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Single metal isotherm study of the ion exchange removal of Cu(II), Fe(II), Pb(II) and Zn(II) from synthetic acetic acid leachate

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Abstract

A large predicted increase in population growth and dwindling phosphate resources has led to sewage sludge being an attractive alternative to commercial fertilisers. Among other contaminants, heavy metals are a barrier to unrestricted use of sewage sludge or sewage sludge ash as a phosphate source. This study will focus on the equilibrium isotherm behaviours of Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} towards C107E, MTS9301 and TP214 resins within acetic acid media, fit to the two parameter Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) isotherm models. C107E and MTS9301 were both found to have comparable monolayer capacities for Cu^{2+} and Fe^{2+} (5±1 vs 4.3±0.7mmol · g^{-1} and 2.1±0.8 vs 2.3±0.8mmol · g^{-1} for Cu^{2+} and Fe^{2+}, respectively). The Freundlich model implied heterogeneous binding for Pb^{2+} and Zn^{2+} adsorption to C107E and MTS9301. The monolayer capacities of MTS9301 for lead and zinc were calculated as 2.1±0.2mmol · g^{-1} and 3±1mmol · g^{-1}, respectively. MTS9301 returned larger D-R free energy values than C107E, with the largest difference being Zn^{2+}, displaying energies of 14.0 and 5.5kJ · mol^{-1}, respectively. TP214 displayed the lowest capacity for metals with Fe^{2+}, Pb^{2+} and Zn^{2+} returning D-R energy values closer to physisorption mechanisms (6.0±0.5, 7.1±0.4 and 7.8±0.5kJ · mol^{-1}, respectively), with copper returning a D-R energy relating to chemisorption (17±1kJ · mol^{-1}). Overall, it was observed that the similarity of the C107E functionality to the free acetate anion led to the highest level of hindrance, seconded by the interaction between Fe^{2+}, Pb^{2+} and Zn^{2+} to TP214, while copper displayed strong interaction with TP214 and MTS9301 displayed little or no hindrance by the acetate complexes in solution, with solution phase complexes affecting the homogeneity of binding within any ion exchange reaction.

Keywords; transition metals, weak acid, isotherm, remediation, ion exchange

1   Introduction

The population of the Earth is increasing from roughly 7.7 billion in 2019 to a predicted 9.4 to 10.1 billion by 2050[1]. This large population increase is causing a rapid decrease in the reserves of the critical raw material: phosphate[2–4]. As phosphate is one of the major components within commercially available fertilisers, this increases fears surrounding food security, with current predictions for exhaustion of phosphate reserves ranging from 50-200 years[3, 4]. Treatment of municipal waste water generates a sludge, which contains phosphate (up to 44% of quantity found within commercial fertilisers)[2], which represents a solution to the shortage, and also converts waste into a sustainable, valuable resource.

While sewage sludge is a rich source of phosphate, source combination of waste streams can lead to the infiltration of many toxic heavy metals[5]. Among these metals are copper, zinc and lead (average EU levels reported as 337 ppm copper, 124 ppm lead and 1222 ppm zinc)[6], being especially prevalent within the sewage sludge ashes[7]. In many cases where sewage sludge is currently used as a fertiliser it is assumed that these metals are immobilised[5], however, atmospheric conditions can lead to sulphide-sulphate oxidation, reducing the pH of soils and mobilising metals[8, 9].

Struvite precipitation and phosphate recovery circuits are already implemented commercially for the recovery of nutrients from sewage sludge[10, 11], however creating a residual base metal contaminated waste source. Removal of base metals from the sewage sludge, not only generates a metal-free phosphate source, but also a secondary valorisation stream through stores of the metallic bi-product. Success using strong mineral acids, weak organic acids[12–14] and strong oxidising agents[15] has generated a potential solution for the removal and recovery of these metals. One area that has been overlooked within these studies, however, is the removal of metals from the slurry post dissolution.

Previous work by our research group[16] proposed a hypothetical "resin-in-pulp" system for the removal of heavy metals from weak acid leached sewage sludge and ash (a hypothetical schematic is displayed in Figure 1). This study showed that acetic acid would lead to lower suppression of metal recovery by ion exchange, whilst also minimising unfavourable hydrolysis reactions. pH dependent speciation of the metals allowed for the tuning of solution conditions to selectively recover certain species. The pH dependence on species selectivity of C107E, the high affinity for copper, lead, iron and zinc of MTS9301 and the proposed

redox reaction between copper and the thiourea functionality of TP214 all require further study, and will therefore lend these resins as the focus of this paper.
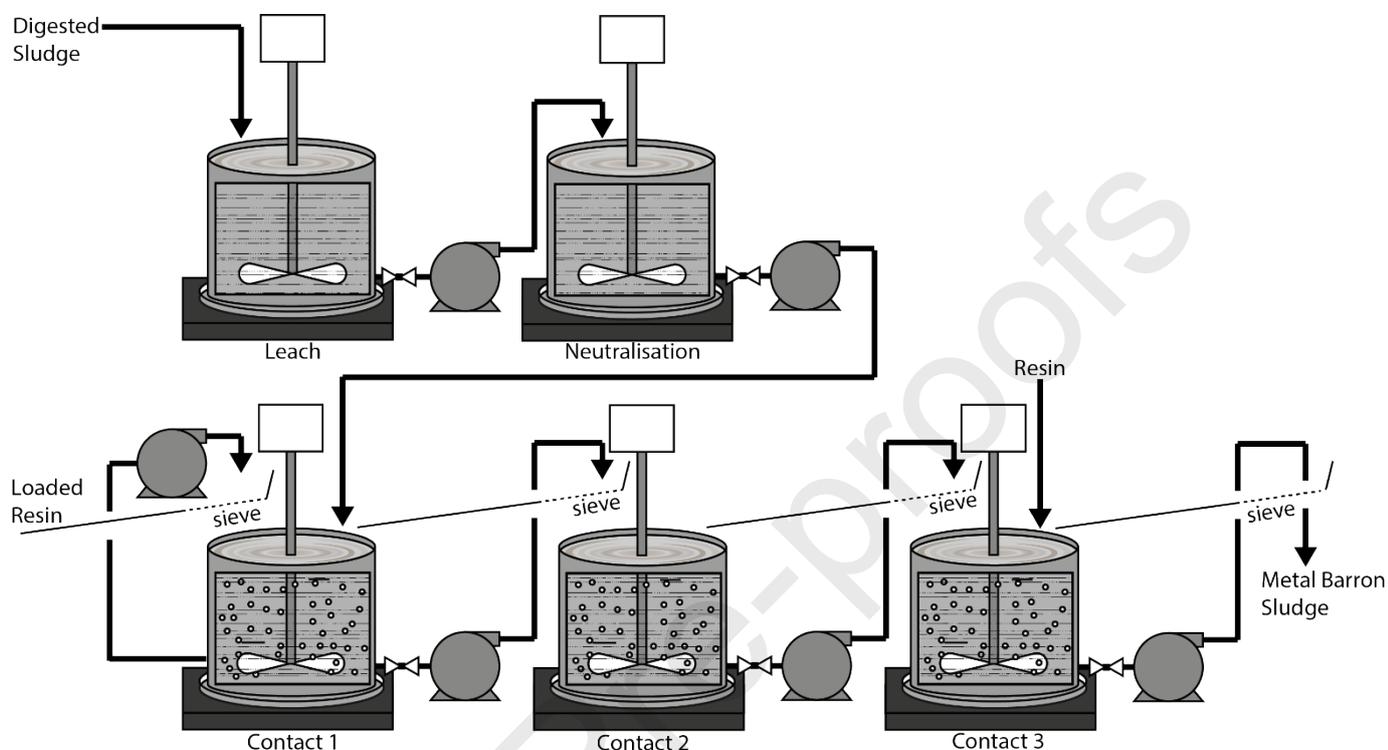

Figure 1: A schematic of the hypothetical resin-in-pulp process for the removal of heavy metals from sewage sludge, containing an arbitrary 3-stages.

The work presented in this paper follows on from the previous work by attempting to understand the chemistry governing the reported ion exchange behaviour; through isotherm loading experiments within the presence of the complex-forming acetic acid, and as an understanding of resin capacity is required to determine the number of stages required within a completed process (Figure 1 displays an arbitrary 3-stage process), this study is imperative[17]. The novelty of this research is derived from a new understanding of the competition between functionality and complexing weak acid, departing from the generally studied strong mineral acid media (HCl, HNO$_3$ and H$_2$SO$_4$)[18]; adding to the body of literature an analysis of the effect the complexing nature of acetic acid can have on resin capacity and thermodynamic behaviours. This work is, in part, towards the understanding of ion exchange processes proposed for a technique for the removal of base metals from sewage sludge for recycling of both heavy metals and the phosphate within sewage sludge.

2 Methods

2.1 Reagents and stock solutions

All chemicals used were of analytical grade or higher and purchased from Sigma-Aldrich apart from glacial acetic acid, which was purchased from VWR. MTS9301 (iminodiacetic acid functionality) and C107E (carboxylic acid functionality) were supplied by Purolite, and Lewatit MonoPlus TP214 (thiourea functionality), which was supplied by Lanxess (Table S1, Figure 2). Ion exchange resins were preconditioned to the protonated form by 24-hour contact with 1 M H_2SO_4 (10 bed volumes) prior to washing with 50 bed volumes of deionised water, then stored under deionised water.
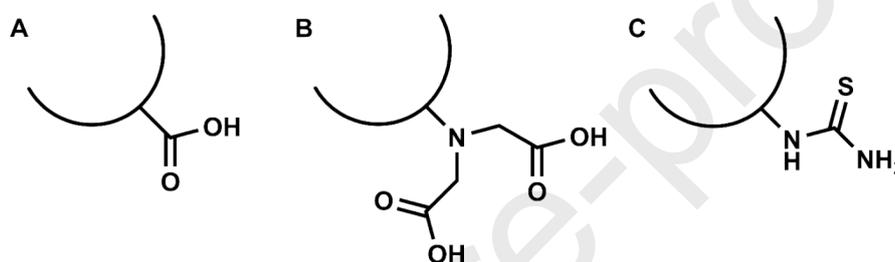

Figure 2: Chemical structure of the functionalities of the ion exchange resins tested throughout this study (A = C107E, B = MTS9301, C = TP214; semicircles represent the matrix).

2.2 Isotherm Loading Studies

Single metal contacts were conducted by contacting 2mL of wet settled resin with 50mL of solution. Experiments were left for 24h to reach equilibrium on an orbital shaker (250 rpm) at 20°C. Single-metal solutions were made up, with concentrations from 50-3000ppm with either the chloride salt of copper, iron(II) and zinc or lead nitrate. Each solution was made to 0.5M acetic acid and 0.5M NaCl in order to lower the impact of varying ionic strength and then adjusted to pH 4.5 using NaOH due to performances within the previous study and the proximity to acetic acid's pK_a, allowing for dissociation of the acetic acid and complexation of the acetate species. All samples were diluted in 1% nitric acid and analysed using AAS (Perkin Elmer Atomic Absorption Spectrometer), experimental error was calculated as two standard deviations of triplicate measurement of each pre-contact solution. All pH measurements were conducted using a commercially available Ag/AgCl electrode, calibrated using a four-point calibration.

