

Polyethyleneimine functionalized mesoporous diatomite particles for selective copper recovery from aqueous media

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ABSTRACT

To date, the quest for cost-effective methods for removal of dissolved metals from aqueous solutions remains a daunting challenge for many industries. This paper reports on the development of an effective, hybrid adsorbent for selective copper recovery from aqueous solutions under industrially relevant conditions. The work involved (i) purification and functionalization of diatomaceous earth (DE) particles with glutaraldehyde(GA)-crosslinked polyethyleneimine(PEI), (ii) physicochemical characterisation of the product and (iii) metal adsorption from solutions containing Cu(II)/Ni(II)/Fe(II)/Ca(II)/Mg(II)/Mn(II)/Al(III)/Na ions and their subsequent elution behaviour. Acid leaching of the pristine DE led to a significant reduction in its metal oxide (e.g., Al₂O₃, Fe₂O₃) constituents and a concomitant increase in both SiO₂ content and specific surface area. Upon functionalization with GA-crosslinked PEI, the DE particles' interfacial chemistry was completely altered to that of the polymer with no change in specific surface area. Isothermal batch adsorption from saline (15g/dm³ NaCl) and non-saline solutions containing 500 and 1000 mg/dm³ of Cu at ~pH 4 revealed >97% Cu(II) removal by functionalized DE within 3 min in both cases. Subsequent water elution tests at pH 1 showed complete release of the adsorbed Cu confirming pH-dependent interaction between dissolved Cu and GA-crosslinked PEI. **The preliminary** batch adsorption/elution tests involving 1000 mg/dm³ solutions of Ni, Ca, Mg, Mn, Fe, Na and Al showed little or negligible affinity of the functionalized DE towards these elements, suggesting good selectivity for Cu. Furthermore, it is shown that the functionalized particles are chemically stable at H₂SO₄ concentrations up to 2 M and may be recycled >10 times without loss in their Cu adsorption/desorption performance.

Key words: Hybrid adsorbent; Polyethyleneimine (PEI); Diatomaceous earth (DE); Copper extraction; Separations; Surface modification

1. Introduction

Selective removal of dissolved metal ions/species from aqueous solutions is an intractable challenge in a wide range of industries, including but not limited to mining and mineral processing, water and wastewater treatment, fuel and power, food, pharmaceuticals, agriculture and manufacturing [1]. For example, there are techno-economic limitations in the application of existing conventional separation and/or purification methods to address water pollution by toxic or heavy metals resulting from mining, chemical, industrial and agricultural processes and waste disposal [2]. As water is a critical resource and ubiquitous fluid for most domestic, municipal and industrial processes, its increasing complexity and salinity pose major challenges for the conventional water treatment systems in meeting quality standards and recycling or discharge requirement. In the mining industry where conventional separation methods such as solvent extraction (SX) and ion exchange (IX) are heavily used to recover valuable metals (e.g., gold, copper, platinum, zinc etc.), there is a shift towards the use of saline or blackish water due to acute scarcity of portable water in recent years [3-7]. The high ionic strength (>0.8 M) aqueous solutions involved are typically proliferated by a plethora of multivalent ions whose interactions have a striking, deleterious impact on selectivity and process efficiency.

Cognizance of the technical, environmental/safety and economic limitations associated with conventional separation methods (e.g., flammable tertiary amine-based SX) when dealing with complex aqueous solutions (e.g., pregnant leach solutions), there is a growing need to develop new and more effective and benign adsorbents for selective recovery of metals from such aqueous environment. In recent years, the use of functionalized mesoporous silicates/silica substrates as adsorbents for selective removal of metal ions from aqueous solutions has gained significant attention [8-16]. These organic-inorganic composite materials combine both the attractive properties of high surface area, thermally and mechanically stable inorganic

substrate with metal-specific chemical affinity of the organo-functional groups. Despite the numerous, proof-of-concept studies on organosilane-functionalized, synthetic mesoporous silica materials, their scale up for large-scale utilization as adsorbents is not deemed to be economically viable [17]. This is mainly due to costly techniques employed to produce such mesoporous systems.

As an alternative, naturally occurring and cheaper mesoporous materials such as DE particles, which display high metal ion sorption capacity similar to that of the more expensive synthetic adsorbents, are attracting significance attention [17-20]. As fossilized remains of diatoms, DE particles' unique and intricate structural, chemical and mechanical properties (e.g., hierarchical pore structure, high specific surface area, robustness, metal ion sorption capacity, non-toxic and chemical inertness etc.), their abundance in nature and low cost are most desirable. These essential characteristics have also led to the current, rapidly growing interest in its application to water purification [17, 21-24]. For instance, the adsorption behaviour of heavy metal ions (e.g., Ni(II), Pb(II), Cu(II), Cd(II) and Th(IV)) and organic contaminants onto pristine and modified DE particles from aqueous solutions under different conditions (e.g., pH and temperature), have been investigated [25-30].

Studies on the removal of U(VI) and Cr(III) ions by raw and functionalized DE particles from aqueous solution showed that adsorption capacity of the former was increased dramatically [21, 24]. Gao et al. [29] reported that PEI-functionalized DE particles displayed very strong trapping effect for phenol in neutral aqueous solution via the cooperating of strong electrostatic and hydrogen bond interactions. Furthermore, Molinari et al. [31] used the PEI alone as complexing agent to study the complexation-ultrafiltration process in the selective removal of Cu(II) from Ni(II) ions from aqueous media.

Of specific interest to the present work are two recent studies of PEI self-assembly and crosslinking on planar silica [32] and excellent Cu(II) selectivity and binding reported for

nano-thin GA crosslinked PEI films in artificial seawater [33]. To date, there have been a number of studies of DE material-based adsorption of Cu and other heavy metals (e.g., nickel, mercury, chromium) from aqueous media [17, 21-30, 34]. Another recent study has also reported on the removal of Cu(II) from synthetic electroplating rinse water by using PEI impregnated ion-exchange resin [35]. However, no studies of PEI-functionalized DE recovery of Cu(II) species from high ionic strength solutions of Cu, Ni, Ca, Mg, Mn, Fe, Na and Al salts and assessment of multiple use and adsorption efficacy, have as yet been reported. Hence, the aim of this study was to examine the (i) surface modification of DE particles through self-assembly of PEI and subsequent crosslinking with GA, (ii) metal (Cu(II), Ni(II), Fe(II), Ca(II), Mg(II), Mn(II) and Al(III)) adsorption behaviour of this new hybrid adsorbent in Milli-Q water and saline (15 g/dm³ NaCl) solution background and (iii) evaluation of adsorbent regeneration for recycle and metal adsorption performance. The investigations reported herein provide a means for benchmarking the efficacy and the analysis of potential application of PEI modified-DE particles for selective and cost-effective removal of toxic metal ions, with a strong focus on Cu, from saline solutions produced in large streams across several industries.

2. Materials and Methods

2.1 Materials

Fine DE powder, a commercial product, was supplied by Diatomaceous Earth Online TM (Queensland, Australia). The as received sample had a specific BET surface area of 39.10 m²/g with 10th, 50th and 90th percentile size of 1.9, 6.3 and 15.6 µm, respectively (Fig. 1). Sulphuric acid (98 wt.%) (Scharlau Chemie, Australia), branched PEI (Lupasol HF; MW=25000 g/mol; primary:secondary:tertiary amines=1:1:0.7; BASF, Germany) (Fig. 2) and GA solution (25% in H₂O) were used for acid purification and surface modification.

