_2	SNE	R^2
UT	1.4	1.34	0.14	4.18	0.97	1.85	0.09	3.96	0.93
PT	2.05	1.32	0.18	4.25	0.91	2.12	0.07	4.02	0.98

In addition, Figure 7 presents the equilibrium sorption data with their fitted models that was performed over 24 h (with kinetic data confirming that equilibrium conditions had been reached). Generally, based on the graphs in Figure 7, copper sorption using polymer-treated tailings was found to be beneficial, meaning the sorption of copper ions occurred even at the low equilibrium concentration [43]. Application of Langmuir expression to the equilibrium Cu^{2+} data for untreated and polymer-treated samples is presented in Figure 7A,B, and did not provide a satisfactory fit to the experimental data for both sorbents.
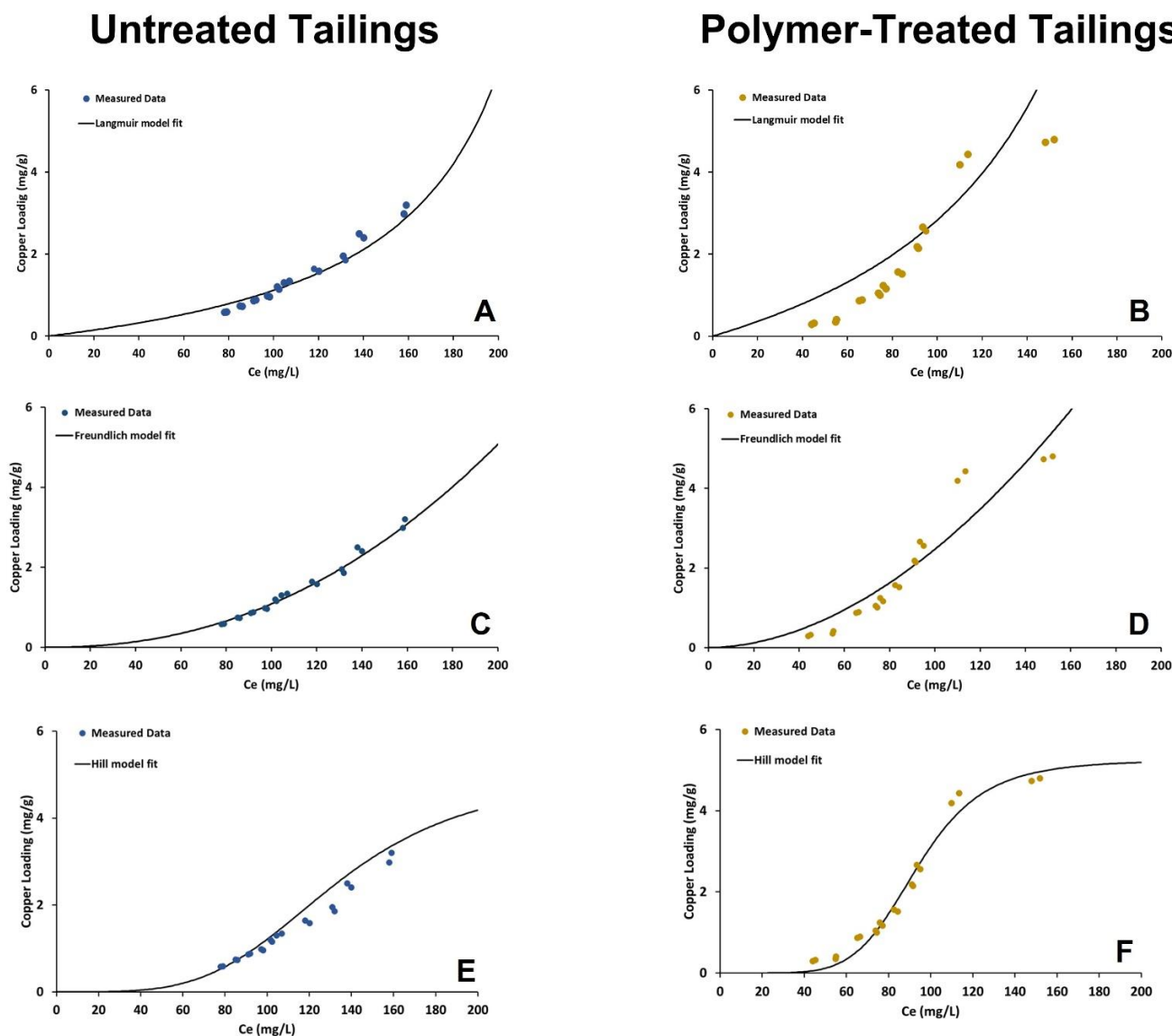