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2.3 Speciation Modelling

PHREEQC calculations were conducted using the Aqion interface for PHREEQC modelling software[19]. Each model was generated as a single metal and metals were entered into the models as chloride salts. All PHREEQC models had a NaCl concentration of $0.5mol \cdot L^{-1}$, an acetic acid concentration of $0.5mol \cdot L^{-1}$, with an open CO_2 system calculated at 298K. The data generated by this modelling is presented within Figure S1.

Predominance diagrams were generated using a combination of the HYDRA[20] and MEDUSA[21] software packages, being a database of logK data (at 25°C) and software to create diagrams, respectively. The data obtained using this software is presented in Figure S2. To determine effect of metal concentration on solution phase speciation, speciation modelling was carried out using the HySS2008 software suite[22]. Speciation was modelled at a metal concentration of 50-3000ppm, with the resultant speciation diagrams displayed in Figure S3. All complex stability constants attained for the modelling were sourced from Bezzina, et al. (2019)[16].

3 Results

3.1 C107E

Plots of collected isotherm data for the extraction of Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} from acetic acid solutions using C107E are displayed in Figure 3. The initial slope of the isotherm for each metal is extremely gradual, bar Fe^{2+}. Pb^{2+} and Zn^{2+} were not seen to reach their experimental maximum loading capacities (q_{max}) under the experimental conditions, whereas Cu^{2+} and Fe^{2+} were. The experimentally observed q_{max} values for Cu^{2+} and Fe^{2+} were 0.004 and $0.002mol \cdot g^{-1}$, respectively.

(a)

(b)

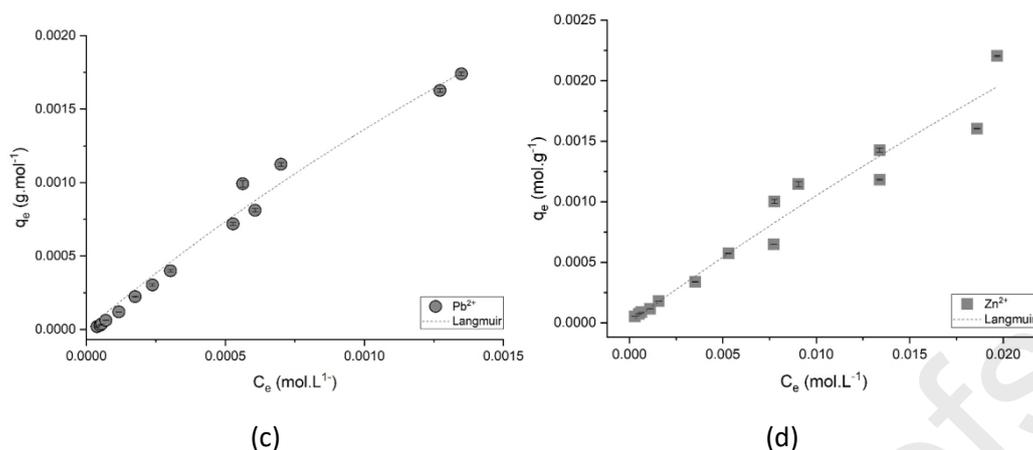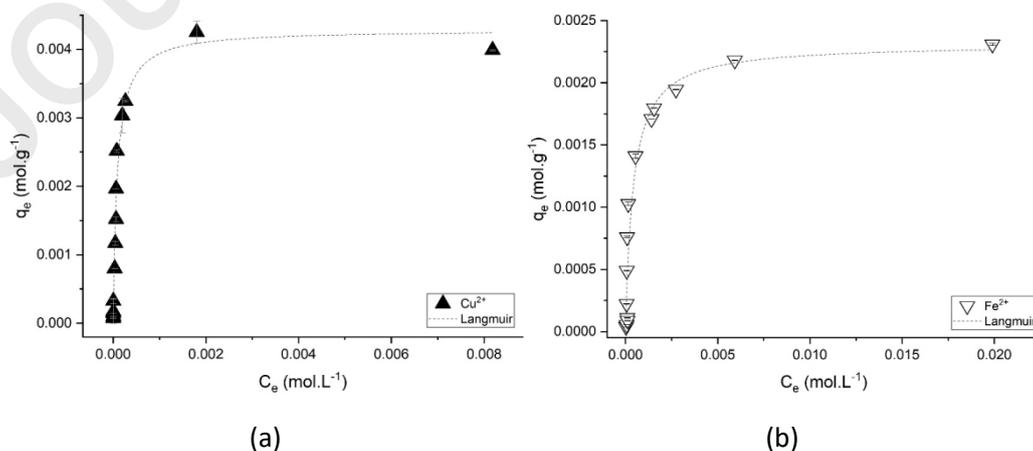(c)   (d)
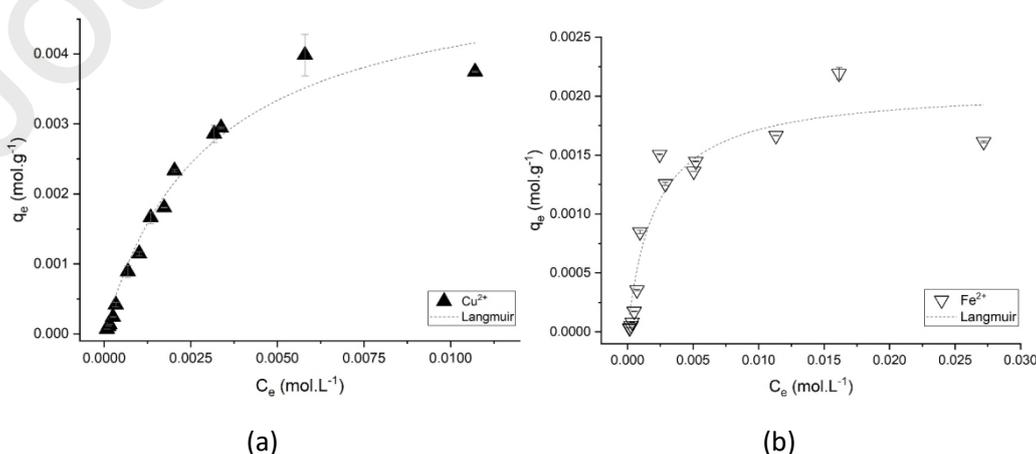
Figure 3: Concentration dependent extraction of copper (a), iron (b), lead (c) and zinc (d) by C107E in acetic acid media (initial concentrations 25-3000ppm; temperature 20°C; 0.5M NaCl; 0.5M acetic acid; 2ml wet settled resin; 50ml solution). The dashed lines in each figure represent the Langmuir model (described later) fitted to the data.

3.2   MTS9301

Plots of collected isotherm data for the extraction of Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} from acetic acid solutions using MTS9301 are displayed in Figure 4. The initial slopes for each metal are much steeper than those observed for C107E, with lead displaying a much less sharp initial slope than the other metals. In this case, both copper and zinc reach an adsorption of $\sim 0.004 \mathrm{mol} \cdot \mathrm{g}^{-1}$, however copper reaches this with an equilibrium solution concentration of $\sim 0.002 \mathrm{mol} \cdot \mathrm{L}^{-1}$, whereas zinc saturates the resin at a C_e five times higher at $\sim 0.010 \mathrm{mol} \cdot \mathrm{L}^{-1}$. Experimentally, both lead and iron(II) reach a similar experimental maximum, both reaching $\sim 0.002 \mathrm{mol} \cdot \mathrm{g}^{-1}$, however iron(II) reaches this with a much lower equilibrium solution concentration, and the sorption of lead seems to continue to increase beyond the range of the isotherm.

(a)   (b)

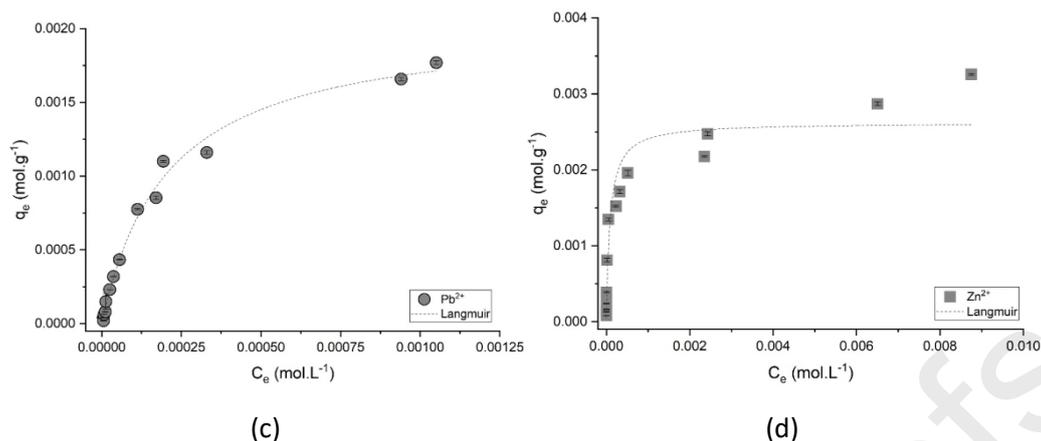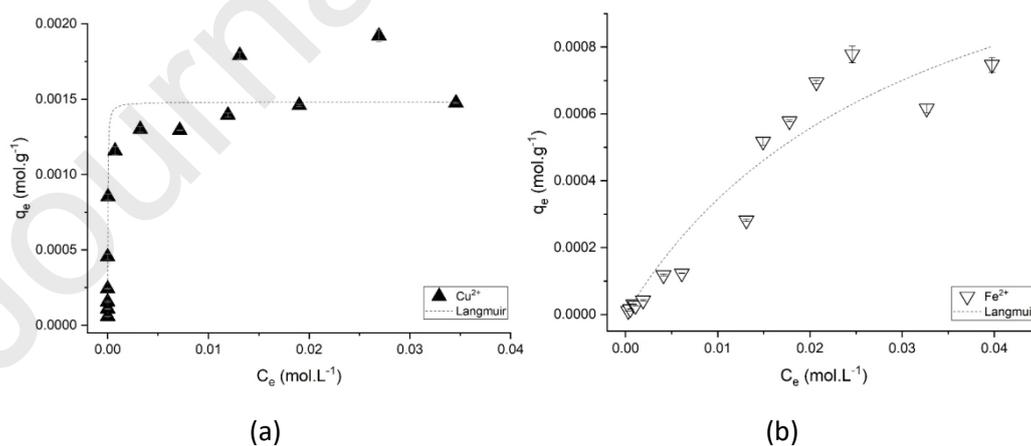(c)   (d)

Figure 4: Concentration dependent extraction of copper (a), iron (b), lead (c) and zinc (d) of MTS9301 in acetic acid media (initial concentrations 25-3000ppm; temperature 20°C; 0.5M NaCl; 0.5M acetic acid; 2ml wet settled resin; 50ml solution). The dashed lines in each figure represent the Langmuir model (described later) fitted to the data.

3.3   TP214

Figure 5 displays the single metal isotherms of the adsorption of copper, iron(II), lead and zinc to the surface of the thiourea based TP214 resin. In this case copper is displays the largest experimental maximum adsorption, with $\sim 0.002 \text{mol} \cdot \text{g}^{-1}$, while all other metals remain $<0.001 \text{mol} \cdot \text{g}^{-1}$. This high maximum is also accompanied by a more definite plateau, while iron(II), lead and zinc maximums are reached either more gradually, or seemingly not at all.

