

2018

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[10.1016/j.heliyon.2018.e00520](https://ro.ecu.edu.au/ecuworkspost2013/4222)

Larsson, M., Nosrati, A., Kaur, S., Wagner, J., Baus, U., & Nydén, M. (2018). Copper removal from acid mine drainage-polluted water using glutaraldehyde-polyethyleneimine modified diatomaceous earth particles. *Heliyon*, 4(2), e00520. Available [here](#)

This Journal Article is posted at Research Online.
<https://ro.ecu.edu.au/ecuworkspost2013/4222>

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Received:
22 June 2017
Revised:
19 October 2017
Accepted:
17 January 2018

Cite as: Mikael Larsson,
Ataollah Nosrati,
Simarpreet Kaur,
Jochen Wagner, Ulf Baus,
Magnus Nydén. Copper
removal from acid mine
drainage-polluted water using
glutaraldehyde-
polyethyleneimine modified
diatomaceous earth particles.
Heliyon 4 (2018) e00520.
doi: [10.1016/j.heliyon.2018.e00520](https://doi.org/10.1016/j.heliyon.2018.e00520)



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Copper removal from acid mine drainage-polluted water using glutaraldehyde-polyethyleneimine modified diatomaceous earth particles

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Abstract

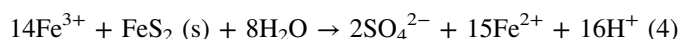
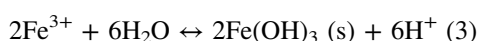
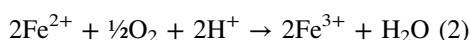
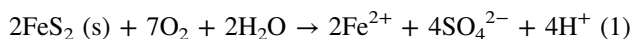
Mine waters and tailings generated from mining and mineral processing activities often have detrimental impact on the local environment. One example is acid mine drainage, in which sulphides in the mining waste react with water and oxygen to produce an acidic environment that subsequently dissolves host rock minerals from the waste containing toxic metals and trace elements. Copper is one such metal of significance, as it is mined at large volumes in sulphide containing ores. It has strong biocidal activity that greatly affects ecosystems. We have previously reported that glutaraldehyde (GA)-crosslinked polyethyleneimine (PEI) has strong affinity and selectivity for copper and that diatomaceous earth (DE) particles can be modified with the material to form a copper-extraction resin. In this study, the copper uptake of GA-PEI-DE particles was investigated from synthetic and real acid mine drainage samples under different pHs and their copper removal performance was compared with that of selected commercial resins. The results

revealed that copper could effectively and preferentially bind to the material at pH 4, and that the copper could be completely eluted by lowering of the pH. In addition, effective copper uptake and elution was demonstrated using real legacy acid mine drainage water from Mount Lyell in Tasmania.

Keywords: Metallurgical engineering, Materials science, Environmental science

1. Introduction

Tailings generated by mining and mineral processing plants account for the largest proportion of global waste from industrial activities [1]. Despite lack of accurate data on the production of mine wastes, some estimations suggest that approximately 20000–25000 million tonnes of solid mine wastes are produced annually around the world [1]. The outflow of acidic water from some mine wastes, known as acid mine drainage (AMD), is one of the unwanted consequences of metal and coal mining activities, creating significant environmental and water quality problems globally [2, 3, 4, 5, 6, 7, 8]. As shown in Equations 1–4, acid drainage occurs naturally in mine waste (e.g., waste rocks and tailings) when residual sulphide minerals such as pyrite (FeS_2) are oxidized in the presence of air (oxygen), water and bacteria to liberate protons (H^+) and thus lower pH [5, 9, 10, 11]. The iron and sulphur oxidizing bacteria are known to catalyse some of these reactions (Eqs. (2), (3) and (4)) at low pH, increasing the rates of reactions by several orders of magnitude [5, 12].



Upon acidification of the water, it can dissolve major constituent elements (e.g., silica, aluminium, iron, magnesium), toxic metals (e.g., copper, lead, cobalt, zinc, cadmium and chromium) and metalloids (e.g., arsenic) from the waste and the contacting rocks, with subsequently release into the surrounding environment; including streams, rivers, ground water, etc. [4, 13]. The discharge of AMD to the environment or its treatment for recycle and reuse is a major economical, technical and environmental challenge faced by most of the mines around the world. For instance, the release of hazardous metals from mine wastes to the environment via acid drainage is a problem that persist long after mining activities have been discontinued [14]. Copper (Cu) is one of those hazardous metals and a key pollutant that often exist in AMD. The acidity and high concentration of dissolved copper makes such AMD toxic to most organisms [14, 15].

To date, a wide range of AMD treatment systems have been developed based on chemical, physical and biological processes, alone or in combination, with systems generally categorised as either “passive” or “active” depending on the process [2, 4, 16, 17]. Examples of processes are: pH control or precipitation, adsorption or absorption, electrochemical concentration, flocculation/filtration/settling, biological mediation, redox control (sulphate reduction), ion exchange and crystallisation [2, 17, 18, 19]. The main difference between these treatment systems is their ability in handling the acidity, flow rate and acidity load (i.e., the product of acidity and flow rate) of the influent AMD [2]. In both passive and active systems, pH control with cost-effective neutralisation reagents (e.g., limestone, pervious concrete) is the most common and low-cost process used [11, 20].

Despite extensive studies on development of different technologies for AMD treatment, AMD still remains a major challenge to the mining industry and the environment due to its significant economic and long-term environmental impacts [2, 6, 15]. For instance, mining activities in general and AMD specifically is one of the most common causes of metal pollution in freshwater. A few examples of environments close to mine sites that are polluted with copper are the Mt Lyell mining area in Tasmania [21], Tsumeb smelter complex in Namibia and Lo Aguirre Mine in Chile [22], the Poura Gold mine in West Africa [23] Katanga, a mining area of the Democratic Republic of Congo [7, 8] and Ingaldhal copper mine in India [24].

Amongst different methods developed for removal of hazardous metals from polluted natural water or industrial wastewater during the last few decades, adsorption is one the most widely used, mainly due to low cost and being environmentally friendly [25, 26, 27]. This might explain why many recent studies have focused on developing new and novel adsorbents such as ion exchange resins [17], activated carbon [28], clay minerals [29] and zeolites [27].

