On copper removal from aquatic media using simultaneous and sequential iron-perlite composites

Mouhammad Shadi Khudr[1*], Yassin Mohamed Elhassan Ibrahim[2*], Arthur Garforth[2], Abdullatif Alfutimie[2]

[1]Faculty of Biology Medicine and Health, The University of Manchester, M13 9PT, UK
[2]Department of Chemical Engineering and Analytical Science, Faculty of Science and Engineering, The University of Manchester, M1 3BB, UK

*Equal contribution

Corresponding author: Abdullatif Alfutimie Email: abdullatif.alfutimie@manchester.ac.uk

Corresponding author: Mouhammad Shadi Khudr Email: scholia_1@tutanota.com

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Author Contributions

All authors wrote the manuscript and accepted the final draft.

Mouhammad Shadi Khudr (MSK) conceived and designed the study, statistically analysed the data, co-produced the figures, and enriched and produced the manuscript.

Yassin Mohamed Elhassan Ibrahim (YMEI) performed the experiment, analysed the samples, and co-produced the figures and the manuscript.

Arthur Garforth (AG) reviewed and contributed to the production and enrichment of the manuscript.

Abdullatif Alfutimie (AA) hosted the work, provided insights on the experimental design, contributed materials and analysis tools. AA contributed to the enrichment and production of the manuscript.

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Abstract

The use of reusable, affordable, and inert adsorbents as a means to mitigate copper pollution, with a lesser burden on the environment, has been attracting some attention. However, aiding the adsorption process of a promising adsorbent, such as expanded volcanic glass (perlite), with a reducing companion, such as solid iron, that can displace and dispose of copper from polluted water has never been tested before. In this laboratory study, we investigated the removal of Cu^{2+}, resulting from contaminating freshwater with copper sulphate pentahydrate, using simultaneous or non-simultaneous (sequential) mixes of expanded perlite and iron coarse powder over 23 hours. The percentage of copper removed was calculated at 15 min, 40 min, 120 min, 300 min, and 1380 min using induced coupled plasma (ICP-OES). A rapid removal of 71% at 120 min was achieved when the perlite and iron were added simultaneously in separate permeable pouches; the application of the iron after the perlite led to 78% of removal at 1380 min that was almost identical to what was accrued via perlite alone (77%). This, therefore, suggests that the presence of iron is most advantageous in the short run as it leads to fast uptake of Cu^{2+}, attributable to the combined action of the reduction of Cu^{2+} by iron and Cu^{2+} adsorption by perlite. Further investigation in support of the results was carried out using Energy-Dispersive X-Ray Spectroscopy (EDAX), X-Ray Diffraction (XRD), Brunauer, Emmett and Teller (BET), and Fourier-Transform Infrared Spectroscopy (FTIR). The findings of this multidisciplinary work provide insights and mechanisms for heavy metal removal from water in a relatively short time using a novel time-specific combination of iron and perlite and thus merit wider testing across different classes of adsorbents, pollutants, and water systems.

Keywords: Perlite, iron, heavy-metal pollution, adsorbents, reactivity series, water treatment

1. Introduction

The ongoing rapid increase in global population, coupled with climate change, has been leading to unprecedented increased demands on water for myriad applications [1,2]. This is alarmingly increasing the burden on the environment especially in urbanised and heavily industrialised areas prone to heavy metal pollution [3]. Despite being essential for life in minimal amounts, copper easily accumulates in the environment and in organisms with far-reaching negative consequences on the terrestrial and aquatic ecosystems [4-7]. Copper pollution can be the result of various natural and anthropogenic causes including the extensive use of copper sulphate pentahydrate $CuSO_4 .5H_2O$ in industries, agriculture, and pond treatment from algae [8,9].

Conventional methods used in the industry for the removal of heavy metal ions in aqueous solutions include chemical precipitation, ion exchange, membrane filtration and adsorption [10,11]. Adsorption is quite effective, easy to apply and economical [11-15]; however, testing the adsorption of heavy metals, such as Cu^{2+}, with companion reactive metals is still largely unexplored. Adsorption processes, at the liquid-solid interface, are central to the chemical industry as they are widely used in lubrication, flotation of minerals, water treatment and oil recovery [12]. The adsorption depends primarily on the characteristics of the adsorbent and the adsorbate but also on variables, such as, contact time, temperature, pH level, and the initial concentration of adsorbates [13].

Adsorption using perlite (amorphous volcanic glass) [14] has been attracting attention due to the promising properties of high porosity, chemical inertness, environmental safety, fast kinetics, low bulk density, and affordability [14-16]. Expanded perlite is chemically treated [15] prior to the extraction of heavy metals from contaminated aquatic media [15,17], with an optimal copper adsorption at pH of 6.5 [17]. Treated and untreated forms of perlite are both shown to be effective in Cu^{2+} removal [15]. However, supporting the perlite adsorption of the target species with copper-displacing electrochemically active metals, such as iron, has been thus far overlooked; perlite-metal combinations may reduce the financial and environmental burden of the conventional perlite pre-treatments. Iron, higher in the reactivity series, can displace copper in solution [18]. Therefore it might be predicted that adding a copper-displacer (iron in its solid form $Fe_{(s)}$) to accompany the adsorbent (perlite) may enhance Cu^{2+} removal. Interestingly, these two copper-removal mechanisms have yet to be tested in simultaneous or sequential fashions.

In this laboratory work, we examined the removal of Cu^{2+}, resulting from contaminating freshwater with 0.07 g/l of copper sulphate pentahydrate $CuSO_4.5H_2O$, using expanded perlite and different mixes of the perlite and iron coarse powder, with the aim of accelerating the amount of Cu^{2+} removal over time.

2. Methods

2.1. Materials

Horticultural medium-grade perlite pellets P35 ($Al_2CaFe_2K2MgNa_2O_{12}Si$) was acquired from Grow Technology© (UK) and used as an adsorbent in the current study; the perlite is brilliant white beads (1-2 mm) expanded under heating (760°C–1100°C) to volumes that are several times bigger than those of the original particle sizes of the siliceous glassy volcanic (magmatic) mineral [15]. The heating causes the structural crystalline water in the perlite to vaporise resulting in rapid expansion yielding high porosity [19,20].