(a)   (b)

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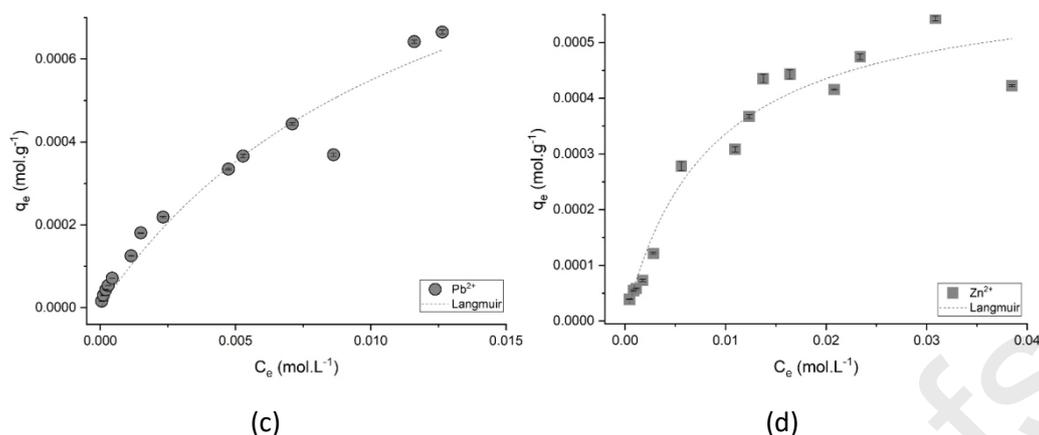(c)   (d)

Figure 5: Concentration dependent extraction of copper (a), iron (b), lead (c) and zinc (d) TP214 in acetic acid media (initial concentrations 25-3000ppm; temperature 20°C; 0.5M NaCl; 0.5M acetic acid; 2ml wet settled resin; 50ml solution). The dashed lines in each figure represent the Langmuir model (described later) fitted to the data.

4   Discussion

In all instances, excessive weak acid has been used in order to determine the effect, if any, that the presence of the complex forming acetate anion has on isotherm performance on each resin. The initial slopes of the isotherms for the carboxylic acid (WA) functionality are extremely gentle, alluding to a weaker interaction between this carboxylic acid functionality and the metallic ions. This becomes of interest due to the similarity between the functionality on the resin and the complexing acetate in solution, creating a competitive equilibrium between the two species. While this is prevalent for the extraction of iron(II), which displays a steep initial slope of the isotherm before a plateau, copper begins to show binding hindrance, while zinc displays behaviour that leads to the assumption of solution stabilisation. Due to solubility restraints regarding lead, saturation was not observed. The behaviour of zinc counters what would be assumed as the low stability constants of zinc acetate species (logβ of 1.79, 2.80 and 3.30 for $CuAc^+$, $CuAc_2$ and $CuAc^-_3$, respectively vs 0.87 and 1 for $ZnAc^+$ and $ZnAc_2$, respectively)[16], as the weak acid functionality has a decreasing affinity for protons towards high pH values, which coincides with its capacity for zinc[23].

Contrarily, the initially weak interaction is not observed towards the iminodiacetic acid (IDA) functionality, most likely due to the high strength of the chelation or bidentate binding mechanism between these metals and the functionality. Lead, however does not show such strong adsorption, leading to the assumption of weaker interactions; creating a hypothesis of a different mechanism due to the high ionic radius of lead preventing the chelation. The adsorption isotherms of lead, zinc and iron(II) for the thiourea functionality

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display the same hindrance seen for the adsorption of lead and zinc to the WA functionality. This is assumed to be due to the weak interactions (inability for ion exchange mechanisms) towards the thiourea functionality, which is further justified by the extremely low experimental q_e values. The copper isotherm for the thiourea functionality, on the other hand, displays a steep initial slope, indicating extremely strong interaction. This supports the previous observation of a redox reaction between copper and thiourea[16].

4.1   Isotherm Modelling

This section will describe models used to analyse data related to the extraction capacities and thermodynamic properties of extraction for adsorbents. In each instance, there are the values C_e (equilibrium solution concentration in mol $\cdot$ L^{-1}) and q_e (equilibrium concentration of adsorbed species in mol $\cdot$ g^{-1}), T is the temperature in Kelvin and R is the universal gas constant (J $\cdot$ K^{-1} $\cdot$ mol^{-1})[24]. The models that will be utilised for the data analysis within this study will be the commonly used two parameter models, the Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherms[25]. In all cases, the best fit was determined by the r^2 value of the fit, and confidence intervals were obtained by the square root of the covariance matrix of each model.

4.2   Homogeneity of Binding

This section will cover the use of the Freundlich and Langmuir models in describing the heterogeneous or homogeneous nature of adsorption with descriptions of capacities and intensity of binding. The Langmuir describes a monolayer adsorption process, with interactions purely between the adsorption species and adsorbent, with no co-extraction and generally more intense binding, while the Freundlich model can be used to describe a system where adsorption includes co-extraction of species and weaker interactions[25]. The Freundlich model describes systems displaying a decrease in energy with increasing binding, a relationship that is exponential[24]. This model is given by:

$$q_e = a_F C_e^{b_F} \tag{1}$$

where a_F and b_F are the Freundlich isotherm constants. The value a_F represents adsorption capacity[26–28] or relative adsorption capacity[25, 29–34]. The parameter b_F is either given as the degree of heterogeneity[25, 27, 29] or intensity of adsorption[26, 30–33]. When $b_F = 0$ the reaction is irreversible, when $0 < b_F < 1$ there is

favourable adsorption and when $b_F > 1$ there is unfavourable or cooperative adsorption[27, 31]; in this capacity the more 'intense' the binding mechanism, the more homogeneous the binding surface, with less intense processes leading to heterogeneous binding[25].

Table 1: Variables obtained by fitting the single metal isotherm data to the non-linear Freundlich model.

Resin	Values	Copper	Iron(II)	Lead	Zinc
C107E	a_F	0.05±0.02	0.008±0.003	0.8±0.3	0.07±0.03
	b_F	0.51±0.06	0.37±0.07	0.92±0.06	0.93±0.01
	r^2	0.905	0.776	0.979	0.956
MTS9301	a_F	0.015±0.005	0.007±0.003	0.05±0.01	0.010±0.002
	b_F	0.23±0.04	0.28±0.05	0.47±0.04	0.24±0.02
	r^2	0.768	0.781	0.958	0.941
TP214	a_F	0.0031±0.0004	0.008±0.004	0.012±0.003	0.0025±0.0007
	b_F	0.17±0.03	0.7±0.1	0.67±0.06	0.46±0.07
	r^2	0.893	0.896	0.970	0.888

The variables obtained by the fitting of the isotherm data to the Freundlich model are displayed in Table 1. The interactions of lead and zinc with the WA functionality displays very reasonable fits to this model (r^2 of 0.979 and 0.956, respectively), with copper displaying a tentative fit (r^2 of 0.905), however the fit to iron(II) was poor, with an r^2 of 0.776. With the very poor fit of iron(II) in mind, the intensities of adsorption generate the trend of Zn>Pb>Cu. The Freundlich isotherm fit to the experimental data for the IDA functionality isotherms displayed poor correlation to both copper and iron(II), while lead and zinc found reasonable fits to this model (r^2 values of 0.958 and 0.941, respectively), with zinc displaying a higher intensity of binding than lead. The adsorption of lead to the thiourea functionality displays a reasonable fit to this model (r^2 of 0.970), no other metals fit the model, with r^2 values <0.9.

The Langmuir model, unlike the Freundlich model, does follow Henry's law as concentration decreases[24], i.e. while at high concentrations it predicts constant adsorption. This model is capable of describing monolayer sorption mechanisms, and is given by:

$$q_e = \frac{q_m a_L C_e}{1 + a_L C_e} \tag{2}$$

In this instance a_L is the Langmuir isotherm constant (L · mol^{-1}), related to the sorption energy (equilibrium constant for the sorption of the species) and q_{max} is the monolayer capacity of the sorbent (mol · g^{-1})[35].

Table 2: Variables obtained by fitting the single metal isotherm data to the non-linear Langmuir model.

Resin	Values	Copper	Iron(II)	Lead	Zinc
C107E	a_L	340±60	500±100	170±90	10±10
	q_{max}	0.005±0.001	0.0021±0.0008	0.009±0.004	0.02±0.03
	r^2	0.976	0.915	0.983	0.955
MTS9301	a_L	11000±2000	2400±600	4800±400	11000±5000
	q_{max}	0.0043±0.0007	0.0023±0.0008	0.0021±0.0002	0.003±0.001
	r^2	0.975	0.928	0.992	0.909
TP214	a_L	50000±20000	30±20	80±30	120±30
	q_{max}	0.001±0.001	0.0014±0.0008	0.0012±0.0005	0.0006±0.0002
	r^2	0.890	0.922	0.955	0.952

The Langmuir fits to the isotherm data of the adsorption of copper, lead and zinc to the WA functionality (Table 2) display reasonable fits (r^2 >0.95), with iron(II) displaying a slightly more tentative fit of 0.915. The calculated theoretical maximum adsorbance calculated by the Langmuir model for the WA functionality dictates that zinc displays the highest capacity, with 0.02mol · g^{-1}, however the high error, along with weak interaction, makes removes any credibility to this value, regardless of the r^2. The capacity trend then follows Pb>Cu>Fe, with lead then showing 0.009 mol · g^{-1}. The Langmuir isotherm fits the data obtained by the IDA functionality isotherm experiments quite well, all metals return r^2 values >0.9, with lead and copper returning values >0.97. The maximum sorption capacities follow a trend of Cu>Zn>Fe>Pb, with copper's theoretical sorption capacity being 0.0043 mol · g^{-1}. Neither the Langmuir nor Freundlich model was capable of fitting the copper adsorption isotherm data for the thiourea functionality, with lead and zinc being reasonably described and iron(II) showing a tentative relationship.

Copper displays more homogeneous binding behaviour for both the WA and IDA functionalities, deriving theoretical q_{max} values closely related to experimental values and poor fits to the Freundlich model. This leads to the assumption that the binding mechanism of both of these resins follows a monolayer coverage with uniform binding energies and a more traditional equilibrium adsorption[27]; while similar to literature descriptions of copper adsorption reactions in strong acid media[23, 36– 41], there is a much lower (although described by a tentative fit) binding intensity for the adsorption of copper towards the carboxylic acid functionality in within this study, emphasising a competition between carboxylic acid functionality and solution phase acetate. Overall, both IDA and WA functionalities have the highest capacity for the adsorption of copper from the resins studied (both within error margins of each other), while thiourea lagged behind in capacity; however, this is taken from an experimental observation as the thiourea functionality data was a poor fit ($r^2 < 0.9$), although this could be due to the degree of scatter within the experimental data.

Iron(II) displays a poor fit to Freundlich towards all functionalities, with the Langmuir providing a better description. Further alluding to monolayer adsorption processes, the Langmuir model was able to predict the maximum loading capacity for both the WA and IDA functionality, however due to the lack of saturation, the values obtained by the fitting of the TP214 isotherms were difficult to compare with certainty. Similarly, to the case of copper, the WA and IDA functionalities displayed the highest capacity for iron(II), with thiourea remaining fairly low despite high K_d values towards lower concentrations[16] and high capacities described in previous studies[26, 42]. Modelling of the thiourea resin isotherm with the iron(II) system poses a challenge due to the possibility of oxidation and iron(III) precipitation; while oxidation is not modelled (Figure S1b) within a closed system, introduction of thiourea functionality and agitation of solution potentially allows for the precipitation of Fe_2O_3 through an alteration in solution oxidation-reduction potential (as alluded to in the predominance diagram in Figure S2).