A review of the literature indicates that significant attention and interest is directed towards the issue of copper pollution in water, and many studies have focused on development of new materials and adsorption-based methods to address this challenge [30, 31, 32, 33, 34, 35]. For example, Ahmadi et al. incorporated a natural product yersiniabactin (Ybt) into a resin within a packed-bed column prototype to selectively remove copper from water samples [30]. Ghaemi fabricated polymeric nanocomposite membranes using polyethersulfone (PES) and alumina (Al_2O_3) nanoparticles and investigated the membranes and their application for copper ion removal from water [31]. It was shown that the ability of alumina nanoparticles to adsorb dissolved metals could improve the copper removal efficiency of PES membranes. Gupta and Gogate studied the application of activated watermelon shell-based biosorbent for the removal of copper from aqueous solutions [32]. They concluded that this new biosorbent can be used as an

environmentally friendly, low cost and highly efficient material for efficient copper removal from water. Rabiul Awual investigated the effectiveness of ligand supported mesoporous silica as conjugate nanomaterials for detection and removal of copper ions from polluted waters [34]. His results suggested that the conjugate nanomaterials could be readily applied to environmental samples for Cu(II) ion remediation. Rikame et al. synthesized a composite cation exchange membrane by phosphorylation of fullerene/sulfonated polyvinyl alcohol (SPVA) and tested its application for removal of copper ions from wastewater [35]. Their synthesized composite membrane showed 10% greater Cu^{2+} removal from water compared with a commercial membrane known as Ultrex.

Despite development of numerous new materials and adsorption-based methods for copper removal from different aqueous systems, most of them face intractable challenges such as high cost, poor selectivity and low copper removal capacity and efficiency. Such limitations make them unsuitable and economically nonviable for large-scale mining applications including AMD treatment. Of interest to this study is the copper pollution of freshwater due to mining activities and the pressing need to develop new, efficient and cost-effective adsorbents for copper removal and value adding selective recovery from such polluted waters. We recently reported that glutaraldehyde (GA)-crosslinked polyethyleneimine (PEI) presented very high affinity and selectivity towards dissolved copper in seawater with pH of 8.1–8.3 [36, 37, 38] and showed that the copper binding was largely unaffected by adsorbed polysaccharides or EDTA as a competing ligand [39]. We further demonstrated that cheap diatomaceous earth (DE) particles could be readily modified with GA-PEI through a feasible self-assembly process to prepare a copper binding resin that could remove copper from saline and non-saline mining-relevant aqueous solutions [38, 40]. The resulting PEI-GA-DE particles have strong affinity towards copper compared to several other metals at pH 3.5–4 [40]. Importantly, the modification is extremely stable so that the bound copper can be eluted under acidic conditions and the particles reused over many cycles [38, 40]. Although the results are promising, the performance of the PEI-GA-DE particles in solutions with pH relevant to AMD and large excess of other metals during the binding remains to be reported on.

The main aim of this paper is to further characterize the copper binding of the GA-PEI-DE particles and investigate the removal and selective recovery of copper from AMD-polluted freshwater. To achieve this goal, PEI-GA-DE particles were investigated for extraction of copper from model solutions relevant to AMD and the performance was demonstrated in real solution from the Mt Lyell area in Tasmania. Specifically, the copper uptake and elution behaviour of GA-PEI-DE particles from synthetic and real AMD under different conditions was determined and the results were compared with those obtained from commercial resins; Metcap 1, Lewatite TP 220, Purolite S930+ and Purolite S985.

2. Materials and methods

2.1. Materials

Commercial fine DE powder was supplied by Diatomaceous Earth Online and has been previously characterized [40]. Sulphuric acid (98 wt.%) was bought from Scharlau Chemie, branched PEI (Lupasol HF; Manufacturer specifications: MW = 25000 g/mol; primary:secondary:tertiary amines = 1:1:0.7) was provided by BASF and GA (25% in H₂O; Grade II) was bought from Sigma-Aldrich. The following metal salts were used to prepare metal solutions: Aluminium Chloride Hexahydrate (Sigma-Aldrich; Reagent Plus), Cadmium Nitrate Tetrahydrate (Sigma-Aldrich; Purum), Copper Sulphate Pentahydrate (Chem-Supply; Analytical Reagent), Iron (II) Sulphate Heptahydrate (Sigma-Aldrich; ACS reagent), Lead(II) Nitrate (May & Baker; ≥ 99%), Nickel(II) Nitrate Hexahydrate (Sigma-Aldrich; Puriss) and Zinc (II) Chloride (Scharlau; Reagent grade). Water used was of Milli-Q grade. Water containing legacy acid mine drainage (AMD) from previous operations was kindly provided by Copper Mines of Tasmania.

2.2. Preparation of PEI-GA-DE particles

Mesoporous DE particles were surface modified with GA-crosslinked PEI as previously reported [40], with slight differences in the protocol indicated. Briefly, the DE particles were treated with concentrated sulphuric acid at 100 °C, followed by thorough washing with Milli-Q water and drying at 100 °C. Subsequently, DE particles and PEI were mixed with 450 g of 0.5 mol/L NaCl solution for final concentrations of 10 wt% and 1 wt%, respectively. The pH was set to 9 and the dispersion was mixed for 30 min using a magnetic stirrer, the ultrasonication step was excluded. Particles were separated from solution and washed with Milli-Q water, after which GA-crosslinking was performed by dispersion in 450 ml of 0.5% GA solution and mixing for 30 min using magnetic stirrer. Finally, the particles were washed 1X with Milli-Q water, 2X with pH 1 H₂SO₄ solution and 2X with Milli-Q water, followed by drying over night at 80 °C.

2.3. Confirmation of surface modification

Successful surface modification was confirmed using thermo-gravimetric analysis (TGA) on a Discovery TGA (TA Instruments). Acid washed DE particles and PEI-GA-DE particles were analysed in the temperature range 25–550 °C. Two measurements were conducted for both DE and PEI-GA-DE particles and the weight loss for acid treated DE particles was subtracted from that of the PEI-GA-DE particles in all four combinations. Subsequently, wt% PEI-GA material was calculated from the weight change between 100–550 °C.