Analytical reagent grade nickel(II) nitrate hexahydrate (Sigma Aldrich), sodium chloride, copper(II) sulfate pentahydrate, magnesium sulphate heptahydrate, calcium sulphate, manganese sulphate monohydrate, iron(II) sulphate heptahydrate and aluminium sulphate 14-hydrate (Chem-supply, Australia) were used in solution preparations for the metal adsorption tests. High purity Milli-Q water (specific conductivity $<0.5 \mu\text{S}\cdot\text{cm}^{-1}$, surface tension at $20\text{ }^\circ\text{C}$ of $72.8 \text{ mN}\cdot\text{m}^{-1}$ and pH of 5.6) was used for the preparation of all solutions and dispersions. The DE sample was (i) purified by acid treatment, (ii) surface modified by GA crosslinked PEI and then (iii) used for removal of dissolved metal ions from solution.

2.2 Methods

2.2.1 Purification of DE via acid treatment

200 g of as received DE powder was first dispersed in 1 dm^3 of 1 M sulphuric acid solution and agitated at 600 rpm and $100\text{ }^\circ\text{C}$ for 2 h in a well-sealed, acid resistant cylindrical borosilicate glass vessel. Then, the slurry was centrifuged at 4000 rpm for 5 min and the solid product was re-pulped in 1 dm^3 of 3 M sulphuric acid solution and agitated at 600 rpm and $100\text{ }^\circ\text{C}$ for 20 h [36, 37]. The acid treated DE product obtained after centrifugation was first washed with pH 1 sulphuric acid solution and then repeatedly with Milli-Q water until the pH of filtrate reached 5.5. The final solid product was then oven dried at $100\text{ }^\circ\text{C}$ overnight and stored in a sealed bag at room temperature for analysis or use.

2.2.2 Surface modification of DE particles

For functionalization of purified DE with PEI, known amount of the purified DE particles was dispersed in 40 ml of PEI containing 0.5 M NaCl solution (at 1, 3 or 10 wt.% solid) in 50 cm^3 Falcon tubes, keeping the PEI to DE ratio constant. The dispersion was first ultrasonicated for 15 min in a sonication bath (Soniclean, Australia), followed by 30 min mixing on a rotary tube mixer (Ratek, Australia) at room temperature ($\sim 23\text{ }^\circ\text{C}$) for self-assembly of PEI on the surface

of DE particles. Then, the dispersion was centrifuged for 5 min at 4700 rpm (using Sigma 416K centrifuge) for solid-liquid separation. The solid product was re-dispersed in 100 cm³ of Milli-Q water for 5 min to remove free and unbounded PEI from DE particles and then centrifuged for solid-liquid separation. After repeating this washing procedure three times, the final solid product was re-dispersed in 40 ml of 0.5% GA in water solution for stabilizing crosslinking of the PEI with GA. The dispersion was subsequently incubated for 30 min on rotary tube mixture before centrifugation for solid-liquid separation. An interesting observation that confirmed the successful surface functionalization at all DE solid loadings (1, 3 and 10 wt.%) was that after the stabilizing crosslinking with glutaraldehyde, the particles changed colour from slightly dark cream in Fig. 3A to the purple in Fig. 3B.

After the stabilizing crosslinking with GA, the solid products were washed twice with 100 cm³ of Milli-Q water. Then, they were re-dispersed in 40 cm³ of PEI containing 0.5 M NaCl solution (used for the first step known as PEI self-assembly) for 30 min to react with unreacted GA on the surface of modified particles. The final solid product (PEI modified DE particles referred to as f-DE in the rest of this manuscript) was washed with Milli-Q water for multiple times before centrifugation and was dried at 100 °C overnight. The dry f-DE powder was stored in sealed container. To enable accurate comparisons at the same concentration in subsequent experiments, the DE particles' solid contents in the final dispersions were determined using an infrared moisture balance (AD-4715, A&D, USA). Details on the concentrations of different components of the different dispersions used are given in Table 1.

2.2.3 Thermogravimetric analysis

To determine the mass fraction of the PEI-GA layer on the surface modified DE particles, the mass loss upon heating from 23 °C to 600 °C at 10 °C/min rate was recorded using a Hi-RES Modulated TGA 2950 Thermogravimetric analyzer (TA instruments), with a balance and oven N₂ purge flow of 45-55 cm³/min. The mass% of organofunctional groups resulting from the

surface modification was calculated by subtracting the mass loss of non-modified DE from mass loss for the surface modified DE and quantifying the mass loss step occurring in between 100 °C and 550 °C.

2.2.4 PEI-GA nanoparticles

Under ultra-sonication in a sonication bath (Soniclean, Australia), 5 cm³ of 0.5% GA aqueous solution was added to 5 cm³ of 1% PEI aqueous solution. The ultra-sonication was maintained for 30 min at room temperature, thereafter the sample was aged for 2 d. Subsequently, the sample was filtered through a Minisart-GF pre-filter before zeta potential and dynamic light scattering characterization of the PEI-GA nanoparticles.

2.2.5 Zeta potential measurements

As received, acid treated (purified) and f-DE particles' zeta potential (ζ) in dilute dispersions (0.1 wt.% solid in 10⁻³ M KNO₃ solution) was determined using the Nano-ZS Zetasizer in electrophoretic light scattering mode (Malvern Instruments Ltd., Worcestershire, UK). The instrument determined the zeta potential values from the dynamic mobility data using the Smoluchowski model. The dispersion pH was adjusted to desired values with dilute (<0.1 M) HNO₃ and KOH solutions, allowing equilibration time of 5 min before each zeta potential determination. To achieve good reproducibility of results, all zeta potential measurements were replicated three times and the pure errors determined to ± 2.5 mV for the large values around 50-60 mV and to ± 1.0 mV for the values smaller than 20 mV and are reported at 95% confidence interval.

2.2.6 Metal uptake and elution studies

Preliminary metal uptake capacity was determined for (i) 500 and 1000 mg Cu(II)/dm³ both in Milli-Q water and synthetic saline water (15 g NaCl/dm³) background. The details of uptake tests are as follows: in a 30 cm³ polystyrene container, 2 g of dry surface modified DE powder

(adsorbent) was dispersed in 20 cm³ of the metal/s containing solution. The dispersion was stirred using a magnetic stirrer (with a stirrer bar size closely matching the diameter of the container) at 600 rpm while maintaining its pH at ~4. At predetermined time-points (0, 3, 9, 27 and 81 min) about 2 cm³ of the dispersion was removed isokinetically for supernatant analyses. Solid-liquid separation was carried out by centrifugation at 4700 rpm for 3 min. The supernatants were filtered using 0.2 µm Minisart High-Flow syringe filters before subsequent analysis of the solution for metal content using atomic absorption spectroscopy (AAS). To investigate the elution of loaded metal ions from the adsorbent, (i) solid-liquid separation was carried out at the end of each uptake test, (ii) the solid product (e.g., Cu loaded, modified DE particles) was washed and re-dispersed in Milli-Q water, (iii) the dispersion was acidified using concentrated H₂SO₄ and (iv) samples were taken at different pH values for solid-liquid separation and determination of released Cu concentration in solution. Further uptake and elution tests were conducted on 1000 mg/dm³ solutions (in Milli-Q water) of Cu, Ni, Ca, Mg, Mn, Fe and Al to compare their adsorption behavior and selectivity/affinity towards surface modified DE.