Lead displays a reasonable fit to the Freundlich and Langmuir isotherm (this is true for all three resins), with little deviation from literature capacities (0.923[43], 1.27[41], 0.912 mmol $\cdot$ g^{-1}[45] for WA, IDA and thiourea functionalities, respectively). The WA functionality isotherm data, displays a similar fit to both models with a low sorption intensity and the allusion to heterogeneous binding. IDA displayed behaviour better fit to the monolayer sorption model with a binding intensity indicative of more homogeneous behaviour. The thiourea functionality displays a low binding intensity (although higher than the WA functionality), leading to the assumption of a homogeneous binding mechanism. The heterogeneous nature

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being alluding to a speciation dependent binding (with PbAc⁺, PbAc₂ and PbAc₃⁻ present in solution), and similar functionalities describing more homogeneous behaviour [23, 36, 40, 41, 45 – 48].

Zinc displays interesting adsorption behaviour, with little adsorption to the WA resin, a closer fit to Freundlich for IDA functionality and a bias towards Langmuir behaviour for the thiourea functionalised resin. Within both WA and thiourea isotherm experiments, saturation was not reached due to complex competition leading to low equilibrium adsorption at this pH (K_d values for such systems have previously been reported as 0.174 for the WA functionality and 0.053 for TP214)[16]; therefore, comparison of experimental and modelled capacities is not possible. The maximum capacity determined by the Langmuir fitting of the IDA functionality data is closer to the experimentally observed maximum, with the largest experimental value being ~0.003 mol · g⁻¹, this coupled with the low stability constants of each zinc-acetate complex leads to the assumption of homogeneous binding.

4.3 Sorption Energies and Interaction

The D-R isotherm model (and the Temkin to a much lesser extent) can be used to determine the energy associated with adsorption. From this, the adsorption process (physisorption, ion exchange or chemisorption) can be determined and therefore, to a small extent, the reversibility of the reaction as well as the potential selectivity of a functional group for one ion over another. The Temkin model describes systems that are heterogeneous in binding nature, similar to that of the Freundlich model[50], however with a linear, not exponential decrease in energy[24, 51]. This isotherm is given by:

$$q_e = \frac{RT}{b_T}\ln\left(a_T C_e\right) \tag{3}$$

where R is the gas constant, T is the temperature of the experiment, b_T is the Temkin isotherm constant relating to the heat of sorption (J · mol⁻¹)[52] and a_T is the Temkin equilibrium sorption isotherm constant (L · mol⁻¹) relating to the maximum adsorption capacity[53]. As with many of isotherm models this model was devised for predicting gas-solid equilibrium isotherms, however in this case is often a poor descriptor of liquid-solid adsorption[25], not only this but the Temkin isotherm is assumed to only fit within a small region of the isotherm (ignoring high and low values of concentrations)[27, 31]; therefore, this model is often ill equipped to describe a system effectively and will be used as supplemental to the D-R isotherm.

Table 3: Variables obtained by fitting the single metal isotherm data to the non-linear Temkin model.

Resin	Values	Copper	Iron(II)	Lead	Zinc
C107E	b_T	2800±200	5900±600	5500±600	5900±900
	a_T	7000±1000	5000±1000	15000±3000	1600±500
	r^2	0.922	0.842	0.859	0.787
MTS9301	b_T	4300±400	6100±600	7600±500	7100±300
	a_T	$4±1×10^5$	$3±1×10^4$	$12±2×10^4$	$5±1×10^5$
	r^2	0.911	0.908	0.953	0.980
TP214	b_T	1700±100	1500±200	2200±300	2100±200
	a_T	$3±2×10^6$	1300±500	7000±3000	1700±400
	r^2	0.925	0.813	0.825	0.924

The Temkin model is unable to describe the data obtained for the adsorption of iron(II), lead and zinc to the WA functionality, with copper displaying the tentative r^2 of 0.922 (Table 3), with a binding energy of 2.8±0.2kJ $\cdot$ mol^{-1}. This model displays reasonable fits to the sorption of lead and zinc to IDA, as both display the most heterogeneous behaviour towards this functionality, with r^2 values of 0.953 and 0.980, with copper and iron(II) having more tentative fits. The tentative trend of sorption energies obtained therefore follows Cu<Fe<Zn<Pb. The Temkin model returned tentative fits to both copper and zinc isotherms (r^2 0.914 and 0.931, respectively) with binding energies of 1.7±0.1 and 2.1±0.2kJ $\cdot$ mol^{-1}, respectively, while both iron(II) and lead returned poor fits with this model (r^2 0.831 and 0.847, respectively).

The Dubinin-Radushkevich (D-R) isotherm is used to determine the binding energy of a specific sorption process, allowing characterisation of the adsorption mechanism[24, 25]. This isotherm is described by:

$$q_e = q_D exp^{\left(-B_D\left(RTln\left(1+\frac{1}{C_e}\right)\right)^2\right)} \tag{4}$$

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where q_D is the capacity (mol · g^{-1})[27, 31, 54], R is the gas constant and T is the temperature at which the experiment is conducted. The constant B_D related to the free energy of adsorption, E (kJ · mol^{-1})[24, 34], of the sorbate species to the surface of the resin. This can be calculated using:

$$E = \frac{1}{\sqrt{2B_D}}$$ (5)

Using this calculation, assumptions can be made of the binding mechanism of the adsorption. If E is <8 kJ · mol^{-1} the binding mechanism is assumed to be physical (physisorption), 8 kJ · mol^{-1} <E <16 kJ · mol^{-1} it is assumed to be ion exchange and if E is >16 kJ · mol^{-1} then the adsorption mechanism can be assumed to be chemical (chemisorption)[38, 55].

Table 4: Variables obtained by fitting the single metal isotherm data to the non-linear D-R isotherm model.

Resin	Values	Copper	Iron(II)	Lead	Zinc
C107E	q_D	0.011±0.002	0.0034±0.0006	0.027±0.005	0.009±0.002
	B_D	7.0±0.7×10^{-9}	6±1×10^{-8}	1.02±0.06×10^{-8}	1.6±0.2×10^{-8}
	E	8.4±.4	9.4±0.8	7.0±0.2	5.5±0.3
	r^2	0.943	0.842	0.985	0.953
MTS9301	q_D	0.007±0.001	0.0039±0.0005	0.0067±0.0007	0.0044±0.0003
	B_D	2.5±0.4×10^{-9}	3.7±0.6×10^{-9}	4.5±0.3×10^{-9}	2.5±0.2×10^{-9}
	E	14±1	11.6±0.9	10.5±0.3	14.0±0.6
	r^2	0.852	0.853	0.977	0.965
TP214	q_D	0.0019±0.0001	0.0020±0.0004	0.0020±0.0003	0.0009±0.0001
	B_D	1.8±0.3×10^{-9}	1.4±0.2×10^{-8}	1.0±0.1×10^{-8}	8±1×10^{-9}
	E	17±1	6.0±0.5	7.1±0.4	7.8±0.5
	r^2	0.919	0.918	0.961	0.928

For copper, lead and zinc, the D-R model fits quite well to the WA data (Table 4), as these metals return r^2 values of 0.943, 0.985 and 0.953, respectively, however iron(II) returns a low value of 0.842, therefore the

values obtained are more tentative. The free energies of adsorption for metals on the surface of this resin follow a different trend, with the derived values following the trend Fe>Cu>Pb>Zn, opposite to that of the Temkin values (with the omission of the extremely tentative iron(II) value), which is to be expected if the Temkin energies relate to the energy required for binding. The isotherm data of lead and zinc adsorption to IDA was adequately described by the D-R isotherm, with both iron(II) and copper showing far less correspondence to the model (r^2 ~0.85), leading to the tentative trend in energies of adsorptions of Cu>Zn>Fe>Pb. The thiourea functionality isotherm data for all metals returned a fit to the D-R model with r^2 values >0.91. The free energies of adsorption of this resin displayed a different trend, with iron(II), lead and zinc displaying free energies within similar regions (6, 7.1 and 7.8kJ · mol^{-1}, respectively), while copper returned an energy of 17kJ · mol^{-1}.

Copper displays an ion exchange mechanism for the adsorption to both IDA (while tentative, it agrees with literatures values[38, 39]) and WA functionality (14±1 and 8.4±0.4kJ · mol^{-1}). The free energy is tentatively much larger for MTS9301, rationalised by a bidentate binding mechanism theorised by this resin, forming much more stable chelation complex, while increasing the entropy of the system, from the potential release of not only acetate ions but also two protons from the IDA functionality; agreeing with a lack of interference of the acetate species to copper extraction by IDA. The WA functionality does not produce energy values that agree with literature sources, which allude to strong ion-exchange extraction mechanisms (~15kJ · mol^{-1})[39], whereas in this study the competition between carboxylate functionality and solution-phase acetate reduced binding energy to 8.4±0.4kJ · mol^{-1}. The Temkin binding energy for copper to the WA functionality is much lower than that of IDA, due to a greater extent of ligand transfer when adsorbed by the IDA functionalised resin.

The argument for a redox reaction between copper and thiourea can be further justified by the calculation of high sorption free energies (17kJ · mol^{-1}), alluding to a chemisorption process, with the better fit to the Temkin isotherm (over Langmuir and Freundlich) alluding to a heterogeneous binding mechanism, supported by the multitude of species formed by the redox reaction between aqueous thiourea and copper(II)[56, 57]. Studies within strong acid media (but low ionic strength) do not display trends describing a similar redox process (free energy of 5.28kJ · mol^{-1}[48, 58]). However, thiourea has been previously observed to out compete the binding of copper with solution phase citrate and lactate complexes, having a high affinity for this ion over iron(II), lead and zinc[16], alluding to high ionic strengths facilitating the reaction.

The poor fits of the WA and IDA functionality data to the D-R isotherm for iron(II) leads to tentative assignments of the mechanisms as ion exchange. With respect to the thiourea isotherm, the low oxidation-reduction potential required for oxidation and precipitation at this pH throughout the isotherm concentration range leads to the assumption of Fe_2O_3 formation (Figure S2). Due to the high concentration of iron within sewage sludge being deleterious to the adsorption of other species, this precipitation is beneficial for the removal of the other metals.

Lead returned a free energy value closer to physisorption (7 kJ · mol^{-1}) for the carboxylic acid functionalised resin, despite the ability of this resin to extract lead selectively from other complexing media[16]. The competition of lead-acetate complexes (being 25% PbAc$^+$, 50% PbAc$_2$ and 25% PbAc$^-_3$) and the WA functionality led to a free energy of binding value higher than that of strong acid media values (3.5kJ · mol^{-1})[47]. The much higher free energy reported for IDA functionality is potentially due to the diacetic acid functionality creating a bidentate ion exchange process, breaking the acetate complexation, which can be supported by the Temkin binding energy, which is high, relative to the other metals studied. Thiourea functionality displays physisorption binding energies towards lead, again concurrent with the lack of exchangeable ions; interestingly, higher energy than that of literature values[48].

Zinc still displays far lower free energy of adsorption and binding energy towards the WA resin, which could be explained by the extremely low stability constants of zinc to carboxylic acid complexes[16], with a ligand transfer between the carboxylic acid groups on the resin surface and solution phase acetate. The free energy of adsorption related to the sorption to the IDA functionality implies a strong ion exchange interaction, most likely to do with the chelating effect of this functionality, allowing for the interaction between the nitrogen atom as well as both carboxylic acid functionalities. Thiourea functionality displays physisorption towards this metal through both free energy of adsorption, with the lowest overall capacity calculated. Weak Van der Waals forces are the most likely present, supported by the low Temkin binding energy calculated.