The perlite beads were enclosed in permeable inert polyester copolymer (lycra) mesh, purchased from a local retailer (Manchester, UK), customised as pouches and sealed with elastic bands). As perlite has a lower density than water, the pouches were kept submerged by attaching them to the bottom of the beaker using Quick Tack adhesive putty (inert non-hazardous synthetic rubber) acquired from Q-connect© (UK). Iron coarse powder, obtained from Eisco Labs© (USA), was used alone and in combination with perlite simultaneously and sequentially as specified below.

2.2. Experimental medium

Freshwater (Aqua, hereafter) was simulated artificially *sensu* [21] by using three laboratory stock solutions, namely; stock solution A (117.6 g/l, calcilum chloride dehydrate $CaCl_2.2H_2O$ [Fisher Scientific©, UK]), stock solution B (25.2 g/l, sodium bicarbonate $NaHCO_3$ [Honeywell©, Germany]), and stock solution C (0.07 g/l, selenium dioxide SeO_2 [Merck KGaA©, Germany] plus 0.33 g/l sodium chloride NaCl [ChanteSel©, UK], all dissolved in high purity milli-Q water with a pH ~7.

2.3. Contaminant

Aqua was contaminated with 0.07 g/l of copper sulphate pentahydrate $CuSO_4.5H_2O$ (Sigma-Aldrich©, UK) to mimic possible copper contamination associated with industrialised activities. The removed copper from the treated solution at each sampling time was proportionally calculated relative to the initial copper concentration before treatment.

135 *2.4. Experiment design*

136 The perlite only treatment (*Ads*, hereafter) included 2g of perlite in the pouch; whereas
137 1.5g of perlite and 0.5g of iron were used in the iron-perlite pouches (*Ads-Fe*, hereafter); the
138 iron only treatment (*Fe*, hereafter) included 0.5g of iron in the pouch. The beakers were
139 covered with cling-film to minimise evaporation. The respective combinations (*Ads*, *Ads-Fe*,
140 *Fe*) were tested in the copper sulphate contaminated Aqua for the removal of copper ions. The
141 combinations were divided into three categories: 1) independent (*Ads* or *Fe*: perlite or iron
142 were respectively applied alone in the beaker); 2) simultaneous (*Ads-Fe:* perlite and iron were
143 applied together as a physical mixture in one pouch, or perlite and iron were added in
144 individual co-occurring pouches; 3) sequential (either the application of perlite pouch preceded
145 the application of the iron pouch with a time lag of 40 min or *vice versa*). The treatment of the
146 contaminated Aqua (300ml, as specified above) in PVC beakers (500 ml) was tested under the
147 said combinations at 20℃-22℃.

148 *2.5. Sampling time*

149 For each repeat (specified below) of every treatment, 5 samples were taken in a span of
150 23h. The adsorption of Cu^{2+} has been shown to be most effective with agitation during the first
151 two hours [16]. For this reason, a shaker (Infors Ltd.©, UK) was used for the first 5 hours to
152 ensure good contact between the Aqua and the content of the pouch. As such, 10 ml samples
153 were taken using fresh volumetric pipettes with an emphasis on shorter, yet effective, Cu^{2+}
154 removal times (15 min, 40 min, 120 min, 300 min, and 1380 min), from each repeat then
155 temporarily stored in Falcon tubes prior to analysis.

156 *2.6. Characterisation of the removed* Cu^{2+}

157 An inductively coupled plasma optical emission spectrometry (ICP-OES, hereafter)
158 was used to measure the concentrations of Cu^{2+} in the aqueous solutions at the 5 different
159 sampling times. The elemental composition of the perlite beads was determined using Energy
160 Dispersive X-Ray Spectroscopy (EDAX); Brunauer, Emmett and Teller (BET) was used to
161 measure the average pore diameter and the surface area of the perlite adsorbent; Fourier-
162 Fransform Infrared Spectroscopy (FTIR) was used to monitor changes in the functional groups
163 that characterise the interaction of Cu^{2+} with the adsorbent, and X-Ray Diffraction (XRD) was
164 used to investigate any structural changes that may have occurred to the perlite.

165 In sum, the primary focus of the ICP-OES analysis of this work was quantifying the
166 amount of Cu^{2+} removed to determine the effectiveness of *Ads*, *Fe* and *Ads-Fe* for mitigating

the copper pollution. In addition, the pH and conductivity (t = 0, t = 5h and t = 23h) of the Aqua were determined using a probe (Eutech PC 2700, Thermo Scientific©).

2.7. Statistical analysis

Descriptively, the arithmetic (mean) and standard error of the mean (SEM) were calculated for the percentage of Cu^{2+} removal (obtained from the ICP-OES) per treatment combination and sampling time. A mixed effect generalised linear fit (GLMM, logistic regression) by maximum likelihood (Laplace approximation) was applied in R [22], using the package *lme4* [23] and a model optimiser *bobyqa* [24], to test the Cu^{2+} removal as a function of the treatment combination (predictor 1) and sampling time (predictor 2), and their interaction. The treatment combination was made up of 6 levels (*Ads* [perlite alone, baseline], *Fe* [iron alone], *Ads-Fe* (Sim1) [simultaneous application of perlite and iron as a mix in a single pouch], *Ads-Fe* (Sim2) [application of *Ads* and *Fe* as separate yet co-occurring pouches], *Ads-Fe* (Seq1) [sequential application of the perlite pouch (*Ads*) 40 minutes after the application of the iron pouch (*Fe*), both pouches then remained until the end of the experiment], *Ads-Fe* (Seq2) [sequential application of the iron pouch *(Fe)* 40 minutes after the application of the perlite pouch *(Ads)*, both pouches then remained until the end of the experiment]). The sampling time was a categorical variable of five levels (15 min [baseline], 40 min, 120 min, 300 min, 1380 min). The beaker was randomised (random effect) in this repeated measure analysis. Predictor 3 was the time lag of 40 min, a categorical variable referring to the absence of the simultaneous application of the perlite and the iron (No [baseline]) or the presence of their simultaneous application (Yes). The main effects of the model were revealed by applying an Anova command using the R package *car* [25]. In total, there were 6 treatments x 3 repeats x 5 sampling times = 90 readings; the omission of 8 values across treatment readings due to errors resulted in a total of 82 readings.