3. Results and Discussion

3.1 DE purification (via acid treatment) and surface functionalization

The chemical compositions of the as received (pristine) and acid treated DE particles are shown in Table 2. SiO₂ (~63 %w/w) and Al₂O₃ (~16 %w/w) appear as the main oxide components in the pristine DE sample with Fe₂O₃ as minor and CaO, MgO, TiO₂, K₂O and Na₂O as trace impurities. The ~16% loss on ignition (L.O.I) observed indicates the presence of chemisorbed water and volatile impurities such as carbonates and organics. Two-stage acid treatment at 100 °C for overall 22 h led to incongruent leaching of the non-siliceous species resulting in a significant increase of SiO₂ content to ~88.2 %w/w in the product (Table 2).

The results show that the concentrations of Al_2O_3 , Fe_2O_3 , CaO , MgO and L.O.I. decreased by ~85%, 94%, 98%, 96% and 50%, respectively, after the acid treatment. Thus acid treatment significantly altered the DE particles' composition before being functionalized with PEI. Powder X-ray diffraction analysis of the particles before and after acid leaching indicated them to be substantially amorphous in structure, consistent with previous studies [17, 18]. Typical SEM micrographs of the as received, purified (acid treated) and PEI functionalized DE particles (Fig. 4) showed that a large fraction of irregular-shaped, colloidal particles were fractured and the finer fractured particles are aggregated. The unfractured DE frustules exhibited perforated, cylindrical shells (15–20 μm length \times 5-10 μm diameter) morphology with an opening at one end. Regularly spaced rows of pores of ~300 nm diameter are located along the frustule shell wall. The morphologies and sizes of the unfractured DE particles appear to be substantially the same before and after acid treatment and surface modification. Slight decrease in the fraction of fine particles upon acid treatment (Fig. 1) suggest the complete solubilization of some of finer gangue mineral particles present in the as received sample, consistent with the data presented in Tables 2 and 3.

The data in Table 3 show that the BET specific surface area of DE powder increased by ~50% upon acid treatment. This is mainly attributed to the removal of less porous impurities (e.g., clays) which increased mass fraction of DE particles in the purified sample. The data also show that the BET specific surface area of purified DE sample remained substantially the same after surface modification.

3.2 Particle zeta potential: effect of acid purification and surface modification

The zeta potential of silica-based particles such as DE is expected to be negative over a wide pH range (2-14) with the magnitude of the negative charge decreasing with decreasing pH due to protonation of surface silanol (SiOH) groups [32]. In contrast, the zeta potential of

PEI, or surfaces coated with PEI, is expected to be positive below \sim pH 9, with the magnitude of the positive charge decreasing with increasing pH due to deprotonation of amine groups [29, 38]. Taking into account that particle zeta potential strongly depends on surface chemistry, a zeta potential of the PEI-GA functionalized DE particles comparable to GA-PEI material alone would indicate a comprehensive surface coverage. Hence, to better understand the extent of surface modification of DE particles with PEI, the zeta potential of as received, acid-treated and PEI-GA functionalized DE particles as well as GA-PEI nanoparticles were investigated.

Particle zeta potentials of the as received, acid treated (purified) and surface modified DE in dilute dispersions measured as a function of pH are shown in Fig. 5. For the as received DE dispersion (with pristine pH of 7.5) the magnitude of negative zeta potential decreased slightly with decreasing pH, however, no isoelectric point (iep) was observed (Fig. 5A). In return pH sweep, as the dispersion pH was raised from 2 to 11, the particles displayed quite similar pH-zeta potential trend albeit with zeta potential slightly greater in magnitude. The observed zeta potential-pH behaviour lies between those of pure silica and alumino-silicate clays (e.g., smectite), consistent with DE's chemical/mineralogical composition. Also, the moderate negative zeta potentials of -20 to -40 mV and absence of apparent iep in the pH range 2 – 11 displayed the raw DE particles is attributed to the pH-independent, permanent negative charge due to the presence of isomorphously substituted alumino-silicate clay mineral [39, 40]. For the acid treated DE powder, the zeta potential varied with pH and an iep at \sim pH 2 was displayed, in the manner of silica particles [41]. These observations are consistent with the efficient removal of most of the impurities (mainly clay) upon acid treatment [29].

To probe the extent and quality of the surface modification of purified DE particles with GA crosslinked PEI under two different conditions (1 and 10 wt.% DE dispersions), their zeta

potentials recorded as a function of pH, before and after PEI functionalization, are shown in Fig. 5B. Furthermore, the zeta potential of PEI-GA nanoparticles, which were synthesized as part of this study, was measured under the same conditions for comparison. The results in Fig. 5B clearly show that PEI-GA functionalization of the purified DE particles led to iep shift from pH 2 to ~pH 11 and charge reversal. This interfacial chemistry change suggests a close to complete surface coverage with electropositive PEI-GA molecules/species via strong specific adsorption or chemisorption. The results also show that the zeta potential-pH behaviour of the f-DE particles obtained from 1 and 10 wt.% solid dispersions are very similar to that of synthetic PEI-GA nanoparticles. The observed pH-zeta potential trend for f-DE particles is also in good agreement with literature [29]. Successful and efficient PEI functionalization of DE particles in 10 wt.% dispersion is promising in terms of large scale process for surface modification of DE particles.

3.3 Effect of dispersion solid loading on DE surface coverage with PEI

To quantify the amount of crosslinked PEI on the surface of functionalized DE particles, samples produced by different preparations were also characterized by TGA. Fig. 6 shows that the mass fraction of crosslinked PEI decreased from 8 to 6% upon decreasing the initial DE dispersion solid loading from 10 to 1 wt.%. This indicates that at similar PEI to particle surface ratios, better surface coverage is achieved at higher solid concentrations most likely due to increased number of particle-PEI collisions. **This observation is in good agreement with the zeta potential data shown in Fig. 5B where the magnitude of positive zeta potential of DE particles surface modified in 10 wt.% dispersion is slightly greater than that of DE particles surface modified in 1 wt.% dispersion.** However, the zeta potential data of the functionalized particles in Fig. 5B **still** suggest that at both low and high DE solid loadings reasonably good coverage of particles' surface with GA-crosslinked PEI was achieved.

3.4 Metal ion adsorption from solutions

3.4.1 Copper uptake and elution behaviour

Fig. 7 shows the uptake results for the removal of dissolved Cu(II) by f-DE particles from Milli-Q water based solution and synthetic saline solution (15 g/dm^3 NaCl) as a function of time. The data clearly show that in both solutions, >97% of dissolved Cu was taken up and retained by particles almost momentarily (<3 min) which is indicative of reasonably fast adsorption kinetics (Fig. 7). The results may also indicate that 3-5 min is an optimum contact time for efficient Cu removal. The similar Cu adsorption behaviour of f-DE particles at solutions with comparable pH (4.1 and 4.5), but with significantly different ionic strengths (0 and 15 g/dm^3 NaCl) indicates that the binding between dissolved Cu(II) and GA-crosslinked PEI is through hybridization with the free electrons of the nitrogen and not through electrostatic interactions, where the latter is commonly screened by the presence of other ions. In other words, the chelation between PEI's amine groups and dissolved Cu(II) (formation of N-Cu(II) complexes) seems to be the main binding mechanism not affected by the solution ionic strength [42]

Based on the TGA results, neglecting any contribution to the mass of the modification from GA, assuming a monomer MW of PEI of 44 g/mol and using the molecular weight of copper, the N:Cu ratio is calculated to be 12. This number is, however, larger than the true ratio, as the films are highly cross-linked with non-nitrogen containing GA. The ratio is also 2-3 times larger than that reported at saturation for systems in solution [33, 43-45], and about 30% larger than reported for thin films of GA-crosslinked PEI in dilute copper solutions [33, 43]. Overall, the copper uptake was considered highly effective and it was concluded that the PEI in the system adsorbed copper to a level close to saturation.