4.4 Correlation of Physical and Chemical Parameters to Modelled Values

Summaries of the comparisons of values derived by isotherms to the ionic radii, the average ΔH and ΔS of metal-acetate complex formation and electronegativity are included in Table S2, with the important findings displays in Figures S7 - S10 in order to generate tentative correlations between ionic properties and isotherm values. With the exception of zinc, the WA functionality seems to have the trend of increasing capacity with

electronegativity (Figure S8), intensity of binding and energy of binding however display a tentative decreasing trend towards increasing electronegativity (Figures S9 and S10). This is understandable, as this functionality relies purely upon the attraction to a negative charge for extraction, and the behaviour of zinc corresponds to the extremely low stability constants of zinc acetate complexes[16].

The q_{max} of the IDA functionality for metals depends, exponentially, on the ionic radius of the metal observed; the smaller the ionic radius, the higher the capacity (Figure S7). The rationale for this is the chelating nature of the resin. This trend is again observed, linearly, when comparing the intensities of binding; leading to the assumption that the equilibrium for this resin is dictated entirely by ionic radii. The thiourea functionality results could be skewed due to the redox reaction that occurs between thiourea and copper(II).

4.5 Capacities and Resin Performance

While mechanisms of binding and specific interactions of resins with a species is fundamentally interesting; in order to gauge the relative performance of a resin within the conditions specified, each system will be required to be compared to other similar ion exchange systems. This section will focus on such a comparison, using either the derived Langmuir or D-R capacities (dependent on which was best-fitting). Within this section, all values of capacity will be converted from $mol \cdot g^{-1}$ to $mg \cdot g^{-1}$ for comparison with the literature. These can be used as justification for the choice and usage of a resin within the proposed resin-in-pulp system.

The carboxylic acid and IDA functionalised resin displayed monolayer ion exchange mechanisms towards copper(II), their capacities are 320 ± 60 $mg \cdot g^{-1}$ and 273 ± 40 $mg \cdot g^{-1}$, respectively, both being within error of one another; both resins displaying capacities well beyond that of the bispicolylamine functionalised M4195 (although recorded at pH 2)[59], which is an effective copper(II) extractor at low pH values[18]. For the extraction of copper(II) from solution, the IDA functionality is more prevalent within the literature among the commercially available[37, 38, 40, 60] (which include S930[38] and S930+[60], predecessors to the MTS9300 and MTS9301 resins) and novel adsorbents[41, 61, 62]. However, the extraction within this study is higher than many literature values double that of S930[38] and double that of the manufacturer's specifications, giving rise to the suggestion that two Cu^{2+} ions bind to one IDA functionality. Comparable literature capacities have been achieved with the weak acid functionalised resin NDMC (novel) and C106 (Purolite), at 239.9 and 236.7$mg \cdot g^{-1}$, respectively[39], with these values within error of the MTS9301 and C107E data from this study (C107E being comparable to C106, though being described as a 'potable water grade' resin by the manufacturer data sheet).

Interestingly, the C106 resin displayed a free energy of copper adsorption almost double that of C107E ($15.04 \, kJ \cdot mol^{-1}$ vs $8.4 \pm 0.4 \, kJ \cdot mol^{-1}$), with the NDMC resin, C106 and IRC748 having free energy of adsorption $>1 \, kJ \cdot mol^{-1}$[39] higher than that of MTS9301 within acetic acid media; assumed to be due to the stabilisation of the acetate complexes within solution. This alludes to the reason for the decrease in capacities of the resins. The thiourea functionalised resin, with a speculated redox reaction adsorption mechanism has the lowest capacity of all three with a D-R isotherm capacity of $121 \pm 6 \, mg \cdot g^{-1}$, which is comparable to many modified silica and chitosan adsorbents[48, 52, 58, 63]. The difference lies with the large free energy value $17 \, kJ \cdot mol^{-1}$, especially when considering the other thiourea functionalised adsorbents[48, 58]. While the stronger adsorption of TP214 would be preferential for extraction from a sewage sludge pulp (due to the pregrobbing from sewage sludge organic matter[64]), the far superior capacity and the higher likelihood of regeneration of the MTS9301 resin makes it a better choice.

Extraction of iron(II) was low for these resins, with all three functionalities displaying lower affinities for iron(II) than all other metals. While this would not be favourable with respect to the other metals, the low affinity for iron(II) is a positive attribute for the resins to have in order to eliminate competition; as iron is of low value and has no agricultural restrictions[6], it is not necessarily advantageous to remove from the sludge. If iron(III) were to remain in solution, however, there would be a tendency for thiourea functionalities to maintain a higher capacity for this species, over iron(II); as a study conducted on functionalised chitosan displayed a $71.9 \, mg \cdot g^{-1}$ capacity for iron(III) compared to a $48.3 \, mg \cdot g^{-1}$ capacity for iron(II), however this was synthesised with an iron(III) template[26], with unmodified chitosan having higher capacity for iron(II) at $51.81 \, mg \cdot g^{-1}$[42]. This could also, however, be explained by the potential for precipitation of Fe_2O_3 (Figure S2).

The calculated capacities of C107E and TP214 for lead were unreliable, due to the under-saturation, and the potentially heterogeneous mechanisms. The extrapolation required for C107E and TP214 devalues calculated values for capacities, leaving the only reliable capacity being that of MTS9301 returning a capacity of ~$400 \, mg \cdot g^{-1}$. The high capacity of MTS9301 for lead within this study unperturbed by the acetate complexes, being on par with commercial and novel macroporous alternatives[23, 36, 40, 41, 45–47], and outperforming cheap, alternative sorbents (activated carbon, inorganic sorbents and biomass materials[65, 66, 68]).

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At the pH that these experiments were conducted at, zinc did not display high distribution coefficients towards the C107E resin[16], due to this low equilibrium it was difficult to convincingly predict maximum capacities for zinc to the surface of the resin, as a maximum value was not reached. Therefore, the highest maximum value calculated for zinc was via D-R isotherm, calculated at 600±100 mg · g^{-1}. However, again, due to the poor K_d values obtained, these capacities are unreasonable to assume as correct. MTS9301, on the other hand displays capacities that are reasonable at 200±70 mg · g^{-1} assuming homogeneous binding (Langmuir behaviour), also displaying double the milliequivalent capacity of the manufacturer specifications, alluding to the binding of two Zn^{2+} ions to each IDA functional group. Both of these resins display, experimentally, a higher capacity for zinc than the thiourea functionalised resin, which was reported to have a monolayer capacity of only 40±10 mg · g^{-1}. Interestingly, the thiourea functionality was found to display the highest capacity from the literature, with the IDA functionalised IRC748 displaying only 19.7 mg · g^{-1}[37], but a novel thiourea functionalised adsorbent displaying a capacity well beyond that of this study with 226.32 mg · g^{-1} (although at pH 7)[49], also out-competing studies conducted on strong acid functionalised resins, with capacities of ~40 mg · g^{-1} to 70 mg · g^{-1}[55, 70].

Interestingly, while the acetate moiety does affect the performance of each resin, it is not necessarily deleterious to the entire performance of each resin. The carboxylic acid functionalised C107E is effective at the removal of lead from solution, with saturation not reached within this study, whether there are kinetic limitations with this extraction or not will need further research. TP214 displays an extremely strong affinity for copper, while lacking in capacity for all other metals. The strength of binding between the thiourea functionalised resin and copper, apparent towards much lower pH values, generates the possibility of a highly selective process for the removal of copper from a sludge high in copper concentration with potential for high returns. Overall, however, the most effective extractant was MTS9301, with reasonably high free energies of binding and high capacities. The capacity for lead wasn't as high as for C107E, but on par with literature sources. Within the resin-in-pulp process, each of these resins could be utilised for their own purpose, depending on the contaminant metals, and whether the focus is extraction of value from metals or from phosphate nutrients.

5 Conclusions

Single metal isotherm analysis of C107E, MTS9301 and TP214 has been conducted for copper, iron(II), lead and zinc. This is in part of work towards the removal of metals from sewage sludge by resin-in-pulp. Consideration of the effect of acetate complexation on performance and mechanism has been discussed.

Copper was found to undergo a homogeneous binding mechanism to the surface of C107E and MTS9301, both having free energies of adsorption (calculated by the D-R isotherm, however with a poor fit to the MTS9301 data) relating to ion exchange mechanisms; the acetate media hindering the weak acid resin performance. TP214, displayed a free energy of adsorption relating to chemisorption, higher than the other metals studied, further alluding to a proposed redox reaction. The C107E and MTS9301 resins both displayed capacities for copper that were similar to those reported in literature sorbents, while TP214 lagged behind in performance (while maintaining a large free energy).

While there is a possibility for iron(II) to oxidise and precipitate, it was assumed throughout the study that iron(II) would likely remain the dominant species in solution at this pH. This species still, however, displayed poor performance throughout. While this metal had the lowest reported capacities, extraction of this metal is not a required feature of the selected resin, therefore advantageous to the proposed system resin-in-pulp system.

For all resins studied within this body of work, lead was observed to display the most heterogeneous binding to the resin surfaces because of the variety of complex species in solution. The capacity of MTS9301 for lead was similar to that described by literature, while saturation was not attained by either C107E or TP214, due to competition between adsorption and acetate complexation. In both cases, this competition increased the reported D-R free energy of adsorption relative to strong acid media.

For C107E and TP214, zinc loading was not observed to reach saturation, assumed to be hindered by acetate media due to weak interactions with functional groups. C107E and MTS9301 both returned relatively close fits to Langmuir and Freundlich models, returning values relative to high homogeneity. The most reliable capacity value returned from the monolayer sorption model was that of MTS9301 which is comparable to the higher literature values, while TP214 was found to perform poorer than literature thiourea studies.

Of the resins studied within this body of work, MTS9301 was the best overall performer. The selectivity of thiourea for copper (and the strong interactions between), warrants further inspection, while C107E displayed a higher capacity for lead and had similar performance for copper, however poor performance with regards to zinc. The complexing nature of MTS9301 has given this resin a strong recommendation in the selection of a resin within the resin-in-pulp system.