3. Results and Discussion

Overall, the most effective and rapid mitigation of copper pollution of 50% was achieved after 15 min of application with *Ads-Fe* (Sim2) (simultaneous separate *Ads* and *Fe* pouches), which was remarkably 13% and 39% more effective than *Ads* (1-2mm perlite bead size) and *Fe* (iron coarse powder of 0.841 mm), respectively. The highest copper removal was reached as early as 120 min under *Ads-Fe* (Sim2) (71%), suggesting an additive effect of the *Ads* and *Fe* in this combination as is at least 15% more effective than each constituent of the combination when applied alone. Further, the highest levels of Cu^{2+} removal at the end of the

experiment (1380 min) were achieved under *Ads-Fe* (Seq2) (78%) (sequential application of *Ads* 40 min following the application of *Fe*) that was closely followed by *Ads* (77%), Figure 1.

3.1. Ads vs Fe

Ads removal of copper from the medium, via adsorption [15,17], gradually increased over time from 37% at 15 min to 77% at 1380 min. By contrast, although Cu^{2+}removal by iron in the *Fe* treatment, via displacement resulting in copper precipitation, showed a similar trend at 300 min, the differences in removal between sampling time points under *Fe* were more apparent than those observed under *Ads*. However, at the end of the experiment (1380 min) copper removal under the *Fe* decreased by 13% when compared to the reading at 300 min, Figure 1. This can be attributed to reaching a saturation point in the case of the *Fe* up to 1380 min; also the Cu^{2+} removal differed between the perlite (lower density with high porosity) and the iron (higher density), irrespective of the iron weight (0.5g) that was ~ 33% of the weight of perlite in any combination that included both perlite and iron). In our study, the perlite in the *Ads* functioned through adsorption [26]: 1) physisorption caused by the Van der Waal's forces attracting Cu^{2+} to the solid porous surface of the perlite, and 2) chemisorption of Cu^{2+} caused by valence forces onto the perlite surface through spontaneous formation of chemical bonds. In particular, the adsorbed M^{2+} (Cu^{2+} or Fe^{2+}) onto the perlite surface can be explained by the following reactions that suggest an increased positive surface charge as the amount of adsorbed cations increases [15]:

$$-SiOH + M^{2+} \rightleftharpoons SiO-M^{+} + H^{+} \quad \text{Eq. 1}$$

$$SiOH + M^{2+} + H2O \rightleftharpoons SiO-MOH^{0} + 2H^{+} \quad \text{Eq. 2}$$

$$2\,SiOH + M^{2+} \rightleftharpoons (SiO)2M^{0} + 2H^{+} \quad \text{Eq. 3}$$

As for the solid iron $Fe_{(s)}$, its interaction with the copper salt dissolved in the medium, and the consequential deposition (precipitation) of copper, can be explained through the following equations [27]:

$$Fe_{(s)} + CuSO_{4(aq)} \rightarrow FeSO_{4(aq)} + Cu_{(s)} \quad \text{Eq. 4}$$

$$\tfrac{1}{2}\,Fe_{(s)} \rightarrow \tfrac{1}{2}\,Fe^{2+}{}_{(aq)} + e^{-} \quad \text{Eq. 5}$$

$$\tfrac{1}{2}\,Cu^{+}{}_{(aq)} + e^{-} \rightarrow \tfrac{1}{2}\,Cu_{(s)} \quad \text{Eq. 6}$$

The negative charge of the perlite surface due to the OH^{-} may decrease with increasing ionic strength in the medium as the latter affects the activity coefficients for OH°, leading to less adsorbable Cu^{2+} onto the perlite surface [15]. The iron has two possibilities: the first is oxidation and displacement of Cu^{2+} as explained in Eqs.4-5, and the second will follow the

pathway as in Eqs.1-3; however, when Fe^{2+} and Cu^{2+} coexist in the medium the Fe^{2+} will be preferably adsorbed onto the surface of the perlite because iron is more reactive than copper according to the reactivity series [27]. Put differently, the fate of the Cu^{2+}, whether it is displacement (Eqs.4 and 6) or adsorption (Eqs.1-3), or both, will be dependent on the manner of the spatial as well as the temporal application of iron (copper-displacing metal) and perlite (the adsorbent), possible interference or synergy between the two processes, and other properties of the involved substances and solutions (*e.g.* concentrations, pH, kinetics, and saturation).

3.2. Sim1 vs Sim2

The breakthrough point (53%) for the *Ads-Fe* (Sim1) was recorded at 300 min, while it reached (71%) at 120 min for *Ads-Fe* (Sim2), and throughout Cu^{2+} removal under (Sim2) was always better than what was achieved under (Sim1) over time. A possible explanation is that the application of perlite and iron as co-occurring separate pouches in (Sim2) led to more surface area contact between the perlite (highly porous adsorbing substance) and the iron $Fe_{(s)}$ (the displacer), Figure S1. However, the adsorption of heavy metal ions has been shown to increase gradually following the first minutes of contact and reaches an equilibrium over time [28].

3.3. Seq1 vs Seq2

Both *Ads-Fe* (Seq1) (perlite applied 40 min after the iron application) and *Ads-Fe* (Seq2) (iron applied 40 min after the perlite application) resulted in a gradual increase in Cu^{2+} removal after the sequential application at 40 min; the Seq1 effect was more rapid and pronounced at 120 min (66%) compared to that of the Seq2 (43%). This is underlain by the iron companionship of perlite for 80 minutes following its sequential addition to the perlite, meaning that the performance of the perlite (Cu^{2+} adsorption) was boosted as per the iron effect (Cu^{2+} displacement and precipitation as $Cu_{(s)}$) by approximately 10% at 120 min. However, this was not quite the case for Seq2 as it required more time for the effect of the sequential addition of perlite to boost the performance of the removal; Seq2 slightly bested Seq1 at 1380 min leading to overall 78% of Cu^{2+} removal (the highest accrual across all treatments). In other words, in the short run, the application of perlite, when preceding the application of iron, appears to be more effective in Cu^{2+} removal, the opposite may be, however, more beneficial in the long run, Figure1 and (Supplemental Information Figure S1). In other words, the advantage of accompanying perlite with iron resides in the fast uptake of the target pollutant, as in the

long run the iron-perlite mix may just yield similar outcome to the application of the perlite alone.