Figure 7. Non-linear least squares (NLLS) model fits for copper ion sorption for untreated and polymer treated materials. (**A**) Langmuir model fit-UT, (**B**) Langmuir model fit-PT, (**C**) Freundlich model fit-UT (**D**) Freundlich model fit-PT, (**E**) Hill model fit-UT, (**F**) Hill model fit-PT.

The Freundlich isotherm only showed good fitting to the sorption data of copper exchange (Figure 7C) with untreated tailings with the maximum copper loading value of 3.43 mg/g. Freundlich model fitted the copper sorption data sufficiently with the Freundlich exponent value of higher than 1 (1.45) which indicates the exchange process between copper ions and the protons on the untreated slurry sites. The model assumption of the heterogeneous surface with not equivalent and independent binding sites was also proven. In contrast, the Freundlich isotherm model was found to be unfavourable for polymer-treated tailings sample (Figure 7D). The empirical factor ($1/n$), which indicates the favourable sorption when sitting within the range of ($0.1 < 1/n < 1$), were 0.67 and 1.9 for the untreated and polymer-treated materials, respectively.

The Hill equation provided a better fitting to the experimental data of copper sorption by polymer-treated sample compared to the untreated sample. Hill equation fitting to equilibrium data of PT sample was satisfactory in the isotherm system at low equilibrium concentrations with R^2 value of 0.98 and maximum copper loading of 5.24 mg/g.

3.3. Effect of Sorbent Mass on Sorption/Desorption of Copper Ions

The sorption and desorption percentage of copper ions on untreated and polymer-treated material are presented in Figure 8. As was expected based on the morphological studies and BET data, the polymer-treated sample having a more porous structure and more active sites for ion exchange of copper ions showed higher percentage of sorption over different masses of sorbent with an increasing trend. In fact, by adding the polymers into the tailings slurry, particularly at high salinity (in our study 0.6 M NaCl), the polymer chains are expected to be more mobile and flexible on the colloidal surface, which allows the restructuring of aggregated clusters to proceed unhindered. This interpretation is consistent with previous research examining aggregate size-density relationships in freshwater and seawater for different MW polymers [44]. This kind of behaviour of the polymer chains in flocculating the tailings particles provides the situation to expose more surface of the minerals to the copper ions during the sorption and ion exchange processes.
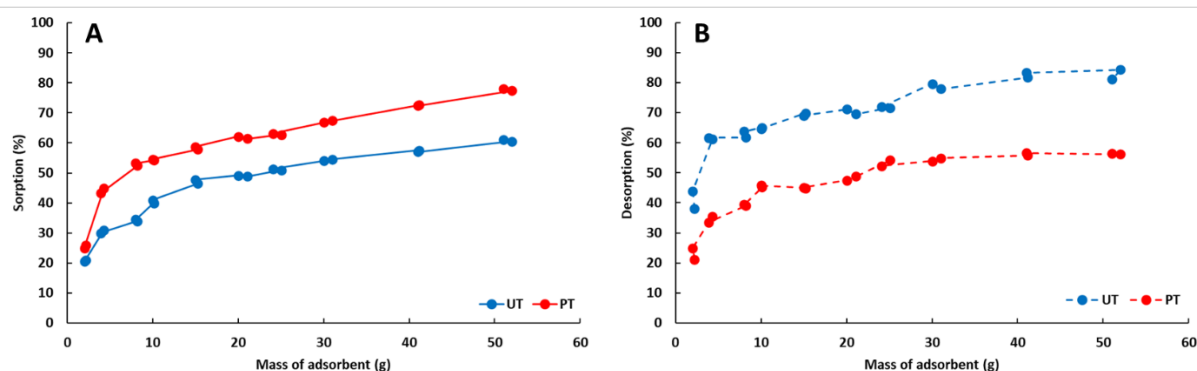

Figure 8. (**A**) Sorption and (**B**) desorption percentage for untreated and polymer treated tailings.