2.4. Scanning electron microscopy, focused ion beam etching and EDX analysis

Samples for SEM and Energy-dispersive X-ray spectroscopy (EDX) analyses were prepared by spreading out a drop of Milli-Q water with dispersed particles on a conductive carbon sticker on top of an SEM stub, followed by drying at room temperature. SEM imaging of gold sputtered (ca. 2 nm) powders were conducted using a Carl Zeiss Microscopy Merlin SEM with a GEMINI II Column and an Everhart-Thornley secondary electron detector, operated at 2 kV in high-resolution column mode. For determination of copper distribution within a single particle 0.05 g of PEI-GA-De particles were dispersed in 30 ml of 50 mg/L copper solution in 50 ml falcon tubes and the pH of the solution was set to 4 using H₂SO₄ and NaOH. The particles were agitated for 24 h to ensure equilibrium copper uptake had been achieved and were washed 5X by separating them from the solution through centrifugation (as described above) and redisperse them in Milli-Q water. Finally, the particles were dried at about 60 °C and were stored in a desiccator until analysis. Generation of a cross section was carried out by dual-beam FIB/SEM (FEI Helios Nanolab 600). A layer of platinum (20 nm) was deposited on samples to protect the surface during selective etching. Etching of the target area was performed under vacuum using a high-energy gallium ion beam and real-time monitoring in both electron and ion beam. High current (21 nA at 30 KV) was used for rough etching, followed by gentle polishing with subsequent low currents (6.5 nA, 2.8 nA, 0.92 nA, 0.28 nA and 93 pA at 30KV). Distribution of copper at the surface and over the cross section of an etched particle was determined through EDX (EDAX) integrated in the FIB-SEM (FEI Helios NanoLabTM 600 DualBeam).

2.5. Metal extraction

Metal extraction tests were conducted as follows: Requisite amounts of Al, Cd, Cu, Fe, Pb, Ni and Zn were mixed in pH 1 aqueous solutions from the salts listed in section 2.1 to achieve concentrations in the range 50–500 mg/L. The pH was set with HCl or H₂SO₄. Uptake of metals by PEI-GA-DE particles was investigated using two methodologies. To investigate binding as a function of pH, 50 ml of metal solution was added to a beaker with and without 0.94 g PEI-GA-DE particles. Under stirring the pH was varied from 1 to 5 using NaOH and HCl. At each selected pH, the solution was equilibrated for >2 min and a 2–3 ml sample was extracted for analysis of metal content. The extracted solution was filtered through a 0.45 µm PTFE filter. For uptake at a fixed pH, PEI-GA-DE particles (0.19 g unless otherwise indicated) were added to 50 ml centrifuge Falcon tubes, followed by addition of 10 ml of metal solution, with or without pre-centrifugation of the solution at pH 4 using 4000 rpm for 5 min using a Sigma 4–16 K centrifuge. The desired pH was subsequently set using NaOH and H₂SO₄, after which the

dispersions were mixed for about 5 min on a dispersion mixer. Subsequently, the samples were centrifuged at 4000 rpm for 5 min and one ml was extracted for analysis of metal content. The total time between finalizing the pH and starting the centrifugation was >20 min. After centrifugation, the pellet was washed twice by re-dispersion and mixing for 5 min in 30 ml Milli-Q water, with the pH either unadjusted or set to 4 with NaOH and H₂SO₄, followed by centrifugation at 4000 rpm for 5 min. Subsequently, copper was eluted by re-dispersing the samples in pH 1 solution, with the pH set with NaOH and H₂SO₄, and one ml was collected for analysis of metal content.

Copper uptake kinetics was investigated by dispersing 0.51 g of PEI-GA-DE particles in 100 ml of 50 mg/L copper solution in MQ water under constant agitation using an overhead stirrer, with the pH of the solution set to 4.0 using NaOH. Over 24 h samples were extracted at predetermined times and filtered through a 0.45 µm PTFE to separate free from particle-bound copper. Subsequently, 434 microliters of the sample were mixed with 2560 microliters of 0.1% polyethyleneimine solution. The absorbance of the resulting UV-vis-active copper-PEI complexes was determined at 275 nm using a Varian Cary 300 Bio UV/Vis spectrometer and a quartz cuvette. The copper concentration was determined through comparison with a standard curve generated from samples with known copper concentrations within the investigated concentration interval.

2.6. Determination of metal concentrations

From samples extracted for determination of metal concentrations, 1 ml was diluted 50X with Milli-Q water and 3–6 drops of TraceSELECT grade HNO₃ (Sigma-Aldrich) were added. Metal content of samples was analysed from three readings using induction-coupled plasma optical emission spectroscopy (ICP-OES; Perkin Elmer ICP-OES Optima 7300DV). All results were processed with MSF (Multicomponent Spectral Fitting). Calibration standards and QC standards were prepared in 1% HNO₃. To achieve good reproducibility of results, all measurements and analyses were replicated three times and the pure errors determined and reported at 95% confidence interval. It is worth noting that most of error bars shown for data points in Figures may not be easily seen due to their small values.

3. Results and discussion

3.1. Preparation of PEI-GA-DE particles and confirmation of surface modification

Fig. 1 shows a typical SEM image of the surface modified DE particles. SEM analysis confirmed that the DE powder contained a mixture of intact particles and particle fragments and that the structural content was similar before and after the

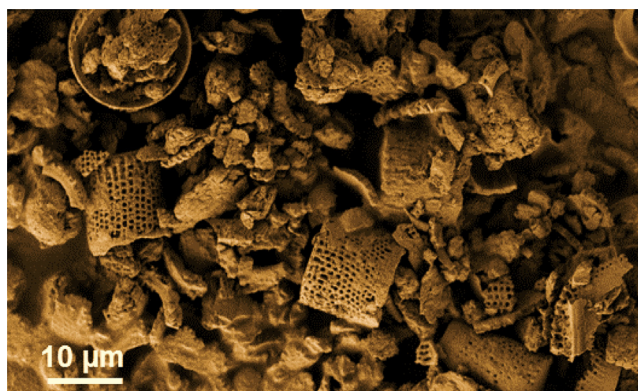


Fig. 1. SEM image of PEI-GA-DE powder.

modification, in line with previous report [40]. The successful preparation of the PEI-GA-DE particles was confirmed visually by colour change from grey to red-brown. The mass of PEI-GA on the particles was determined by TGA to $6 \text{ wt}\% \pm 0.5$ (min/max from mean, $n = 2$). See Fig. 2 for exemplifying TGA-thermogram.