Sims vs Seqs

At 120 min, Sim2 had the best result of Cu^{2+} removal (71%), representing a notable mean reduction of copper from 0.0176 g/l (~9 times larger than the permissible limit in wastewater of 0.002 g/l) to 0.0051 g/l that is only ~ 2.6 times larger than the permitted level (0.002 g/l) by the WHO [29]. This was followed by Seq1 (66%), whilst Sim1 (42%) and Seq2 (43%) were almost identical. Afterwards, at 300 min, Sim1 copper-removal capacity increased to 53%, while Sim2 (70%) and Seq1 (67%) capacity remained consistent, but Seq2 showed a considerable capacity increase from 43% (120 min) to (70%) (300 min). This pattern continued, with a clear boost of Seq2 capacity (reached 78%, 0.0039 g/l of copper that is only ~2 times larger than the permissible limit), by the end of the experiment at 1380 min. It can be deduced from the findings that the best combination of perlite and iron, in terms of time and efficiency of Cu^{2+} removal, is Sim2 despite that eventually Seq2 (followed by *Ads*) may lead to the highest levels of removal. This is again assignable to more chance for kinetics in the case of Sim2 (separate simultaneous pouches of perlite and iron) due to the combination of two processes, *i.e.*, adsorption and metal-displacement, which appeared to work the best between 40 min and 120 min as our results suggest. This implies that this efficiency of the perlite and iron combination is not only time-dependent but also contingent on the way/manner the perlite exists with the iron in the medium. This merits further research to understand the underlying mechanisms further across variable contexts, pH levels, time ranges, and concentrations. It is worthy of note that the ICP-OES measurements showed that the perlite employed in this study was incompatible for the removal of sulphur as there was a negligible change in the concentration of sulphur overtime in the contaminated Aqua due to the negative charges of the $SO4^{2-}$ and SiO^{2-}. Additionally, compared to the non-contaminated Aqua, there were negligible changes in the pH (~6.63 on average) and conductivity (~1.14 on average) at 300 min and 1380 min.

Further, inferentially, our statistical model indicated that the treatment combination, the sampling time, and their interactions highly significantly affected Cu^{2+} removal ($X^2_{(4,51)} = 99.43$, $P < 0.0001$), ($X^2_{(4,51)} = 196.53$, $P < 0.0001$), and ($X^2_{(20,51)} = 85.48$, $P < 0.0001$), respectively; whereas the effect of the 40-min time lag was marginally significant ($X^2_{(1,51)} = 3.65$, $P = 0.056$). Specifically, the model summary revealed the following levels to be significant in terms of Cu^{2+} removal: *Ads-Fe* (Sim1) ($P = 0.01$), *Ads-Fe* (Sim2) ($P = 0.021$), Seq1 ($P = 0.001$), sampling time 1380 min ($P = 0.004$), sampling time 15 min ($P = 0.0007$), *Ads-Fe* (Sim2) x

297 1380 min (P = 0.033), *Fe* x 15 min (P < 0.0001), *Ads-Fe* (Seq2) x 15 min (P = 0.011), *Ads-Fe*
298 (Sim1) x 15 min (P = 0.001); whereas the following were marginally significant: the 40-min
299 time lag (P = 0.056), and *Ads-Fe* (Seq2) x 300 min (P = 0.064); see (Supplemental Information
300 Table S1) for further multiple pairwise-comparisons.

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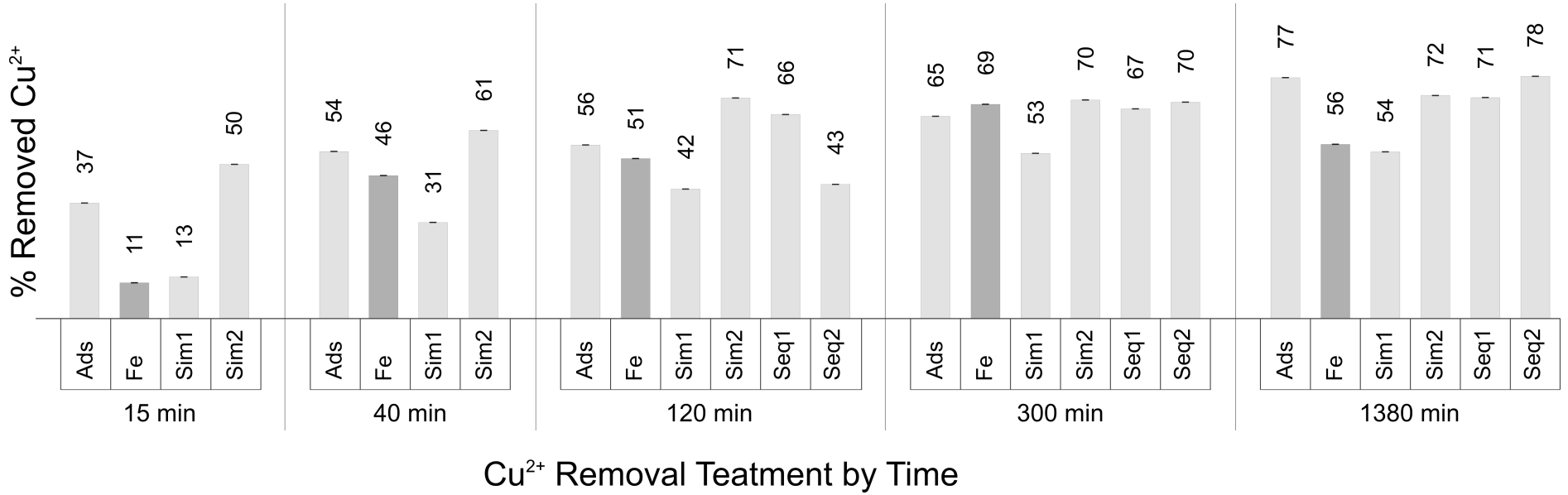

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313 **Figure 1. Percentage of** Cu^{2+} **removed over time.** The bar chart shows the percentage of Cu^{2+} removal from polluted Aqua (Y-axis) at each
314 sampling time (X-axis). There were 6 treatment combinations (*Ads*: perlite alone, *Fe*: iron (coarse powder) alone, *Ads-Fe* (Sim1): perlite and iron
315 are applied simultaneously as a mix in a single pouch, *Ads-Fe* (Sim2): perlite and iron are applied simultaneously as separate pouches, *Ads-Fe*
316 (Seq1): A sequential application where the iron pouch was applied first then followed by the perlite pouch 40 min later, *Ads-Fe* (Seq2): A
317 sequential application where the perlite pouch was applied first then followed by the iron pouch 40 min later. There were 6 treatments x 3 repeats
318 x 5 sampling times = 90 readings (due to the omission of 8 readings the total was 82).