In contrast, the desorption changes by increasing the mass of sorbent of untreated sample was always greater than the polymer-treated sample which indicates that it was hard to desorb the already adsorbed Cu^{2+} on the structure of the polymer treated materials.

The maximum sorption was recorded around 80% at 50 g sorbent sample for the polymer-treated sample in which this amount of the materials at the same condition showed only 56% desorption of copper ions into the DI water. On the other hand, the untreated materials with less capability of copper ion sorption with around 60% removal at the maximum applied sorbent loading (50 g) can readily release the adsorbed ions back into solution (81% after 24 h). This was indicative of the weak binding between the copper ions and active sites of the untreated sample particles and less capability of this material for preserving the adsorbed heavy metal ions within their loosely coagulated structure. In fact, having the constant concentration of metal ions and increasing the mass of the

sorbent is like the situation in which the mass of sorbent is constant, and the metal ions concentration is reducing [45]. By increasing the mass of sorbent, the available surface and porous sites to adsorb Cu^{2+} are increasing which contributed to enhancing the driving force at the solid–liquid interface to increase the sorption capacity until the sorbent reached its maximum capacity and plateaued in the removal percentage graphs, similar to what was presented in previous studies and is consistent with the results in Figure 8 [46,47]. It is worth acknowledging the impact of the polymer itself and without the clay materials on the removal of copper ions that was conducted in a separated study and not included here. Therefore, it is a combination of the tailings particles and the polymer impacts that provide conditions in which the copper ions removal will be improved by having more exposure to the polymer-treated material compared to the untreated sample.

3.4. Effect of the Solution pH on Sorption/Desorption of Copper Ions

Changes in pH may alter the surface charges of the sorbents and the behaviour of the metal ions, so the water pH is widely recognised as an important element affecting the sorption properties of heavy metal ions in aquatic conditions [48]. In this study, the sorption and desorption performance of Cu^{2+} onto the untreated and polymer-treated tailings significantly changed with variation of the solution pH (Figure 9). A substantial increase in sorption percentage was observed for both the untreated and polymer-treated samples by increasing the pH with greater impact for the polymer treated sample up to 98% removal at the maximum applied pH. It is suggested that by increasing the pH, electrostatic interactions might engage in important roles in the sorption of Cu^{2+} onto tailings particles [49]. In fact, by deprotonation of functional groups of the sorbents, the formation of the first-order $CuOH^{+}$ species are increased, which are known to be more surface active than the original Cu^{2+} ions and thus adsorb more readily than Cu^{2+} ions and improve the final adsorbed copper ions from the solution.
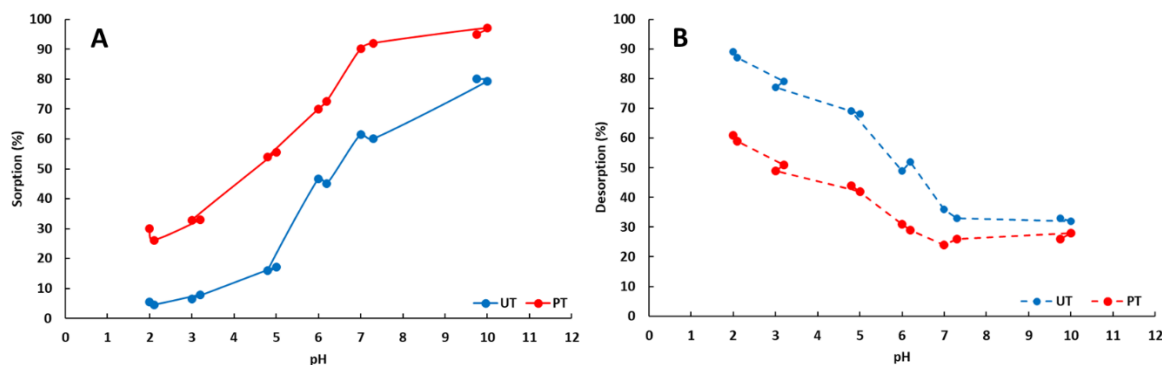

Figure 9. Effect of pH on (**A**) sorption and (**B**) desorption of copper ions on untreated and polymer-treated tailings.