3.2. Single metal binding and precipitation as function of pH

Determination of metal precipitation and metal binding by PEI-GA-DE as a function of pH was critical for three reasons: (i) The quantification of metal bound to the particles relied on separation between solid and dissolved material, thus it was needed to be able to ascribe reduction in dissolved metal content to precipitation or binding to the PEI-GA-DE at each pH. (ii) Taking into account that the extent of Cu removal by surface modified DE particles (PEI-GA-DE) is strongly pH dependent and higher pH is needed for more effective Cu removal, and

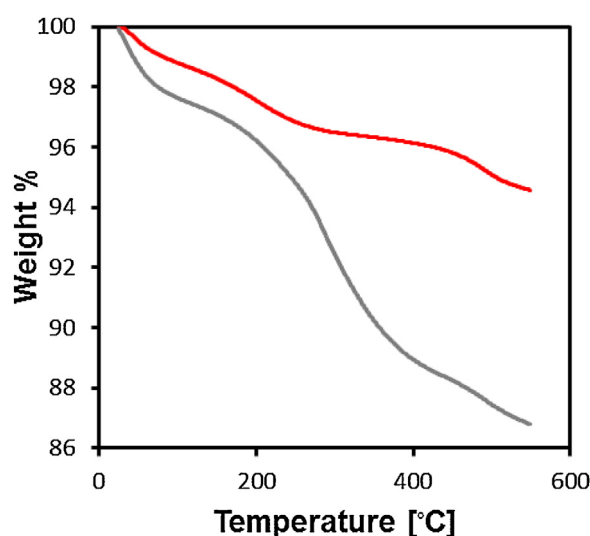


Fig. 2. Exemplifying thermogram of DE (Red) and PEI-GA-DE (Grey) particles.

AMD is acidic and increase of pH for copper extraction is associated with a process cost, it is important to better understand the Cu removal performance of the particles at different pH. (iii) Value could be generated from a copper extraction process by selective extraction of copper and subsequent elution by lowering of the pH, forming purified copper solutions. However, precipitated metal hydroxides formed during Cu extraction process will also be dissolved under acidic conditions, resulting in mixed metal solutions.

The metal precipitation and binding performance of the PEI-GA-DE particles was initially determined between pH 1–5 for solutions of individual metals at about 50 mg/L, with and without PEI-GA-DE. The results revealed that in the absence of PEI-GA-DE, all metals except iron largely remained in solution through the pH interval. However, for iron the amount that remained in solution started to decrease already at pH 2 (Fig. 3a). The removal of iron cations ($\text{Fe}^{2+}/\text{Fe}^{3+}$) from the solution upon pH increase was evidently caused by their hydrolysis and precipitation of hydrolysis products (e.g., ferric hydroxide) [41], reflecting the colour change from clear to yellow and formation of rust coloured flakes [42]. The somewhat uneven trend in iron concentration after filtration at different pH was likely due to variations in capture of the formed aggregates by the filter.

In the presence of PEI-GA-DE particles, the copper concentration started to decrease already at pH 2, at pH 3 only 9% remained in solution, and at pH 4 and 5 $\leq 1\%$ of the copper remained in solution. The amount of iron remaining in solution started to decrease notably from pH 3 in the presence of the PEI-GA-DE particles, and at pH 4 and 5 the remaining fraction was 16% and 2.8%, respectively. The higher Fe removal observed in the presence of the PEI-GA-DE particles is attributed to the availability of their large surface area (substrate) with polycationic

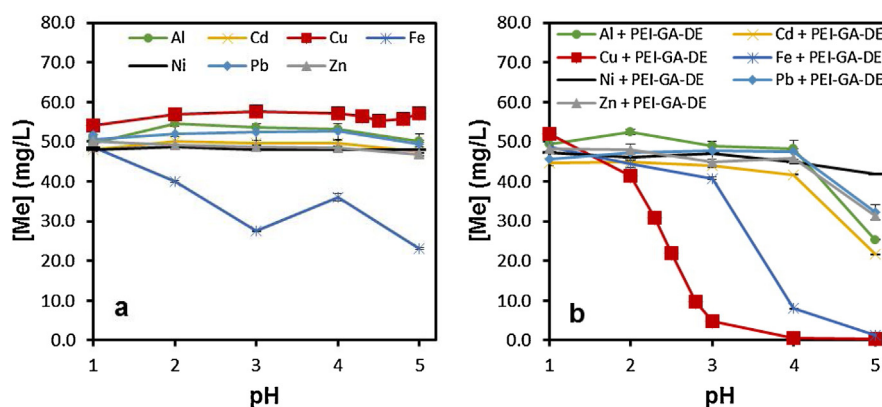


Fig. 3. Metal remaining in single-metal solutions (initially about 50 mg/L) after filtration through a 450 nm filter at different pH in the absence (a) and presence of 19 mg/ml of PEI-GA-DE particles (b). The pH was set from low to high using HCl and NaOH solutions. Error bars indicate one standard deviation between measurements ($n = 3$). Colour figures are available online.

character leading to localized high pH and hence, enhanced nucleation and precipitation rate of Fe(III) hydrolysis products [43, 44]. For other metals, no noticeable change in solution concentration was detected in the pH range 1–4. At pH 5 only a slight decrease was detected for nickel, while for lead, zinc, aluminium and cadmium the remaining fractions were 62%, 62%, 49% and 44%, respectively (Fig. 3b).