3.4. Supportive characterisation of the perlite associated with copper adsorption

The external surface area of the perlite samples increased after treatment from 1.34 m^2/g to 1.3607m^2/g; whereas the total surface area (BET) has decreased from 1.16 m^2/g to 1.03m^2/g, indicating considerable adsorption of the heavy metal into the pores of perlite surface [30]. The mineralogical analysis of perlite determined by XRD (Supplemental Information, Figures S5 and S6), confirmed that the perlite is amorphous with no distinct crystalline phases. The spectra resemble those of glass-like materials [31]; the only detectable feature from the spectrum is a wide curve that is characteristic of the main components of perlite such as quartz (SiO_2) [32]. The EDAX analysis of the post-treatment perlite showed copper attachment to the perlite surface (Supplemental Information, Figure S2).

Additionally, according to the FTIR analysis, certain peak shifts for surface functional groups were detected in the perlite post *Ads* treatment, namely Si-O at 1029 cm^{-1} (pre-treatment) became 1005 cm^{-1} (post-treatment), Al-O bond stretching at 789 cm^{-1} (pre-treatment) became overlapped with a new peak at 561.7 cm^{-1} (post-treatment), assignable to copper adsorption on the perlite surface [32], and at 445 cm^{-1} (pre-treatment) related to Si-O became 410 cm^{-1} (post-treatment) also attributable to copper bonding with silicate [33]. Additionally, uniform peaks were detected at the –OH (hydroxyl) region (3351 cm^{-1}) indicating adsorbed water, and the (1650 cm^{-1}) region characterised free water [33], (Supplemental Information, Figures S3 and S4). Post-treatment FTIR spectra of the simultaneous and sequential *Ads-Fe* treatments showed similar changes.

The combination (Sim2) showed, promising Cu^{2+} removal in terms of time and quantity (ICP-OES data) and EDAX results indicated a considerable amount of captured iron on the perlite surface, as well (Supplemental Information, Figure S2). The oxidation of the iron in the *Fe* pouch in contact with the aqueous copper led to an excess of iron ions (Fe^{2+}) that was captured by the perlite, whilst a considerable amount of Cu^{2+} gained electrons from the oxidised iron to become reduced and deposited on the iron substrate as $Cu_{(s)}$. (Supplemental Information, Figure S2)

4. Conclusions

The effects of Cu^{2+} removal by perlite and perlite-iron mixes over time were investigated through a novel integration of physicochemical processes with simultaneous or sequential applications. Adsorption as a solution to mitigate heavy metal pollution is advantageous when compared to other conventional processes, for technical and economical reasons and the reusability of adsorbents [34]. Moreover, horticultural grade perlite being inert, stable, ultra-light, highly water-retentive, and pH neutral [19] substantiates and adds to the advantage of the adsorption; the addition of iron to perlite in our work proved to have an additive effect on treating copper pollution of water. It is important to highlight that this effect of the iron companionship of perlite appeared to

be considerably functional and thus desirable in the short run in terms of enhancing the speed of copper uptake in the short run (120 min), when the iron and perlite are concurrent but not mixed, then when the iron is applied belatedly after the perlite introduction. This appertains to a synergistic relationship between Cu^{2+} displacement by iron and adsorption by perlite. This work extends the use of perlite beyond agriculture and insulation; our results encourage further research to test the processes and mechanisms highlighted using different classes of adsorbents, reducing metals, and contaminants.

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Data repository

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Supplemental Information

On copper removal from aquatic media using simultaneous and sequential iron-perlite composites

Mouhammad Shadi Khudr[1*], Yassin Mohamed Elhassan Ibrahim[1*], Arthur Garforth[2], Abdullatif Alfutimie[2]

[1]Faculty of Biology Medicine and Health, The University of Manchester, M13 9PT, UK
[2]Department of Chemical Engineering and Analytical Science, Faculty of Science and Engineering, The University of Manchester, M1 3BB, UK

*Equal contribution

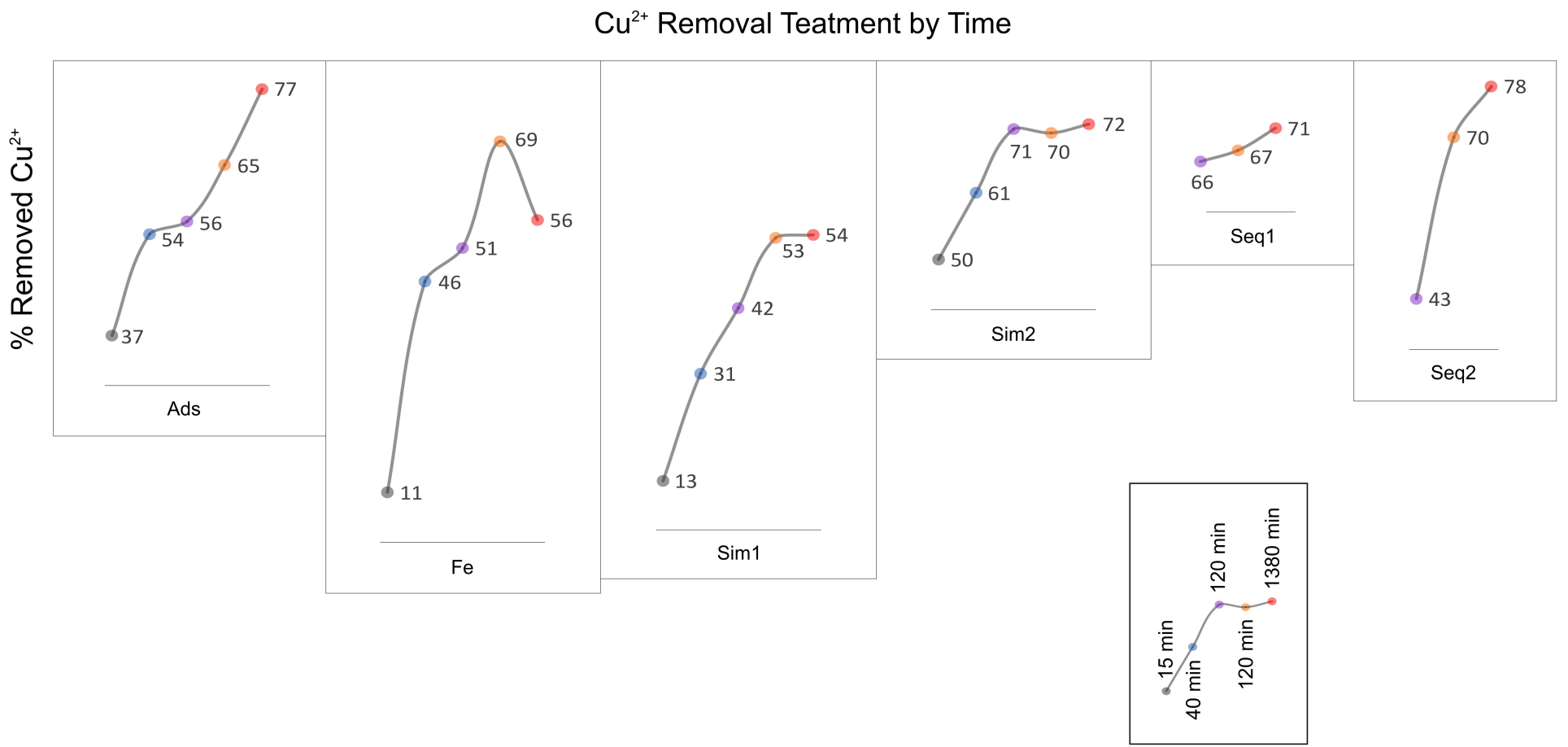
Corresponding author: Abdullatif Alfutimie Email: abdullatif.alfutimie@manchester.ac.uk