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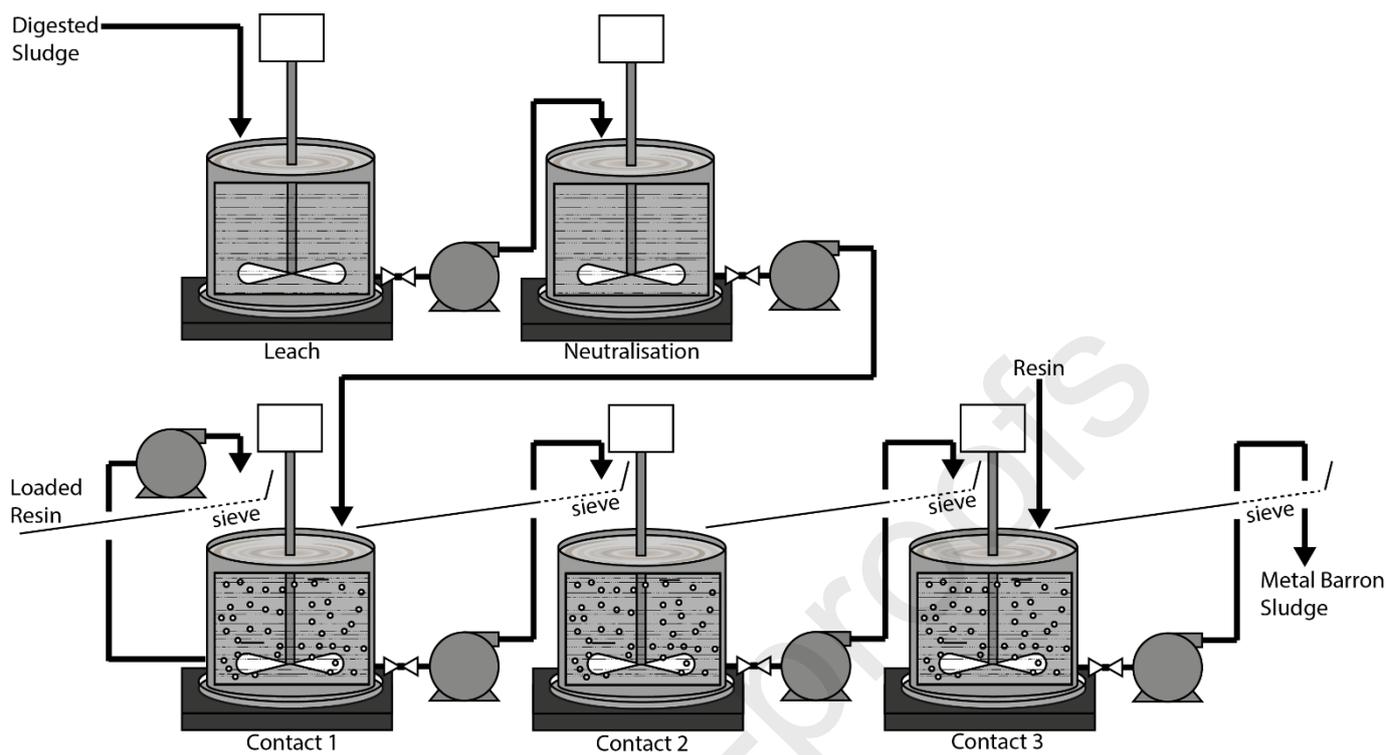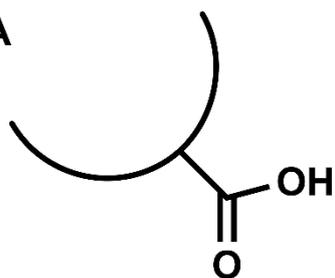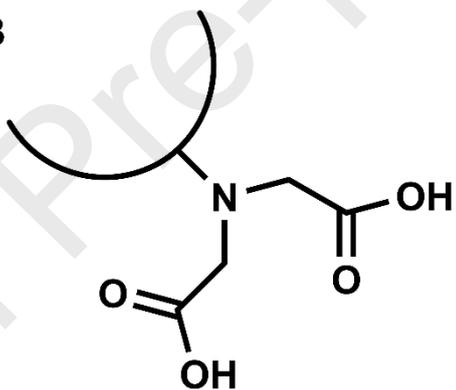