The precipitation of the copper ions onto the surface of the materials was more intense during the desorption process where the increase of the pH resulted in a lower desorption rate of the copper ions into the solution for both samples. For the desorption changes over different pH ranges, opposite to the sorption process, the maximum rate of the desorption was recorded for both samples at lower pH values and was less for the polymer-treated sample, once again demonstrating that the adsorbed copper ions were hard to release. Then, by increasing the pH, the desorption percentage considerably reduced to less than 40% and the two curves tended to converge close to each other.

3.5. Column Leaching Experiments

Batch approach procedure studies have some restrictions and suffer from some undesirable issues such as limited treatment volume [50]. Therefore, sorption of copper ions by untreated and polymer-treated materials was conducted in continuous column experiments

and the results are shown in breakthrough curves (Figure 10). As can be seen, untreated and polymer-treated materials performed differently towards Cu^{2+} sorption. The breakthrough happened after 2 PV (pore volume) and 5 PV for untreated and polymer-treated materials, respectively. The concentration of Cu^{2+} at the breakthrough point was found to be 40 mg/L for untreated tailings and for the polymer-treated sample, it was 16 mg/L. Breakthrough concentration can be shown as the minimum detectable or maximum allowable solute concentration in the effluent. As the process advanced for the PT sample, a continuing rise in Cu^{2+} concentration was seen for 15 PV until the saturation point, which took more time compared to the UT sample as the copper ions needed more time to permeate into the porous structure of the PT sample and it took a longer time to get the sorption saturation.
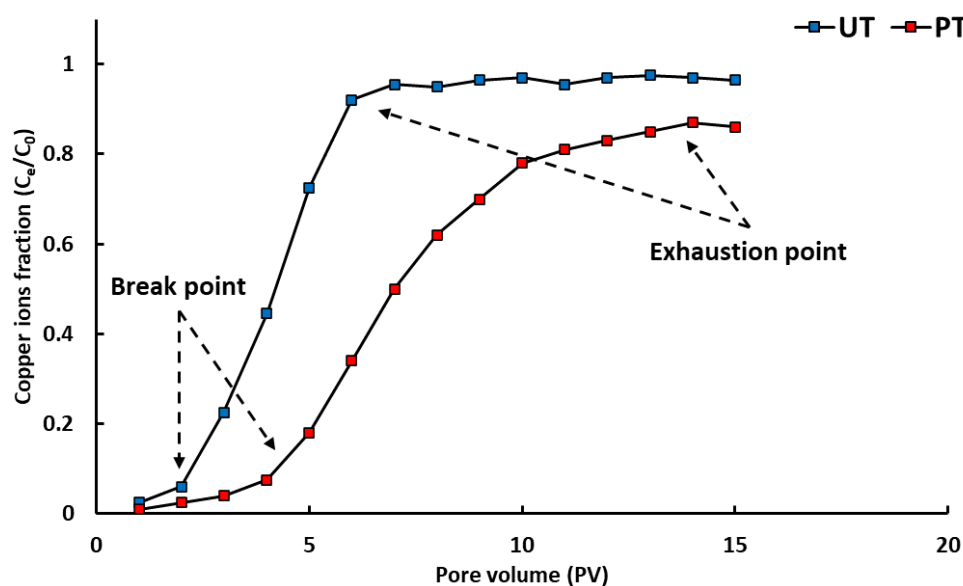

Figure 10. Breakthrough profile for untreated and polymer-treated tailings while treating the copper ions solution (200 ppm).

4. Discussion

In flocculation of mineral particles by inline polymer addition at high dosages, the particles are often bound with suitable cation sorption sites. The highly saline conditions applied in this study (0.6 M NaCl) have practical significance for mineral processing plants utilising seawater in different operations, with mineral surfaces being aggregated through covalent bonding or salt linkages between the anionic groups (e.g., carboxylate) on the polymer chain [22]. Hydrogen bonding may also occur between the polymer's amide groups and OH groups at the mineral surfaces. The resultant highly flocculated clay structures, as presented in the Cryo-SEM images and BET data in Section 3.1, provide further mesoporous media with greater internal voids that can be favourable for sorption of metal ions similar to other applicable mineral materials that are used for the heavy metal ions removal such as copper ions [43,48,51,52]. Moreover, in the presence of high salt, the polymer chains are expected to be more mobile and flexible on the colloidal surface, which allows the unhindered restructuring of aggregated clusters and more contacts with the metal ions to make a new binding to different sorption sites on the mineral particles.