From the amounts metals remaining in solution after filtration at different pHs, in the absence and presence of particles, it was concluded that for individual metals at concentrations of 50 mg/L, precipitation was a concern only for iron. Furthermore, the PEI-GA-DE particles bound copper the most effectively, with excellent removal at pH 4 or higher. Iron was notably precipitated in the presence of the particles at pH 4 and 5, while for the other metals only about 40–60 percent was bound to the particles at pH 5. Although the experiments using solutions of individual metals are informative, real world applications will involve solutions containing mixtures of metals, with copper often being in minority. For example, in the Mt Lyell AMD copper is present in concentrations on the order of 10s of mg/L, with iron and aluminium being present at more than 10-fold and 3-fold amounts, respectively.

3.3. Binding and precipitation from metal mixtures

To further evaluate the PEI-GA-DE particles towards extraction of copper from AMD, tests were conducted using metal mixtures containing about 50 mg/L copper and 500 mg/L each of aluminium, cadmium, iron, lead, nickel and zinc. After preparation of the solution at pH 1, a white precipitate was observed. This was attributed to precipitation of lead since all metals except for lead remained in the solution at their prepared concentrations, as determined by ICP-OES after filtration. For lead, a small decrease in solution concentration was observed immediately after preparation and after 4 days of storage the concentration had dropped by more than 50%.

In the absence of PEI-GA-DE particles, copper remained in solution through the investigated pH range. For nickel and zinc, about 30% decrease in concentrations were observed after filtration at pH 5. The concentration of lead initially decreased between the preparation and initial filtration at pH 1. During the experiment, the lead concentration remained stable until pH 5, at which further decrease in concentration was observed after filtration. A larger fraction of the iron remained in solution compared to the single-metal experiment at 50 mg/L. The noticeable decrease in iron concentration after filtration started at pH 4, and at pH 5 about 60% remained in the solution. Aluminium remained in solution for pHs 1–4, but at pH 5 the concentration after filtration abruptly decreased by about 60% (Fig. 4a).

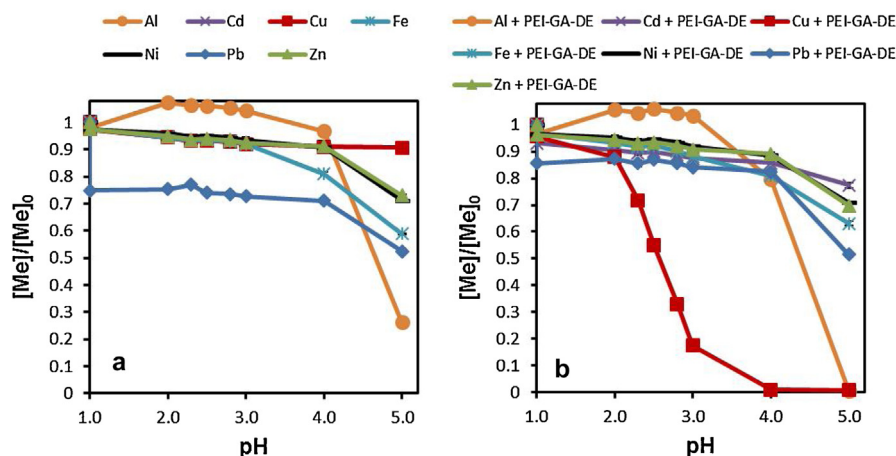


Fig. 4. Initial to final metals ratios for mixed-metal solution (initial concentrations: copper ≈ 50 mg/L; other metals ≈ 500 mg/L) after filtration through a 450 nm filter at different pH in the absence (a) and presence (b) of 19 mg/ml of PEI-GA-DE particles. The pH was set from low to high using HCl and NaOH solutions. Error bars indicate one standard deviation between measurements ($n = 3$). Colour figures are available online.

From the experiments in the presence of PEI-GA-DE particles, it was clear that copper was bound to the particles, while most of the other metals behaved similarly in the presence and absence of the PEI-GA-DE (Fig. 4b). The concentration of copper after filtration started to decrease at pH 2. At pH 3 only about 20% remained in solution after filtration, at pH 4 only 1% remained in the solution and at pH 5 this was reduced to $<1\%$. For aluminium, a small decrease in concentration after filtration occurred at pH 4 and at pH 5 the aluminium concentration was also reduced to $<1\%$, in contrast to the 40% observed in the absence of PEI-GA-DE. A small decrease in the concentration of cadmium, that was not observed in absence of PEI-GA-DE, was also noted at pH 5. Based on the results, it was concluded that the PEI-GA-DE particles effectively bound copper also in the presence of 10-fold excess of several other AMD-relevant hazardous metals. It was decided to use pH 4 for further copper-removal experiments, allowing for strong copper binding while minimizing competitive binding of other metals.

3.4. Copper uptake kinetics, distribution, capacity and Langmuir binding constant

It has previously been reported that the copper uptake of the PEI-GA-DE particles is completed in <3 min when particles are in excess compared to copper [40]. To complement those experiments, we here investigated the adsorption kinetics at pH 4 in a 50 mg/L copper sulphate solution, with copper in excess with regard to the estimated binding capacity of the particles based on PEI-GA content from TGA results and our previous publications on copper binding of PEI-GA in aqueous media [38, 39, 40]. An amount of particles (0.51 g), estimated to bind only a part

of the copper, was added to 100 ml of 50 mg/L copper sulphate solution in MQ water. The concentration of unbound copper was determined over 24 h through UV-vis analysis. As seen in Fig. 5, the concentration of unbound copper decreased with time, from the initial 50 mg/L to equilibrate at around 30 mg/L. After 6 min, the particles had already reached 87% of their copper binding capacity and after 15 min they were saturated with copper.