Corresponding author: Mouhammad Shadi Khudr Email: scholia_1@tutanota.com

Running title: Perlite with iron mitigates copper pollution

contrast	estimate	SE	df	z.ratio	p.value
Ads,No ***VS*** Fe,No	0.3368	0.0647	Inf	5.210	**<0.0001**
Ads,No ***VS*** Sim1,No	0.4889	0.0597	Inf	8.188	**<0.0001**
Fe,No ***VS*** Sim2,No	-0.4681	0.0626	Inf	-7.475	**<0.0001**
Fe,No ***VS*** Seq1,Yes	-0.3556	0.0638	Inf	-5.576	**<0.0001**
Fe,No ***VS*** Seq2,Yes	-0.2972	0.0694	Inf	-4.279	**0.0003**
Sim1,No ***VS*** Sim2,No	-0.6202	0.0575	Inf	-10.790	**<0.0001**
Sim1,No ***VS*** Seq1,Yes	-0.5076	0.0587	Inf	-8.644	**<0.0001**
Sim1,No ***VS*** Seq2,Yes	-0.4492	0.0649	Inf	-6.918	**<0.0001**

Table S1. Cu^{2+} removal, multiple pairwise comparisons. The results of posthoc Tukey, following the GLM model testing copper removal from the contaminated medium over time as specified in the main-text Methods, are shown as multiple pairwise contrasts. There were 6 treatment combinations (*Ads*: perlite alone, *Fe*: iron [coarse powder] alone, *Ads-Fe* (Sim1): perlite and iron are applied simultaneously as a mix in a single pouch, Ads-Fe (Sim2): perlite and iron are applied simultaneously as separate pouches, *Ads-Fe* (Seq1): A sequential application where the iron pouch was applied first then followed by the perlite pouch 40 min later, *Ads-Fe* (Seq2): A sequential application where the perlite pouch was applied first then followed by the iron pouch 40 min later. The time lag of 40 min, a categorical variable referring to the absence of the simultaneous application of the perlite and the iron (No [baseline]) or the presence of the simultaneous application of the perlite and iron (Yes); confidence level used: 0.95, $`pairwise differences of Treatment, TimeLag`.



507

508 **Figure S1. Percentage of Cu^{2+} removed over time.** The chart shows the percentage of Cu^{2+} removal from the medium (*Aqua*) contaminated with
509 copper sulphate pentahydrate (Y-axis) at each sampling time (X-axis) treatment-wise. There were 6 treatments (*Ads*: perlite alone, *Fe*: iron (coarse
510 powder) alone, *Ads-Fe* (Sim1): perlite and iron are applied simultaneously as a mix in a single pouch, *Ads-Fe* (Sim2): perlite and iron are applied
511 simultaneously as separate pouches, *Ads-Fe* (Seq1): A sequential application where the iron pouch was applied first then followed by the perlite pouch
512 40 min later, *Ads-Fe* (Seq2): A sequential application where the perlite pouch was applied first then followed by the iron pouch 40 min later. There
513 were 6 treatments x 3 repeats x 5 sampling times = 90 readings (due to the omission of 8 readings the total was 82).