According to IUPAC (International Union of Pure and Applied Chemistry) classification, the sorption-desorption isotherm of untreated materials can be assigned to the combination of Type II and Type III hysteresis while the polymer-treated materials behaviour only followed the Type III hysteresis model [39]. Type II isotherms are assumed by the physisorption on nonporous surfaces and the shape of the graph is related to the unrestricted monolayer-multilayer sorption up to higher p/p_0 values.

Based on the sorption conditions, the copper ions removal from the solution could have happened through the ion exchange with the cations on the tailings particles or

via the chemical sorption and establishing bounds with the active sites on the surface of the particles or aggregates [47]. If the first chemical sorption layer begins, then due to surrounding effects such as the ion strength from the existed salts in the system or other minerals forces in the slurry, further layers are formed particularly in case of the polymer-treated sample where polymers chains are more flexible for affecting the sorption mechanism by their functional groups elements [53,54].

In the case of a Type III isotherm, there is no Point B (the PT data in Figure 5C) and consequently no detectable monolayer formation and the adsorbed molecules are clustered around the most favourable sites on the surface of a macro-porous solid [55]. The hysteresis loop on the N_2 gas sorption-desorption isotherm occurred in the range of 0.5 to 1.0 P/P_0 which is greater for the polymer-treated sample, implying the presence of more mesopores [56,57].

To understand the dynamic interactions of metal ions in the solution with solid phases and to predict their variation with time, knowledge of the kinetics of these processes is important [33]. Many researchers have linked the fitting of kinetic data to a specific model as an indication of the type of the sorption process to be either chemisorption or physisorption [58–60]. Table 2 showed that the regression coefficient for pseudo-first-order model of the polymer-treated tailings is low and the projected values of q_e was not reasonably close to experimental q_e values compared to that of untreated slurry, suggesting the insufficiency of pseudo-first-order model to fit the kinetic data of polymer-treated sample. On the other hand, the R^2 values for the pseudo-second-order kinetic model are nearly equal to 1 and the predicted values of q_e are comparable to the experimental ones for the polymer-treated sample compared to that of untreated sample. This implies that the sorption of copper ions onto the polymer treated materials is most likely a chemisorption process involving exchange or allocation of electrons mostly between metal ions and functional groups of the aggregates [61]. Although a simple case (single ion sorption) was studied with a certain concentration of the polymer for creating the aggregates, in presence of the salt, the interaction of the polymers with the minerals surfaces are not simple and provide different options for the copper ions sorption. Interactions of the polymers with mineral surfaces can be expected as a hydrogen bonding of the amide groups to neutral sites, covalent bonding, or salt linkage between the anionic groups. This provides a complex situation and why the kinetic experimental data of PT sample cannot be fitted by pseudo-first-order equation, and it is supposed to be a chemisorption phenomenon.

Regarding the pH impact on the sorption and desorption behaviour of copper ions, the electrostatic interaction between the copper ions and the PT or UT materials determines the extent of attenuation and release of ions. According to Low et al. [62], slight sorption of metal ions at lower pH could be attributed to the hydrogen ions competing with metal ions for exchangeable cations on the surface of the materials. Then, in the pH range from 3 to 7, there is an apparent increase of deprotonation of functional groups, particularly for the polymer-treated sample on the sorbent surface, permitting a change for the better sorption of copper ions [13]. Later, in the pH range from 7 to 10, a significant increase of metal removal is observed for the polymer-treated tailings that might be described by the fact that the sorption sites are no more affected by the pH change. In fact, at a higher pH condition, the copper ions precipitate in the form of $Cu(OH)_2$ and that reduces the rate of sorption observed in both UT and PT samples by reduction of copper ions in the solution after the experiment. This can also be supported by the increasing amount of Na^+ in the solution (attributable to pH adjustment by adding NaOH) which compete with the remaining Cu^{2+} on the exchangeable site. However, in a real situation in which a range of components such as organic flotation agents and other heavy metal ions exist, the selectivity sequence of metal ions by the sorbents varies based on the system employed and mainly depend on the initial concentrations of the metal ions and the pH of the solution (Jiang et al., 2010).