To get detailed information on the copper binding capacity and affinity of PEI-GA-DE at pH 4, different amounts of particles were added to a fixed volume of 50 mg/L copper solution, after which particles with bound copper were separated from solution by centrifugation. The amount of bound copper was determined as a function of particle amount, with the results presented in Fig. 6a. If adsorption followed the Langmuir model it should be described by Eq. (5) [45]:

$$\frac{C_f}{q} = \frac{1}{bq_{max}} + \frac{C_f}{q_{max}} \quad (5)$$

Where C_f is the final concentration of the sorbate in solution, q is the mass of adsorbed sorbate per mass of sorbent, q_{max} is the maximum mass of sorbate per mass of sorbent (capacity) and b is an affinity coefficient. A plot of C_f/q against C_f should give a dependence with slope = $1/q_{max}$ and intercept = $1/(bq_{max})$. As seen in Fig. 6b, the data was well described by the Langmuir model with q_{max} and b being determined to 5.4 mg/g and 0.53 L/mg, respectively. To ensure that the DE particles themselves did not bind copper with any significance, 0.18 g of DE particles were mixed with 10 ml of 50 mg/L copper solution at pH 4. After the binding procedure and separation of particles the copper concentration remained

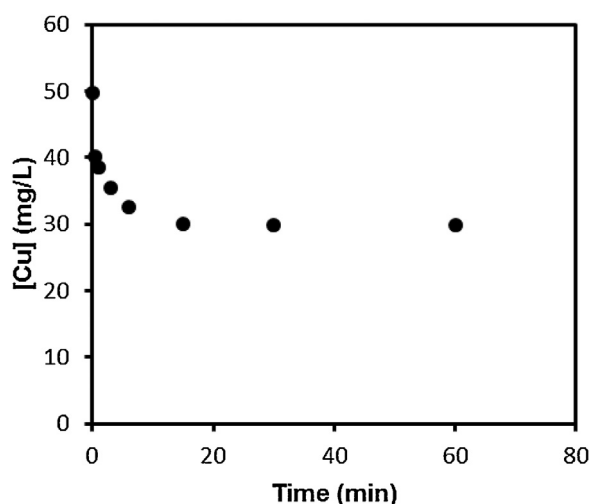


Fig. 5. Copper uptake kinetics from 100 ml, pH 4, 50 mg/L copper solution (copper sulphate) by 0.51 g of PEI-GA-DE particles, as determined by a UV-vis assay.

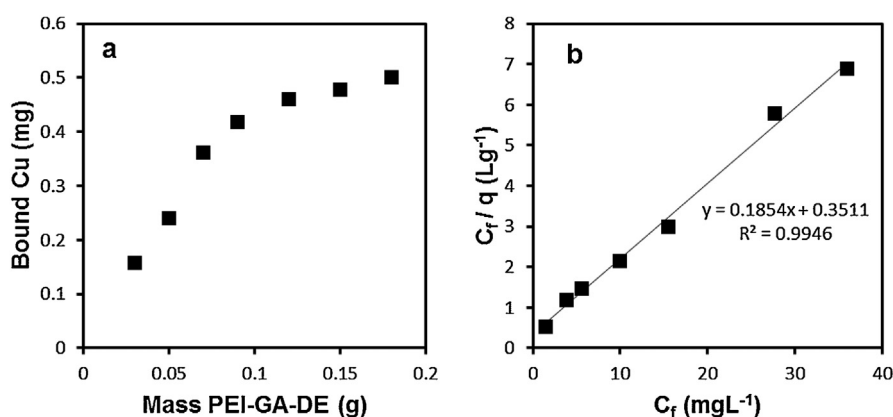


Fig. 6. Copper binding of PEI-GA-DE particles in 10 ml Milli-Q water with pH 4 and 50 mg/L copper (a). Amount of bound copper for different amounts of added PEI-GA-DE particles (b). The pH was set from low to high using HCl and NaOH solutions. Error bars, too small to be seen behind data labels, indicate one standard deviation between analyses ($n = 3$).

close to unchanged (48 mg/L), confirming that the PEI-GA modification was responsible for the copper binding.

To elucidate if copper was bound through the whole volume of the PEI-GA-DE particles, a non-fractured particle, after equilibrium copper loading from 50 mg/L, was identified using SEM (Fig. 7A) and analysed for element distribution using EDX. The analysis revealed that copper was present on the whole particle surface. Subsequently, the particle was etched by FIB to image the cross section (Fig. 7b). The cross section was subsequently analysed for element distribution with EDX. The results revealed that the hollow interior was filled with fractured DE material and that copper was distributed evenly also through the particle. It was concluded that the modification of the DE particles with PEI-GA and the associated copper binding occurred throughout the particles.

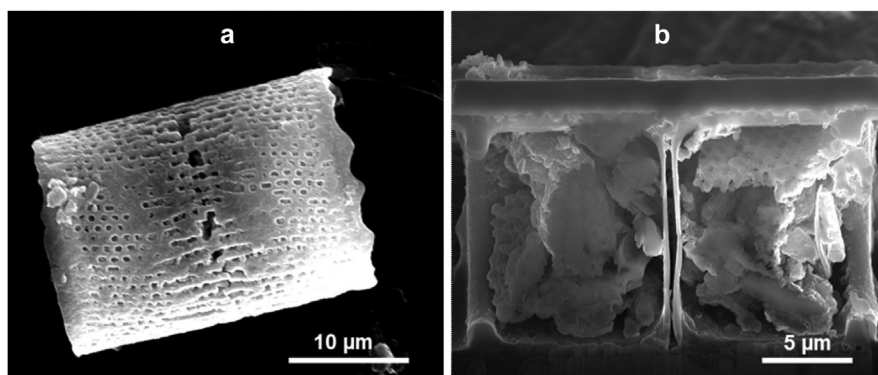


Fig. 7. SEM image of a single PEI-GA-DE particle after equilibrium copper uptake from 50 mg/L in MQ water. (a) Particle surface and (b) cross section after FIB etching.