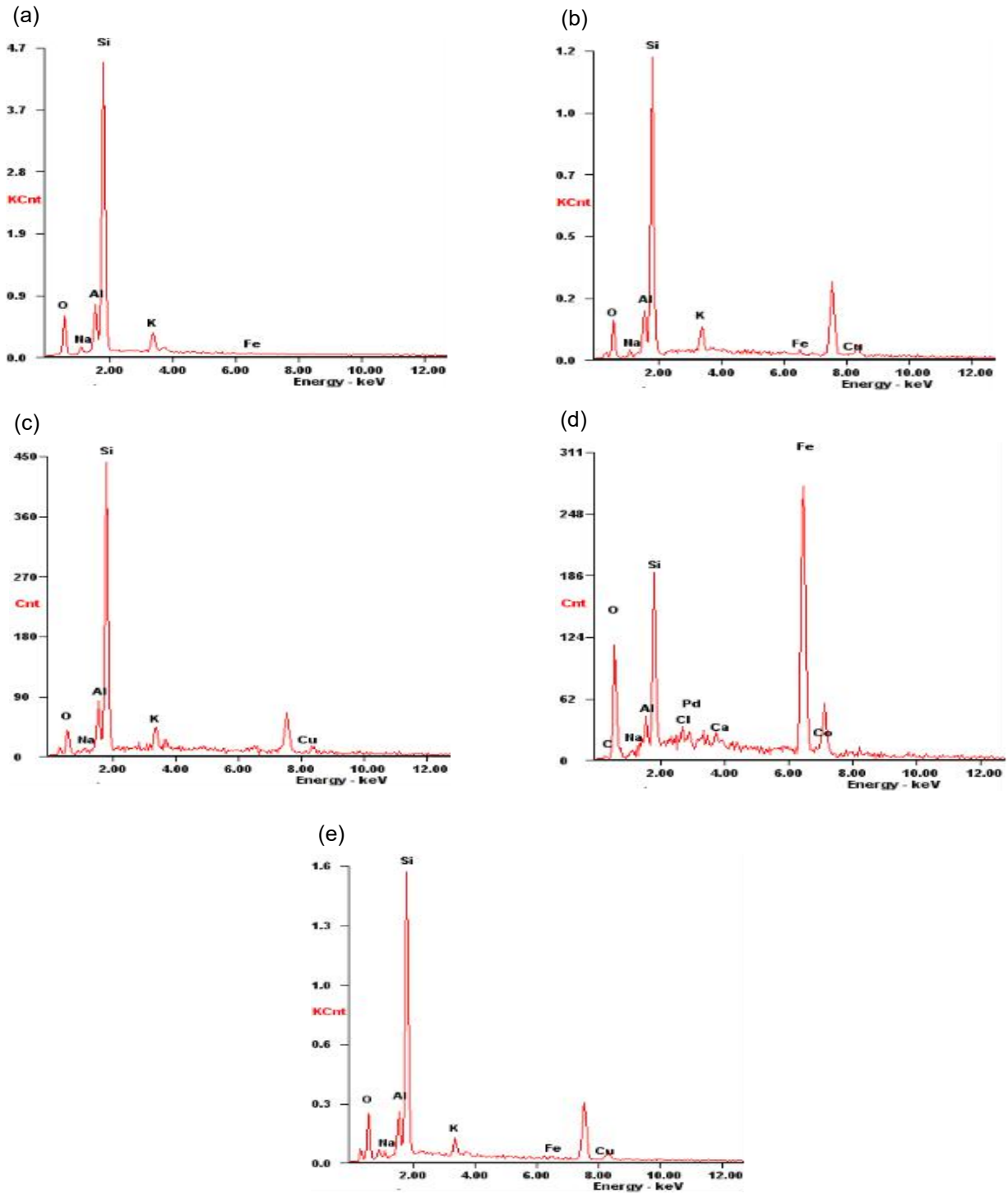
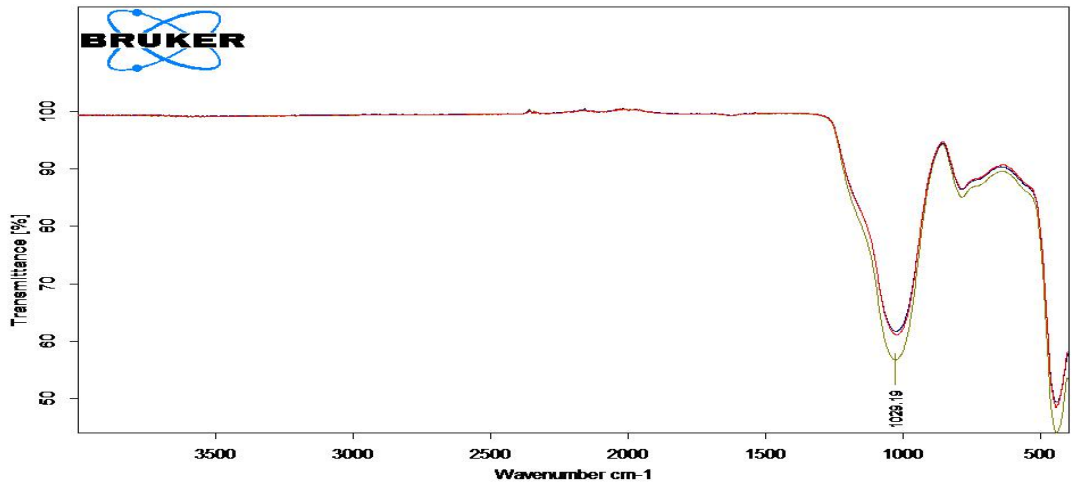


Figure S2. EDAX of perlite (adsorbent). The image collage illustrates the elemental analysis (Energy Dispersive X-Ray Analysis [EDAX]) of the surface of perlite before treatment of the contaminated medium (*Aqua*) with copper sulphate pentahydrate CuSO4.5H2O (a), after the treatment of the contaminated medium at 1380 min corresponding to the respective combinations: (*Ads*: perlite alone (b), *Ads-Fe* (Sim1): perlite and iron are applied simultaneously as a mix in a single pouch (c), *Ads-Fe* (Sim2): perlite and iron are applied simultaneously as separate pouches (d), and *Ads-Fe* (Seq1): A sequential application where the iron pouch was applied first then followed by the perlite pouch 40 min later (e).



549

550 **Figure S3. Pre-treatment FTIR spectrum of perlite (adsorbent).** The figure shows the FTIR
551 spectrum of perlite pre-treatment of the medium (Aqua) contaminated with copper sulphate
552 pentahydrate CuSO4.5H2O. The 3 colours represent 3 repeats of testing the raw perlite pellets
553 before treatment.