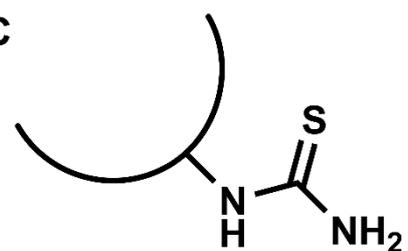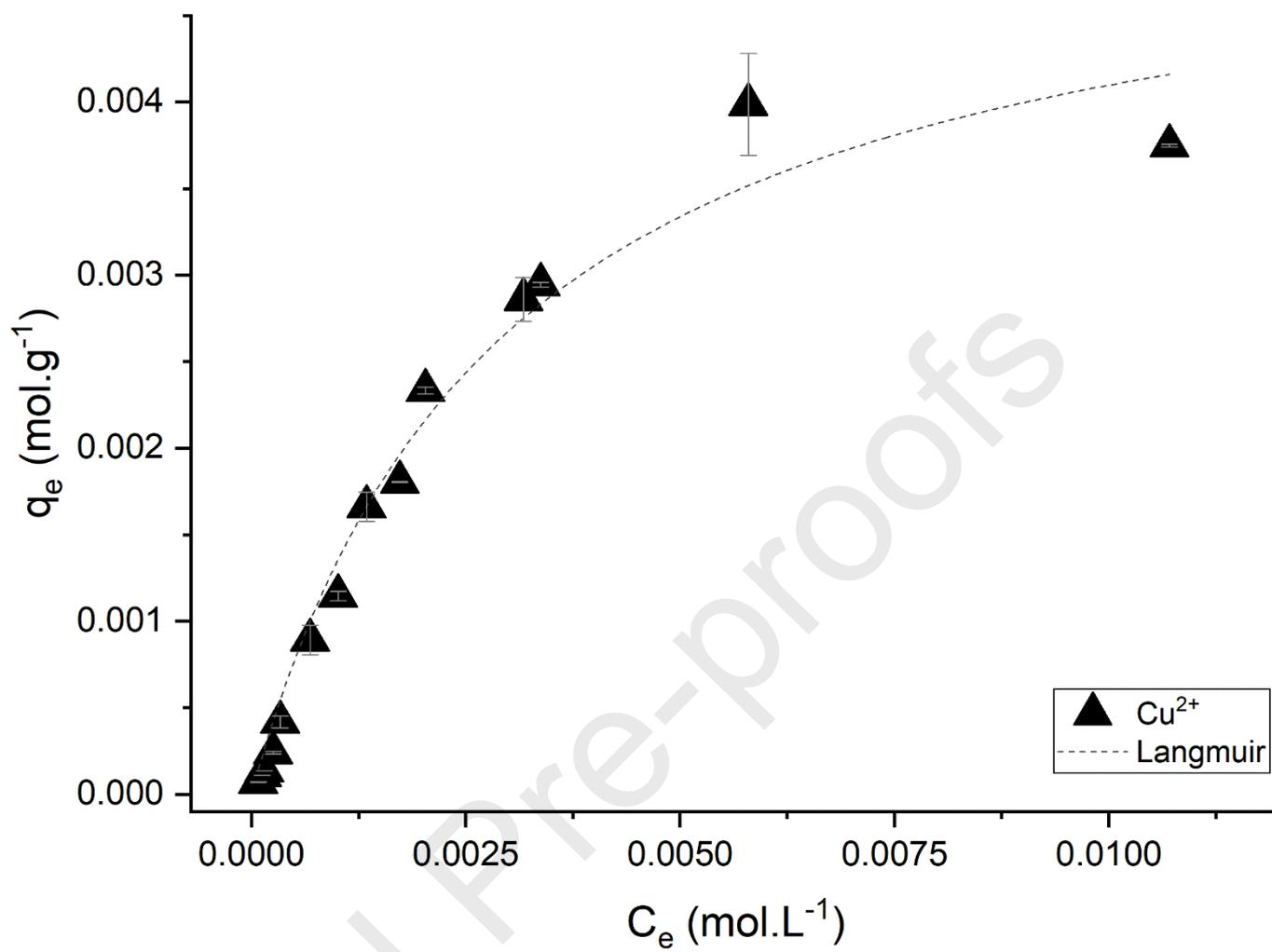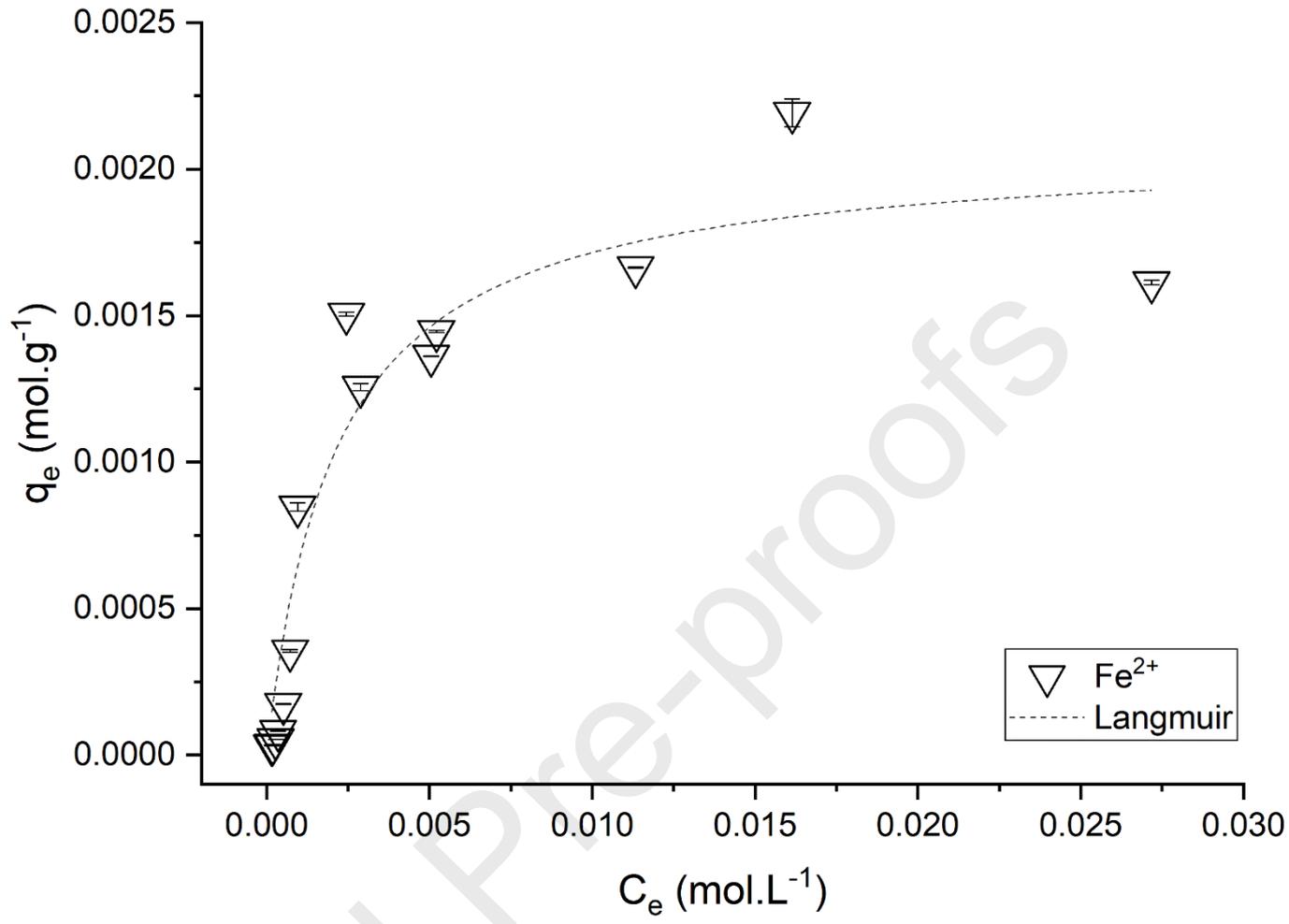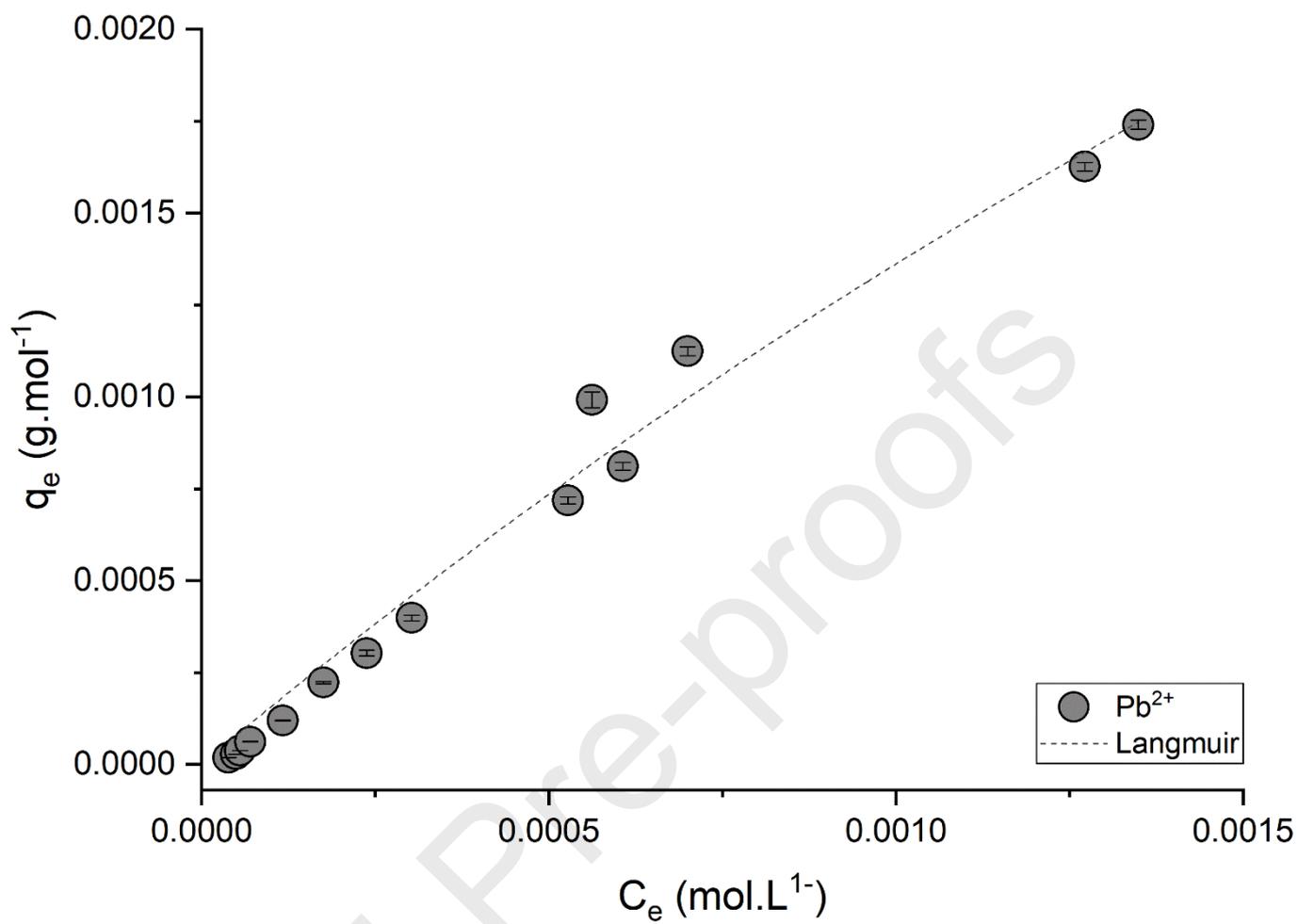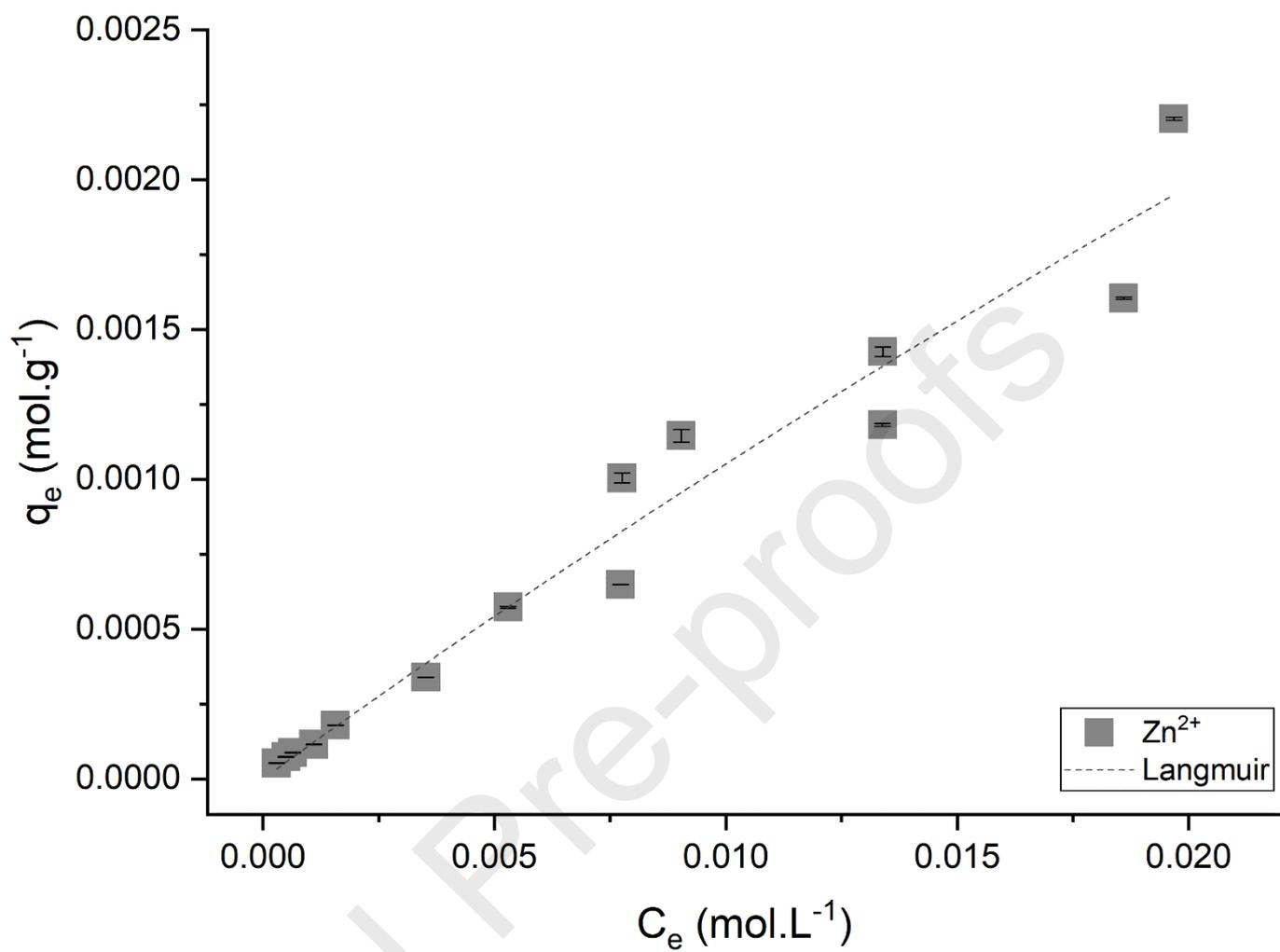