3.5. Comparison with commercial resins

To assess the performance of the PEI-GA-DE particles for copper extraction from complex solutions, containing competing ions at pH 4, metal removal tests were conducted where PEI-GA-DE particles were compared with the commercial resins: Metcap 1, Lewatite TP 220, Purolite S930+ and Purolite S985. The tests were conducted by preparing pH one solution containing 50 mg/L of copper and 500 mg/L of each competing metal, as described above. Subsequently, 0.19 g of sorbent was added and the pH was set to 4. After incubation and centrifugation sorbent free solution was extracted and analysed for metal content. As seen from Fig. 8, PEI-GA-DE was the most effective in extracting copper under those conditions, with Lewatite TP 220 and Purolite S930+ following, achieving final copper concentrations of 4, 5 and 6 mg/L, respectively. Purolite S985 and Metcap 1 only reduced the copper content to 19 and 34 mg/L, respectively. Among the sorbents effective in extracting copper (PEI-GA-DE, Lewatite TP 220 and Purolite S930 +), PEI-GA-DE was the most selective. All sorbents decreased the iron concentration to a certain degree, and PEI-GA-DE and Purolite S930+ also decreased the lead concentration, compared to centrifugation in the absence of sorbent. However, Lewatite TP 220 caused notable reduction in the levels of nickel, cadmium and zinc. Even if Purolite S930+ did not reduce the concentration of those metals to the same extent, it did so significantly more than PEI-GA-DE. It was thus concluded that among the investigated sorbents and under the used conditions, PEI-GA-DE was the most effective and selective in extraction of copper from the solution.

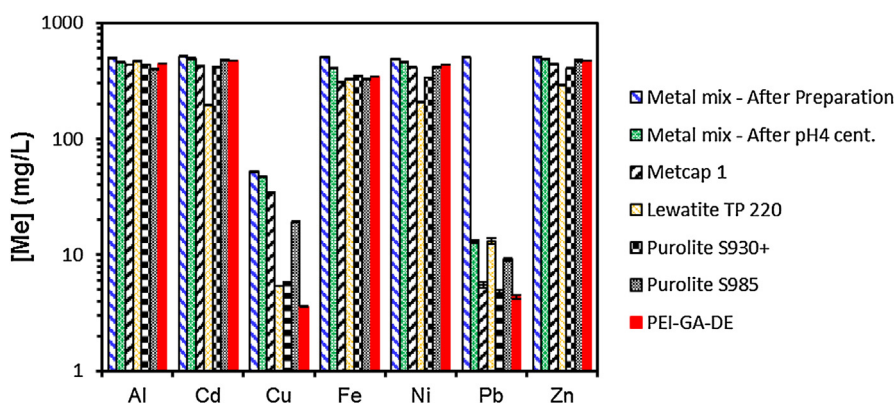


Fig. 8. Metals remaining in mixed-metal solution after uptake and centrifugation at pH 4 in the presence of 19 mg/ml of PEI-GA-DE particles or commercially available metal-chelating resins. Error bars indicate one standard deviation between analyses ($n = 3$).

3.6. Composition of elution liquid

It has been demonstrated that the PEI-GA-DE material is highly stable during elution of bound metals under acidic conditions [38]. It is appealing to use a metal binding resin to extract and purify a target metal, in this case copper. Therefore, the composition of the elution solution was tested after metal uptake, washing and elution for PEI-GA-DE particles (0.019 g/ml). Based on the results for metal binding and precipitation at different pH (Section 3.3), initial experiments were conducted using metal-mix solution, containing about 60 mg/L copper and 500 mg/L of the other metals. Uptake was conducted at 2.6, 3 and 4, followed by washing in Milli-Q water and elution at pH 1. In uptake and elution steps, equal volumes were used, i.e., the metal concentrations are directly comparable in term of recovery. As shown in Fig. 9, 85% of the copper was recovered in elution following uptake at pH 4. The recovery decreased with decreasing pH during uptake, with 16% and 40% recovery for uptake at pH 2.6 and 3, respectively. The concentration of other metals in the elution solution decreased with decreasing pH during uptake, with aluminium and iron being the main contaminants.

To investigate if the presence of other metals in the elution liquid was mainly due to precipitates being separated together with particles and subsequently being re-dissolved in the pH 1 elution solution, or if it was mainly due to binding to the PEI-GA-DE particles, a much smaller mass of PEI-GA-DE particles (1 mg/ml) was suspended in the mixed-metal solution and the uptake-elution cycle was

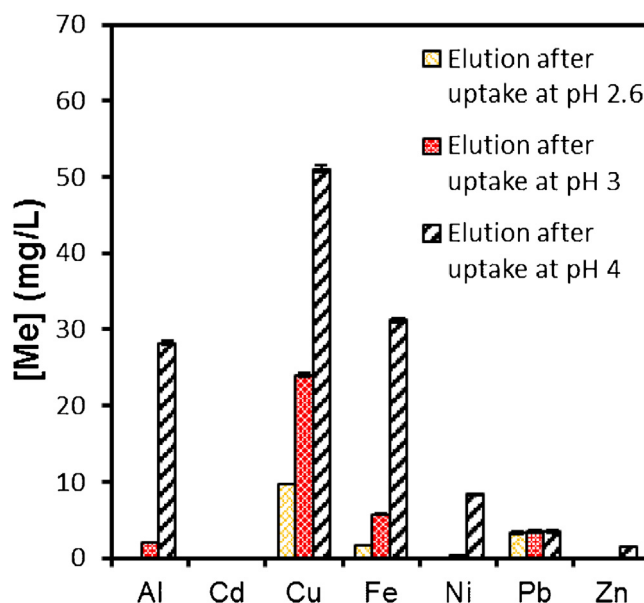


Fig. 9. Metal concentrations in 10 ml of elution solution (pH 1) after uptake by 0.19 g PEI-GA-DE particles in 10 ml pH 4 mixed-metal solution and washing 2X with Milli-Q water. Error bars indicate one standard deviation between analyses ($n = 3$).

performed. The results revealed that in the elution liquid, the copper concentration was greatly decreased while the concentration of other metals remained largely the same. The results thus indicate that precipitation of metals other than copper during uptake test was the main reason for their presence in the elution liquid.

Having established that precipitation was a major factor leading to the presence of metals other than copper in the elution liquid, the mixed-metal solution uptake-elution experiments were conducted with the following adjustments; the mixed-metal solution was pre-centrifuged at pH 4 to remove precipitates prior to adding the 0.019 g/ml PEI-GA-DE particles for uptake. Furthermore, washing was conducted with Milli-Q water with pH set to 4 to minimize precipitation in the slightly higher pH of pristine Milli-Q water. With this methodology, the copper recovery remained high (~80%), but the presence of “contaminating” metals was reduced (Fig. 10a). Aluminium was the main competing metal, followed by iron, but both at reduced concentrations. The aluminium and iron to copper ratios were both about 0.6 for uptake at pH 4 without pre-centrifugation and washing with pristine Milli-Q water. In contrast, the ratios to copper were about 0.3 and 0.06 for aluminium and iron respectively, when using pre-centrifugation and washing at pH 4 (Fig. 10b). It was thus concluded that using the improved methodology, copper could be extracted with increased selectivity.