Having established the efficient copper binding to surface modified DE, it was investigated if the copper could be eluted by simply lowering the dispersion pH, as suggested by the literature [46]. The results in Fig. 8 clearly show the pH-dependent and reversible nature of interactions between dissolved Cu(II) and surface modified DE. Further short-term (3 min) uptake and elution tests conducted at pH 4 and 1, respectively, revealed that almost all of adsorbed Cu at pH 4 can be released into solution at pH 1. Thus it was concluded that both copper binding and subsequent acid induced elution was highly effective. Fig. 8 also shows that in the absence of surface modified DE in 500 mg Cu(II)/dm³ solution, pH-dependent hydrolysis and precipitation of dissolved Cu would mainly occur at pH values >4.5. Hence, the Cu uptake/elution behaviour of f-DE in the pH range 1-4 is mainly due to PEI-Cu interactions and not pH-mediated hydrolysis and precipitation of Cu(OH)₂.

3.4.2 Stability of GA cross-linked PEI layer

To investigate the robustness and stability of the surface modified DE particles, they were subject to the following acidic conditions (i) dilute H₂SO₄ solution (pH 0.5) at ambient temperature for 76 h, and (ii) concentrated (2 M) H₂SO₄ solution (pH -0.5) at 60 °C for 24 h. The subsequent uptake and elution tests conducted using the acid treated, surface modified DE particles showed no decline in their Cu adsorption and elution behaviour at pH 4 and 1, respectively. **The ability of the material to withstand strongly acidic conditions may seem surprising, as GA is known to react with amines to form Schiff 's bases, which commonly are reversible under acidic conditions. However, the high stability with regard to temperature and pH has been explained by aldol condensation and dehydration resulting in ethylenic double bonds conjugated with the imine bonds [47, 48].** Furthermore, the adsorbent showed good stability and reproducible efficiency during repeated uptake/elution cycles for 500 mg Cu/dm³ solution (Fig. 9). The data confirms the stability, reusability and robustness of the

new adsorbent suggesting that it could be used for reasonably large number of cycles while retaining its performance.

3.4.3 Selectivity of PEI modified DE towards copper

Fig. 10 shows the affinity and selectivity of surface modified DE particles towards Cu(II) compared with other divalent and trivalent metal ions used in this study. The results show that the dissolved metal ion adsorption affinity dramatically decreased in the order of Cu>Ni>Al>Fe>Mg>Ca>Mn. While the surface modified DE particles could remove almost 100% of Cu(II) from a 1000 g/dm³ solution and release >97% of that adsorbed Cu into pH 1 solution, they could only remove ~10, 8 and 3% of Ni, Al and Fe from their 1000 mg/dm³ solutions, respectively. The surface modified DE also showed negligible affinity towards Mg, Ca and Mn. Overall, the data in Fig. 10 shows the selective nature of surface modified DE towards Cu compared with Ni, Al, Fe, Mg, Ca and Mn.

4. Conclusions

Purified diatomaceous earth (DE) particles with predominantly amorphous silica were produced by acid leaching of commercial particles at 100 °C for 22 h. Acid treatment significantly increased the specific surface area of the particles without any noticeable morphological changes. The purified particles were surface functionalized with glutaraldehyde-crosslinked PEI. The functionalization was carried out in aqueous dispersions with 1, 3 and 10 wt.% particles and was shown to be more effective at high solid loading, as confirmed by zeta potential measurements and TGA analyses. The functionalized particles (f-DE) showed very good copper adsorption performance in both Milli-Q water and saline solution (15 g/dm³ NaCl) by removing >97% of dissolved Cu(II) at ~pH 4 almost immediately. The adsorption process was pH-dependent and reversible as complete desorption was achieved at ~pH 1. f-DE showed very low absorption affinity towards other

elements including Ni, Ca, Mg, Mn, Fe and Al and was mechanically robust and chemically stable, withstanding 2 M H₂SO₄ at 60 °C and repeated uptake/elution cycles without losing performance. Whilst these preliminary results are very promising, further studies are required to elucidate the possible influential role or impact of other metal ions and their concentration in more complex solutions. It is also important to absorb copper in more acidic solutions because of the conditions in many leaching applications. We believe that this can be achieved by combining the material with an electrically conducting material for tuning of the proton- and copper-binding of the glutaraldehyde cross-linked PEI. This is the next step of development in our group.

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References

- [1] Z. Hubicki, D. Kołodyńska, Selective removal of heavy metal ions from waters and waste waters using ion exchange methods, in: A. Kilislioglu (Ed.), *Ion Exchange Technologies*, In Tech, Croatia, 2012.
- [2] J.H. Duffus, Heavy metals – a meaningless term? *Pure Applied Chemistry*, 74 (2002) 793–807.
- [3] Z. Zainol, M.J. Nicol, Comparative study of chelating ion exchange resins for the recovery of nickel and cobalt from laterite leach tailings. *Hydrometallurgy* 96 (2009) 283–287.
- [4] A. Wilson, M. Fainerman-Melnikova, K. Soldenhoff, What are the options for an integrated IX process to recover uranium from saline and hyper-saline liquors? *ALTA* 2011.

- [5] A.L. Williamson, S. Hall, G.A. Spiers, Biogeochemical extraction for rare earth elements and uranium with minimal mine legacy. The AusIMM Int. Uranium Conference 2011.
- [6] S. Hall, Metallurgical development of the Samphire uranium project. In: proceedings of ALTA 2012 Uranium Conference.
- [7] J.E. Quinn, D. Wilkins, K.H. Soldenhoff, Solvent extraction of uranium from saline leach liquors using DEHPA/Alamine 336 mixed reagent, *Hydrometallurgy*, 134–135 (2013) 74–79.
- [8] H. Zheng, C. Gao, S. Che, Amino and quaternary ammonium group functionalized mesoporous silica: An efficient ion-exchange method to remove anionic surfactant from AMS. *Microporous and Mesoporous Materials* 116 (2008) 299–307.
- [9] K. Northcott, S. Oshima, J. Perera, Y. Komatsu, G. Stevens, Synthesis, characterization and evaluation of mesoporous silicates for adsorption of metal ions. *Advanced Powder Technology* 18 (6) (2007) 751–762.
- [10] M. Iiyama, S. Oshima, H. Kokusen, M. Sekita, S. Tsurubou, Y. Komatsu, Adsorption of divalent transition metal ions with a chelating agent on octadecyl silica gel, *Anal. Sci.* 20 (2004), 1463–1464.
- [11] Z.A. Alothman, A.W. Apblett, Metal ion adsorption using polyamine-functionalized mesoporous materials prepared from bromopropyl-functionalized mesoporous silica. *Journal of Hazardous Materials* 182 (2010) 581–590.
- [12] W. Guo, R. Chen, Y. Liu, M. Meng, X. Meng, Z. Hu, Z. Song, Preparation of ion-imprinted mesoporous silica SBA-15 functionalized with triglycine for selective adsorption of Co(II). *Colloids and Surfaces A: Physicochem. Eng. Aspects* 436 (2013) 693–703.
- [13] M.D. Rabiul Awwal, M.D. Abdul Khaleque, M. Ferdows, A.M.S. Chowdhury, T. Yaita, Rapid recognition and recovery of gold(III) with functional ligand immobilized novel mesoporous adsorbent. *Microchemical Journal* 110 (2013) 591–598.