In our previous research on the same artificial tailings that assessed the hydrological properties of the raw slurry and polymer treated materials [37], the addition of polymer altered the physical characteristics of the materials by creating larger macropore volumes to

drain more water easily. This material has higher infiltration rates in comparison with the raw slurry, which contains finer particles. Practically, addition of the polymer transforms some microporous media to a macroporous structure with the creation of new flow paths allowing the rapid drainage of run-off water [63]. These modifications along with the larger aggregated sizes are linked with the hydraulic conductivity and provide conditions to move water through the structure of the tailings differently in favour of contacting more with the aggregates. In addition, high salinity conditions are important due to the sorption of cations on tailings particle surfaces and are potentially beneficial to the inline flocculation process; however, there is a lack of published information available on the likely impacts of high saline process liquors on polymer performance. The demonstration of the inline flocculation technique in our previous study (Boshrouyeh Ghandashtani et al., 2022) has shown that it is possible to produce the desired highly aggregated network of tailings solids on deposition even in the presence of elevated concentrations of dissolved salts. This has practical significance for mineral processing plants utilising seawater or other brines.

The polymer treated materials has greater potential for removing the ions in the column experiments. Signs of faster exhaustion were observed for the untreated sample after around 6 PV with no more changes in the copper ions fractions by continuing the experiment. The fast saturation of untreated materials could also be related to the lower specific surface area which explains fewer active sites of this sorbent compared to the polymer-treated sample. These observations are consistent with the results of the batch experiments and revealed that the untreated slurry with lower capacity of copper ions removal saturated significantly faster when a higher volume of water was treated. By integration of the area under the breakthrough curve, it was found that 11 mg Cu^{2+}/g of PT sample had been loaded onto the sample after treating 15 PV. This value was calculated to be 6.5 mg Cu^{2+}/g of UT for the untreated tailings bed.

Further development of the underlying science is needed to determine whether non-homogeneous aggregate structures formed through inline flocculation can be beneficial for tailings rehabilitation. Polymer-amended tailings with altered permeability and distribution of aerated and water-filled pores that have the properties for controlling the metal ions release may favour vegetation establishment and growth at mine closure. These properties as well as the geochemical stability of the tailings in regard to release of potential contaminants as seepage could provide insights into the long-term processes for mine closure activities and rehabilitation plans.

5. Conclusions

Polymer-amended tailings through the inline flocculation process have the potential capability for the attenuation of the heavy metal ions due to their porous structure and the chemistry of the aggregates to adsorb heavy metal ions. To this end, a comprehensive study was conducted to investigate the attenuation and release of the copper ions by polymer-treated tailings and compare it with the untreated materials. It was found from the batch experiments that the maximum Cu^{2+} ions uptake capacity of polymer-treated tailings was 25% more than the raw untreated slurry at the equilibrium state. In addition, the Hill isotherm model was fitted on the data of the polymer-treated sample and the Freundlich model showed better fitting for the untreated tailings. This finding plus the behaviour of the material in the dynamic sorption study suggested that the copper ions removal using the polymer-treated sample was a chemisorption phenomenon while the sorption process on the untreated tailings was an unfavourable and reversible sorption. In contrast to sorption experiments at different pH, the desorption of copper ions decreased by increasing the pH. It also was seen that the desorption of copper ions was more difficult for the polymer-treated sample compared to that of untreated slurry. Finally, the fixed bed column experiments showed higher sorption capacity for the polymer treated with a slower saturation/exhaustion and greater maximum loading of copper ions. Therefore, based on the results in this study, the inline flocculation technique is a promising method for producing highly aggregated, porous structures suited for attenuation of the copper ions

released into the solution by the weathering of tailings. This could potentially extend into the removal of the heavy metal ions from tailings pore solutions for rehabilitation activities.

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