3.7. Copper removal and elution from real acid mine drainage

After investigating the copper removal performance of the PEI-GA-DE particles in model solutions, they were also evaluated, using the developed protocol, for removal of copper from real Mt Lyell legacy AMD, followed by elution of bound

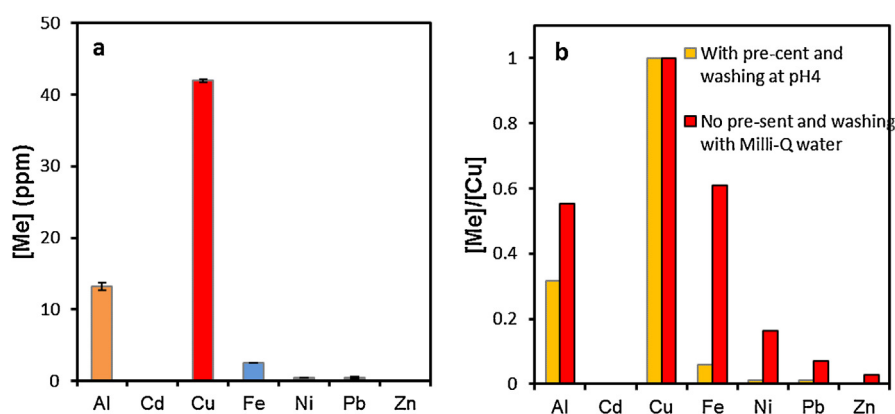


Fig. 10. Metal concentrations in 10 ml of elution solution (pH 1) after uptake by 0.19 g PEI-GA-DE particles in 10 ml of pre-centrifuged pH 4 mixed-metal solution and washing 2X with Milli-Q water set to pH 4. (a) Metal concentration and (b) concentration of each metal relative to that of copper – samples with pre-centrifugation and washing at pH 4 (grey) are compared to samples without pre-centrifugation and washing in pristine Milli-Q water (black). Error bars indicate one standard deviation between analyses (n = 3).

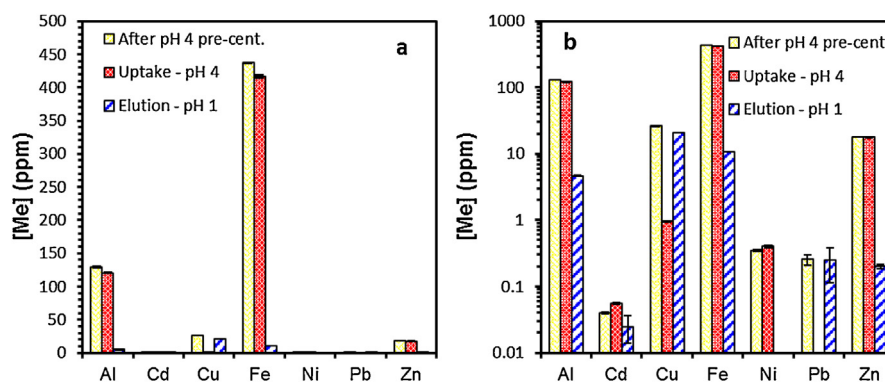


Fig. 11. Metal concentrations in 10 ml of AMD solution from Mt Lyell legacy AMD solution after pre-centrifugation at pH 4, uptake by 0.19 g PEI-GA-DE particles at pH 4 and after elution in 10 ml of pH 1 Milli-Q water. The metal concentration is presented on a (a) linear scale and (b) logarithmic scale. Error bars indicate one standard deviation between analyses ($n = 3$).

metals at pH 1. As seen in Fig. 11, the concentrations of aluminium and iron were more than 100 and 400 mg/L, respectively after centrifugation at pH 4. Copper was present at about 30 mg/L and zinc at about 20 mg/L. All other investigated metals were present at concentrations <1 mg/L. After the metal binding by PEI-GA-DE particles at pH 4, little-to-no decrease in concentration was observed for all metals but copper. On the other hand, for copper the concentration was reduced to 1 mg/L. After washing at pH 4 and elution in an equal volume of Milli-Q water at pH 1, the copper concentration was 21 mg/L (80% recovery). In the elution solution copper was the most abundant metal, with aluminium and iron being the main contaminants at concentrations of 5 and 11 mg/L, respectively. Based on the results it was concluded that the PEI-GA-DE particles were highly efficient in removing copper from real AMD solution and that elution of bound metals resulted in good recovery and great reduction in the concentrations of metals other than copper.

4. Conclusions

It was shown using model and real acid mine drainage (AMD) solutions that PEI-GA-DE particles can be utilized to preferentially extract copper. Furthermore, after elution of bound metals under acidic conditions copper was the major metal present, despite originally being present at much lower concentration than several other metals in the uptake solution. The material holds potential not only for copper remediation of AMD, but also for achieving purified copper solutions. Future work will involve further optimization of the process towards large volume applications and utilization of the material to achieve concentrated pure copper solutions from complex solutions, such as AMD. This will involve developing a methodology to control the particle size so that suitable flow can be achieved in columns and

increasing the capacity of the material by reducing the amount of non-PEI-GA-DE in the particles.

Declarations

Author contribution statement

Mikael Larsson: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Ataollah Nosrati: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Simarpreet Kaur: Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Jochen Wagner and Ulf Baus: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Magnus Nyden: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Funding statement

This work was supported by the Premier's Research and Industry Fund grant provided by the South Australian Government Department of State Development.

Competing interest statement

The authors declare the following conflict of interest: The co-authors of this paper are employees of BASF, the company producing the polyethyleneimine used in this study.

Additional information

No additional information is available for this paper.

Acknowledgements

Our thanks to Dr. Animesh Basak at Adelaide Microscopy for assistance during FIB-SEM.

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