- [14] M.D. Rabiul Awual, I.M.M. Rahman, T. Yaita, M.D. Abdul Khaleque, M. Ferdows, pH dependent Cu(II) and Pd(II) ions detection and removal from aqueous media by an efficient mesoporous adsorbent. *Chemical Engineering Journal* 236 (2014) 100–109.
- [15] B. Fotoohi, L. Mercier, Recovery of precious metals from ammoniacal thiosulfate solutions by hybrid mesoporous silica: 3 – Effect of contaminants, *Separation and Purification Technology*, 139 (2015a) 14–24.
- [16] B. Fotoohi, L. Mercier, Recovery of precious metals from ammoniacal thiosulfate solutions by hybrid mesoporous silica: 2 – A prospect of PGM adsorption, *Separation and Purification Technology*, 149 (2015b) 82–91.
- [17] Y. Yu, J. Addai-Mensah, D. Losic, Chemical functionalization of diatom silica microparticles for adsorption of gold (III) ions. *J. Nanosci. Nanotechnol.* 11(12) (2011) 10349–10356.
- [18] Y. Yu, J. Addai-Mensah, D. Losic, Functionalized diatom silica microparticles for removal of mercury ions. *Science and Technology of Advanced Materials* 13(1) (2012).
- [19] R. Gordon, D. Losic, M. Ann Tiffany, S.S. Nagy, F.A.S. Sterrenburg, The Glass Menagerie: diatoms for novel applications in nanotechnology. *Trends Biotechnol.* 27(2) (2009) 116–27.
- [20] M. Bariana, M.S. Aw, M. Kurkuri, D. Losic, Tuning drug loading and release properties of diatom silica microparticles by surface modifications. *International Journal of Pharmaceutics* 443 (2013) 230– 241.
- [21] A.F.D. de Namor, A.E. Gamouz, S. Frangie, V. Martinez, L. Valiente, O.A. Webb, Turning the volume down on heavy metals using tuned diatomite. A review of diatomite and modified diatomite for the extraction of heavy metals from water. *Journal of Hazardous Materials* 241– 242 (2012) 14– 31.

- [22] E. Li, X. Zeng, Y. Fan, Removal of chromium ion (III) from aqueous solution by manganese oxide and microemulsion modified diatomite. *Desalination* 238 (2009) 158–165.
- [23] P. Yuan, D. Liu, D.Y. Tan, K.K. Liu, H.G. Yu, Y.H. Zhong, A.H. Yuan, W.B. Yu, H.P. He, Surface silylation of mesoporous/ macroporous diatomite (diatomaceous earth) and its function in Cu(II) adsorption: The effects of heating pretreatment. *Microporous and Mesoporous Materials* 170 (2013) 9–19.
- [24] B. Wang, T.R. Smith, Performance of a diatomite-based sorbent in removing mercury from aqueous and oil matrices. *J. Environ. Eng. Sci.*, 6(5) (2007) 469–476.
- [25] G.D. Sheng, J. Hu, X.K. Wang, Sorption properties of Th(IV) on the raw diatomite effects of contact time, pH, ionic strength and temperature. *Appl. Radiat. Isot.* 66 (2008) 1313.
- [26] G.D. Sheng, S.W. Wang, J. Hu, Y. Lu, J.X. Li, Y.H. Dong, X.K. Wang, Adsorption of Pb(II) on diatomite as affected via aqueous solution chemistry and temperature, *Colloids Surf. A* 339 (2009) 159–166.
- [27] T.N.D. Dantas, A.A.D. Neto, M.C.P.D. Moura, Removal of chromium from aqueous solutions by diatomite treated with microemulsion. *Water Res.* 35(9) (2001) 2219–2224.
- [28] M.A.M. Khraisheh, Y.S. Al-degs, W.A.M. Mcminn, Remediation of wastewater containing heavy metals using raw and modified diatomite. *Chemical Engineering Journal* 99 (2004) 177–184.
- [29] B.J. Gao, P.F. Jiang, F.Q. An, S.Y. Zhao, Z. Ge, Studies on the surface modification of diatomite with polyethyleneimine and trapping effect of the modified diatomite for phenol, *Appl Surf Sci*, 250 (2005) 273–279.

- [30] M. Al-Ghouti, M.A.M. Khraisheh, M.N.M. Ahmad, S. Allen, Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: a kinetic study. *J. Colloid Interf. Sci.* 287 (1) (2005) 6-13.
- [31] R. Molinari, T. Poerio, P. Argurio, Selective separation of copper(II) and nickel(II) from aqueous media using the complexation–ultrafiltration process. *Chemosphere* 70 (2008) 341–348.
- [32] W. Tong, C. Gao, H. Möhwald, Poly(ethyleneimine) microcapsules: glutaraldehyde-mediated assembly and the influence of molecular weight on their properties, *Polymers for Advanced Technologies*, 19 (2008) 817–823.
- [33] J.B. Lindén, M. Larsson, B.R. Coad, W. Skinner, M. Nydén, Polyethyleneimine for copper absorption: kinetics, selectivity and efficiency in artificial seawater. *RSC Adv.* (4) (2014) 25063–25066.
- [34] M. Aivalioti, P. Papoulias, A. Kousaiti, E. Gidarakos, Adsorption of BTEX, MTBE and TAME on natural and modified diatomite. *Journal of Hazardous Materials*, 207–208 (2012) 117–127.
- [35] M. Revathia, C.A. Bashab, M. Velana, Removal of copper(II) ions from synthetic electroplating rinse water using polyethyleneimine modified ion-exchange resin. *Journal of Desalination and Water Treatment*, 57 (43) (2016). DOI: 10.1080/19443994.2015.1108234
- [36] H. Mahani, M. Kazemeini, Treatment of diatomaceous earth to obtain its catalyst support. *Scientia Iranica*, 10 (2003) 350–356.
- [37] Y. Yu, J. Addai-Mensah, D. Losic, Development of nano-colloidal diatomaceous earth particles into advanced material for water treatment applications. In: proceedings of Chemeca 2009, Engineering Our Future: Are We up to the Challenge?: 27 - 30 September 2009, Perth, Australia.

- [38] P. Barick, B.P. Saha, R. Mitra, S.V. Joshi, Effect of concentration and molecular weight of polyethylenimine on zeta potential, isoelectric point of nanocrystalline silicon carbide in aqueous and ethanol medium. *Ceramics International*, 41 (3), Part B, (2015) 4289–4293.
- [39] I. Sondi, J. Biscan, V. Pravidic, Electrokinetics of pure clay minerals revisited, *J. Colloid Interface Sci.*, 178 (1996) 514–522.
- [40] S. Nishimura, H. Tateyama, K. Tsunematsu, K. Jinnai, Zeta potential measurement of muscovite mica basal plane-aqueous solution interface by means of plane interface technique, *J. Colloid Interface Sci.* 152 (2) (1992) 359-367.
- [41] M. Kosmulski, E. Maczka, W. Janusz, J.B. Rosenholm, Multiinstrument study of the electrophoretic mobility of quartz, *J. Colloid Interface Sci.*, 250(2002) 99–103.
- [42] J. Wang, Z. Enhanced selective removal of Cu(II) from aqueous solution by novel polyethylenimine-functionalized ion imprinted hydrogel: Behaviors and mechanisms. *Journal of Hazardous Materials* 300 (2015) 18–28.
- [43] J.B. Lindén, M. Larsson, S. Kaur, W. Skinner, S.J. Miklavcic, T. Nann, I.M. Kempson, M. Nydén, Polyethyleneimine for copper absorption II: kinetics, selectivity and efficiency from seawater. *RSC Adv.* (5) (2015) 51883–51890.
- [44] T.D. Perrine, W.R. Landis, Analysis of polyethylenimine by spectrophotometry of its copper chelate, *J. Polym. Sci. A1* (5) (1967) 1993–2003.
- [45] T. Wen, F. Qu, N.B. Li, H.Q. Luo, A facile, sensitive, and rapid spectrophotometric method for copper(II) ion detection in aqueous media using polyethyleneimine, *Arab. J. Chem.*, 2013, DOI:10.1016/j.arabjc. 2013.06.013.