554

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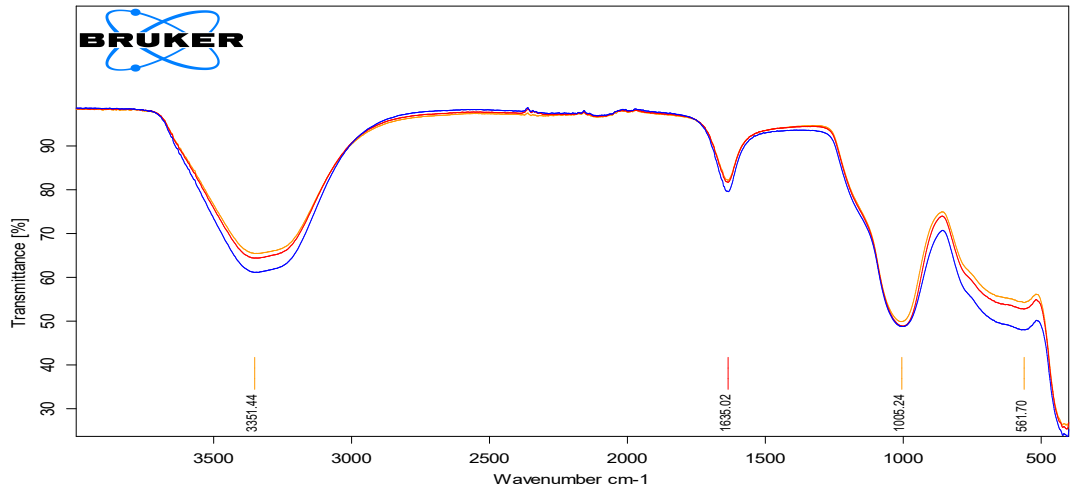

556

557 **Figure S4. Post-treatment FTIR spectrum of perlite (adsorbent).** The figure shows the
558 FTIR spectrum of perlite post-treatment of the medium (Aqua) contaminated with copper
559 sulphate pentahydrate CuSO4.5H2O. New copper peak is visible at 551 cm^{-1}. The 3 colours
560 represent 3 repeats of testing the perlite pellets after treatment. We note that the perlite post-
561 treatment readings for the Sims (perlite and iron are applied simultaneously) and Seqs (perlite
562 and iron are applied sequentially) of the *Ads-Fe* combinations showed similar patterns and thus
563 are not presented herein.

564

565

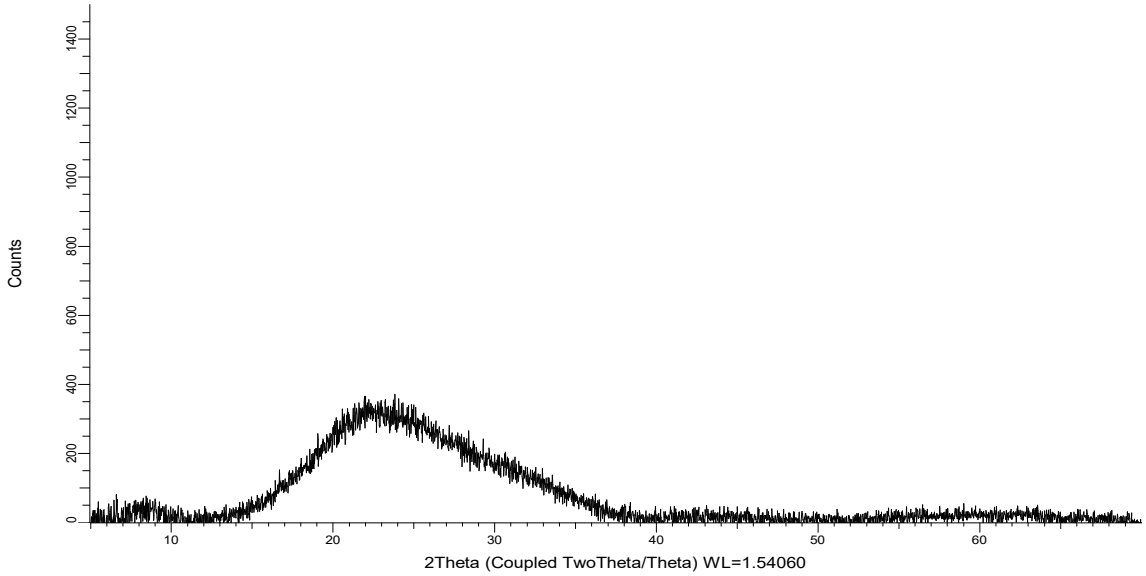

Figure S5. Pre-treatment XRD of perlite (adsorbent). The figure shows the spectrum of the raw perlite before treatment, obtained from X-Ray Diffraction Spectrometry (XRD), indicating the amorphous nature of perlite.

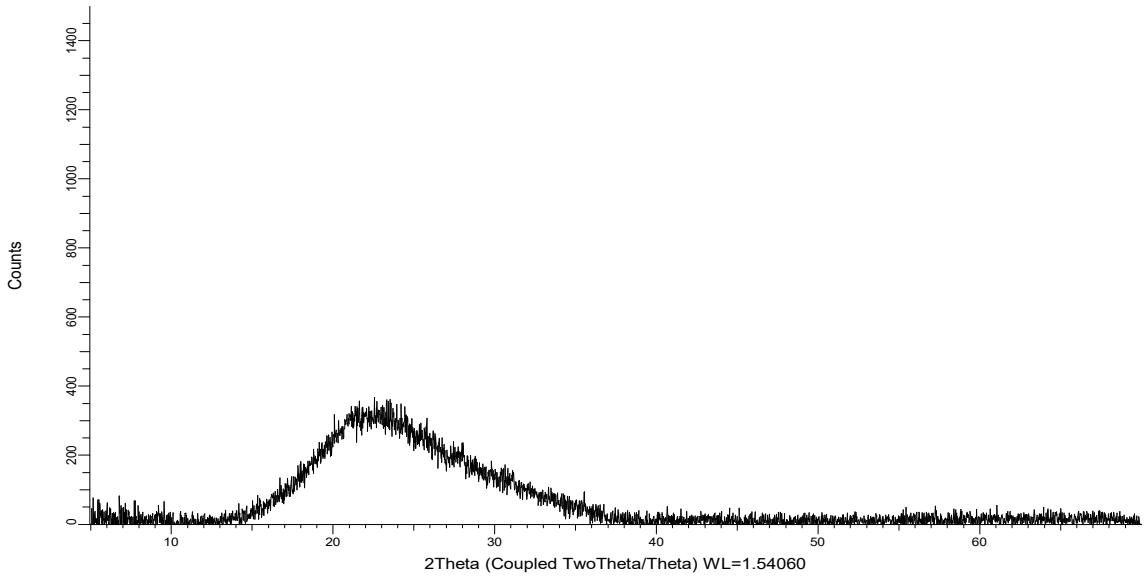

Figure S6. Post-treatment XRD of perlite (adsorbent). The figure shows the spectrum of the perlite following the treatment of the contaminated medium copper sulphate pentahydrate CuSO4.5H2O, obtained from X-Ray Diffraction Spectrometry (XRD), indicating the amorphous nature of perlite.