[46] V.M. Nurchi, G. Crisponi, G. Crespo-Alonso, J.I. Lachowicz, Z. Szewczuk, G.J.S. Cooper, Complex formation equilibria of Cu (II) and Zn(II) with triethylenetetramine and its mono- and di-acetyl metabolites, *Dalton Trans.* 42 (2013) 6161–6170.

[47] I. Migneault, C. Dartiguenave, M.J. Bertrand, K.C. Waldron, Glutaraldehyde: behavior in aqueous solution, reaction with proteins, and application to enzyme crosslinking, *Biotechniques*. 37(5) (2004) 790-6, 798-802.

[48] J.B. Lindén, M. Larsson, S. Kaur, A. Nosrati, M. Nydén, Glutaraldehyde-crosslinking for improved copper absorption selectivity and chemical stability of polyethyleneimine coatings, *Journal of Applied Polymer Science*, 133 (37) (2016) 1-11.

Table 1: Weight percent (wt.%) of the relevant components of the slurries/solutions used during the surface modification (PEI functionalization) of DE particles.

Dispersion	DE particles (wt.%)	PEI (wt.%)	GH (wt.%)
1	1.0	0.1	0.5
2	3.0	0.3	0.5
3	10.0	1.0	0.5

Table 2: Chemical composition of pristine and purified (via acid treatment) DE particles by XRF analysis.

Sample	Chemical and elemental composition wt.%										LOI %
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	K ₂ O	Na ₂ O	P ₂ O ₅	MnO	
	(Si)	(Al)	(Fe)	(Ca)	(Mg)	(Ti)	(K)	(Na)	(P)	(Mn)	
As received	62.9 (29.4)	15.9 (8.4)	2.1 (1.5)	0.6 (0.4)	0.6 (0.3)	0.4 (0.2)	0.2 (0.1)	0.1 (0.1)	(0.01)	(<0.01)	~16
Acid- treated	88.2 (41.2)	2.5 (1.3)	0.1 (0.1)	<0.01 (<0.01)	0.02 (0.01)	0.5 (0.3)	0.1 (0.1)	0.01 (0.01)	(0.01)	(<0.01)	~8

Table 3: BET surface area of DE particles before and after acid treatment and surface modification with PEI.

BET surface area (m ² /g)		
As received DE	Purified DE	PEI surface modified DE
39.1 ± 2.0	60.4 ± 2.5	61.1 ± 2.5

Figure 1

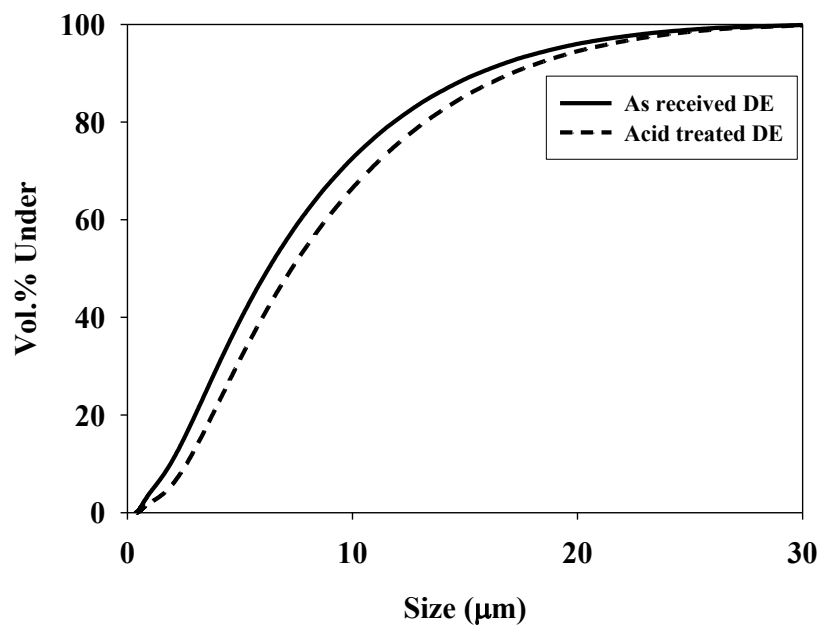


Figure 1: Particle size distribution of DE sample before and after acid treatment (purification).

Figure 2

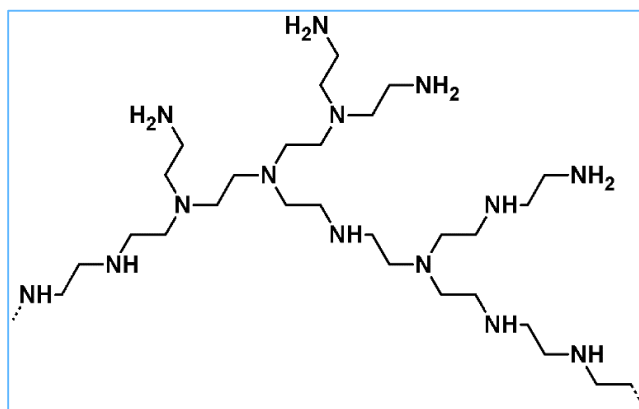


Figure 2: Structure of a typical segment of a branched PEI macromolecule, notice branching through tertiary amines, chain-progression through secondary amines and chain-termination through primary amines.

Figure 3

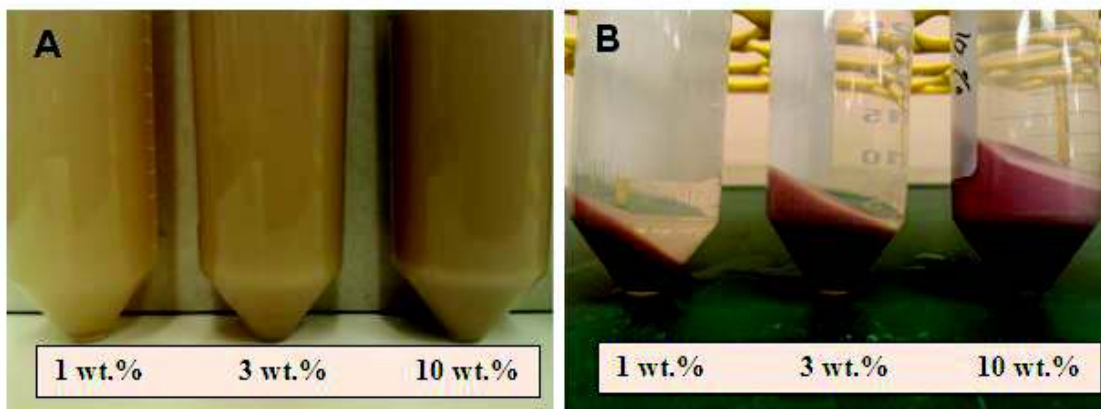


Figure 3: Digital images of 1, 3 and 10 wt.% DE dispersions in Falcon tubes: before surface functionalization (A) and after surface functionalization and centrifugation (B) .

Figure 4

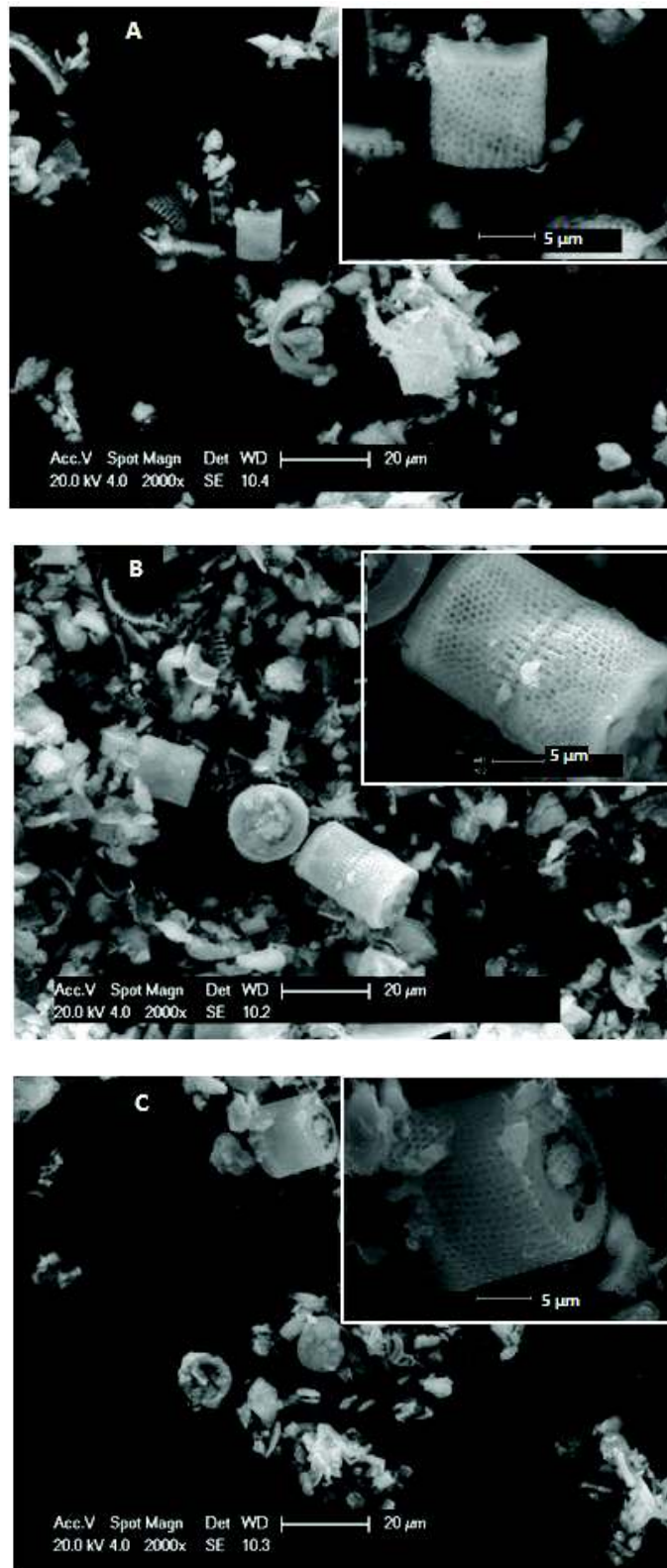


Figure 4: SEM micrographs of (A) raw, (B) purified and (C) surface modified DE sample.

Figure 5

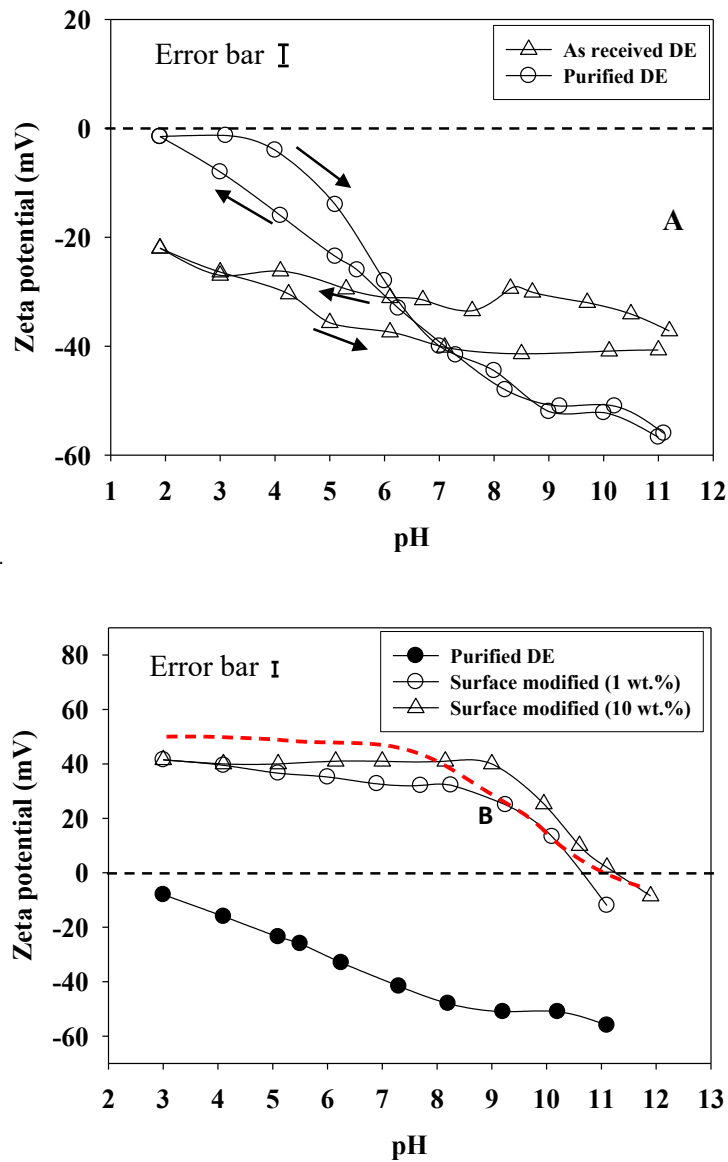


Figure 5: (A) Particle zeta potential of as received and purified, 1 and 10 wt.% solid DE dispersions in 10^{-3} M KNO_3 as a function of pH. The arrows indicate the direction of pH sweep. (B) Particle zeta potential of purified DE dispersions in 10^{-3} M KNO_3 (as a function of pH) before and after PEI-GA functionalization. Chain broken line shows the zeta potentialpH trend for PEI-GA nanoparticles. The errors associated with data points at 95% confidence interval are ± 2.5 mV and ± 1.0 mV for large (50-60 mV) and small (< 20 mV) zeta potential values, respectively. The maximum error is indicated in the figure as a visual aid in interpretation of the data.

Figure 6

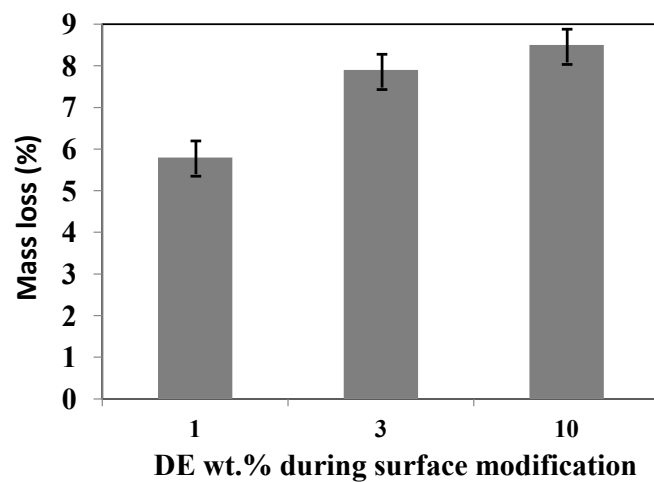


Figure 6: Mass loss (reflecting GA crosslinked PEI mass fraction), as determined using TGA, for surface modified DE particles prepared in 1, 3 and 10 wt.% DE dispersions.

Figure 7

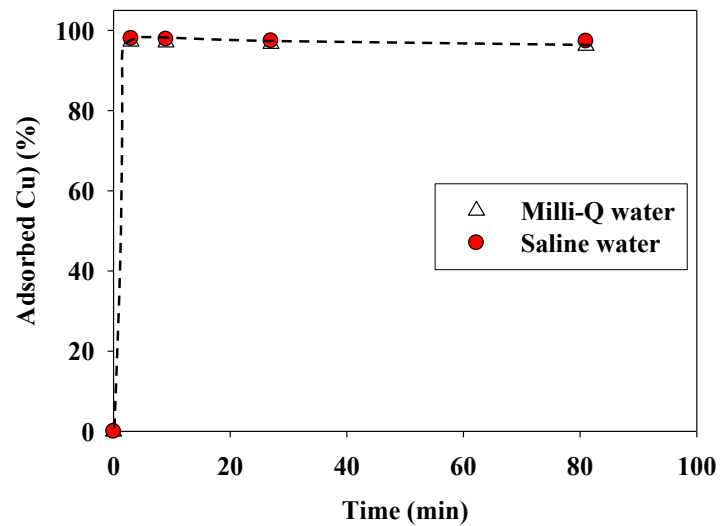


Figure 7: Cu adsorption behaviour of f-DE particles (2 g) from 500 mg Cu(II)/dm³ Milli-Q water based solution and 15 g NaCl/dm³ synthetic saline solution (20 cm³) at 23 °C as a function of contact time at ~pH 4.1 and 4.5, respectively.

Figure 8

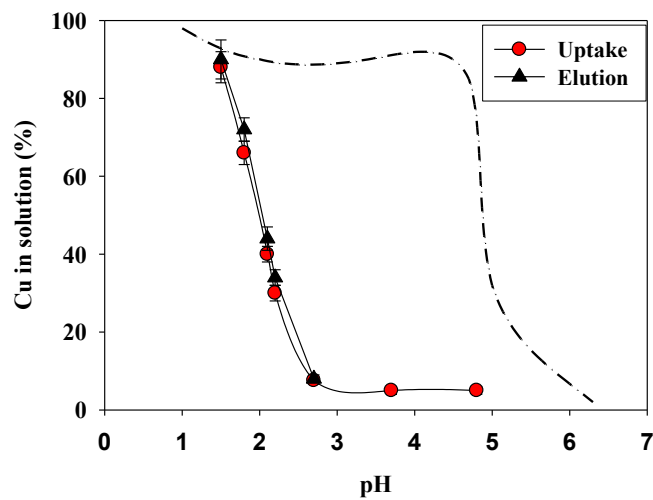


Figure 8: Cu adsorption and elution behaviour of f-DE particles (2 g) in 500 mg Cu(II)/dm³ Milli-Q water (20 cm³) as a function of pH at 23 °C within 5 min. Dash-dot line shows the effect of pH on Cu concentration in 500 mg Cu(II)/dm³ Milli-Q water in the absence of f-DE.

Figure 9

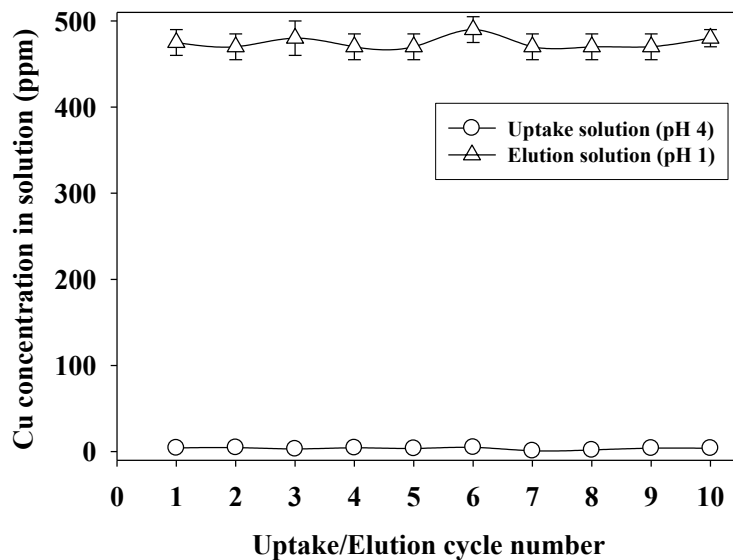


Figure 9: Cu loading/unloading behaviour during repeated cycles with no apparent decrease in the surface modified DE's Cu loading capacity at pH 4 (from 500 mg Cu/dm³ solution) and unloading performance at pH 1 (into pure solution).

Figure 10

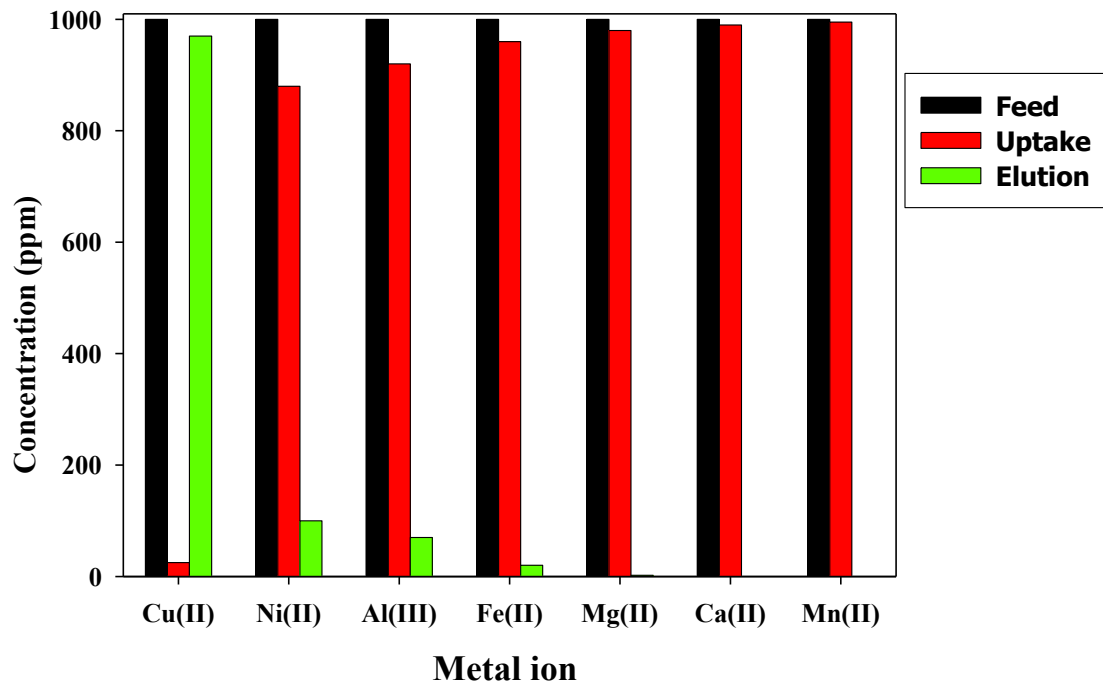


Figure 10: Adsorption and elution behaviour of PEI-modified DE particles (2 g) in 1000 mg/dm³ of Cu(II), Ni(II), Al(III), Fe(II), Mg(II), Mn(II) and Ca(II) solutions (20 cm³). All uptake and elution tests were conducted at pH 3.5-4 (depending on the metal ion type) and 1, respectively, at 23 °C for 5 min.