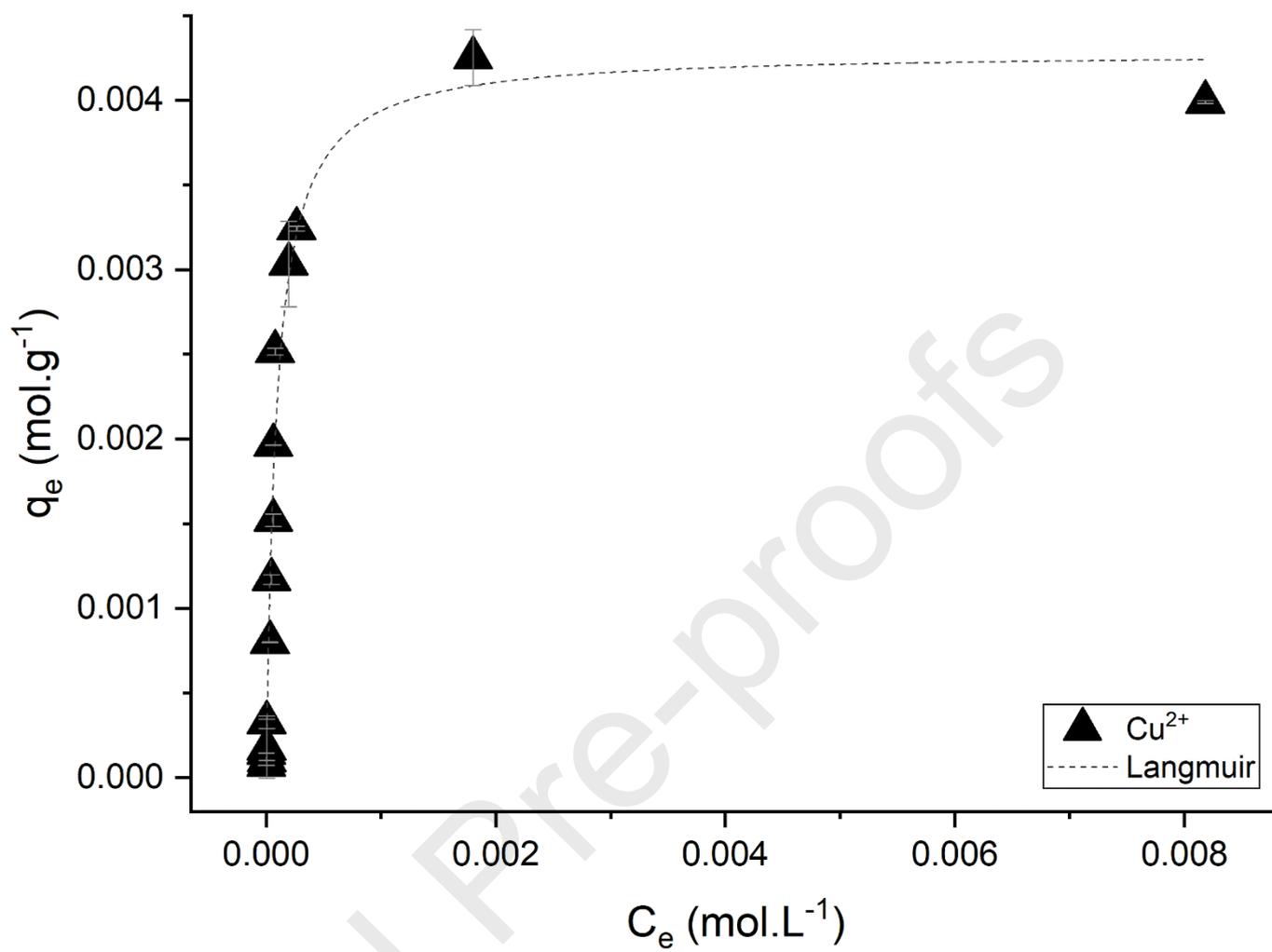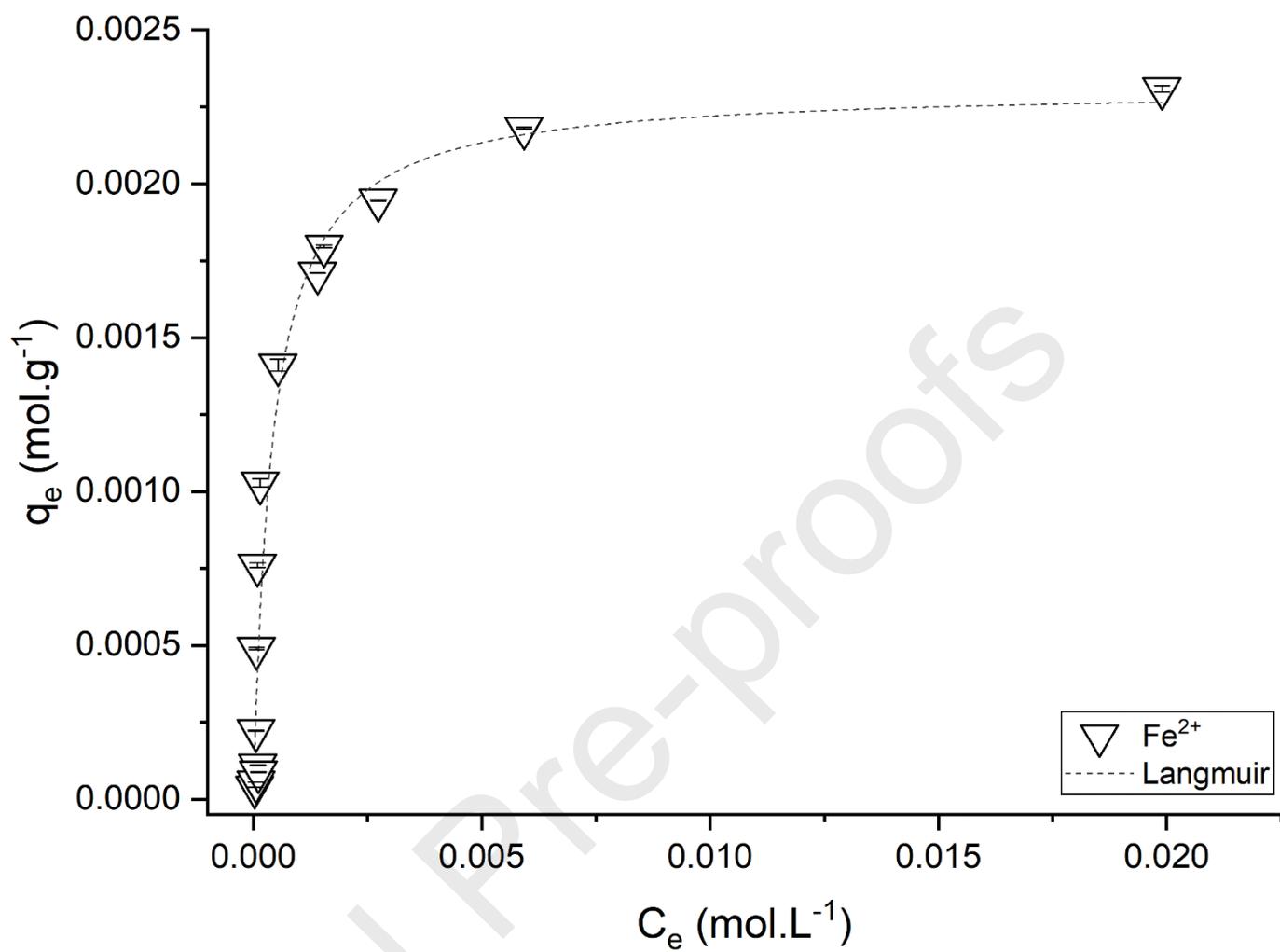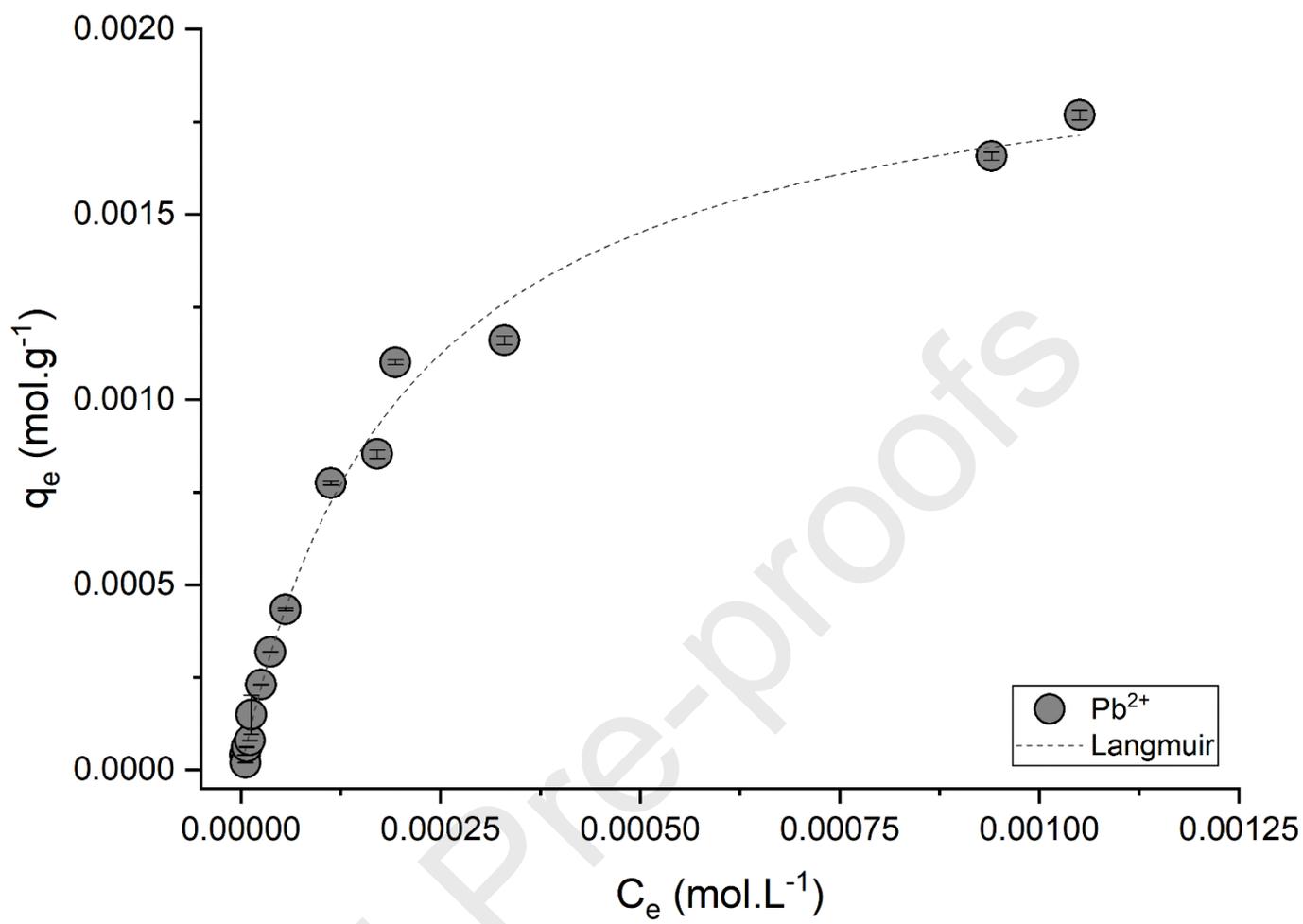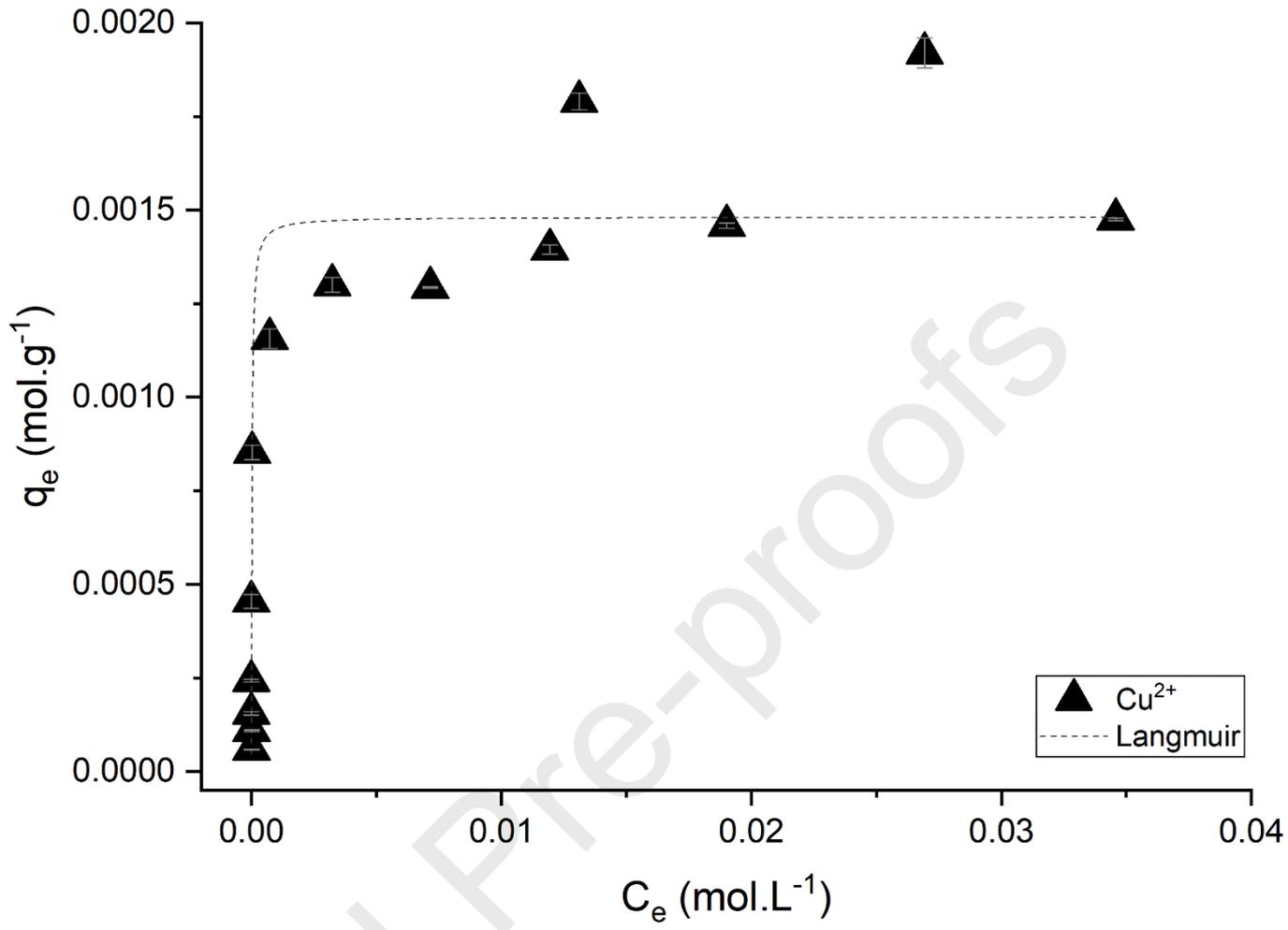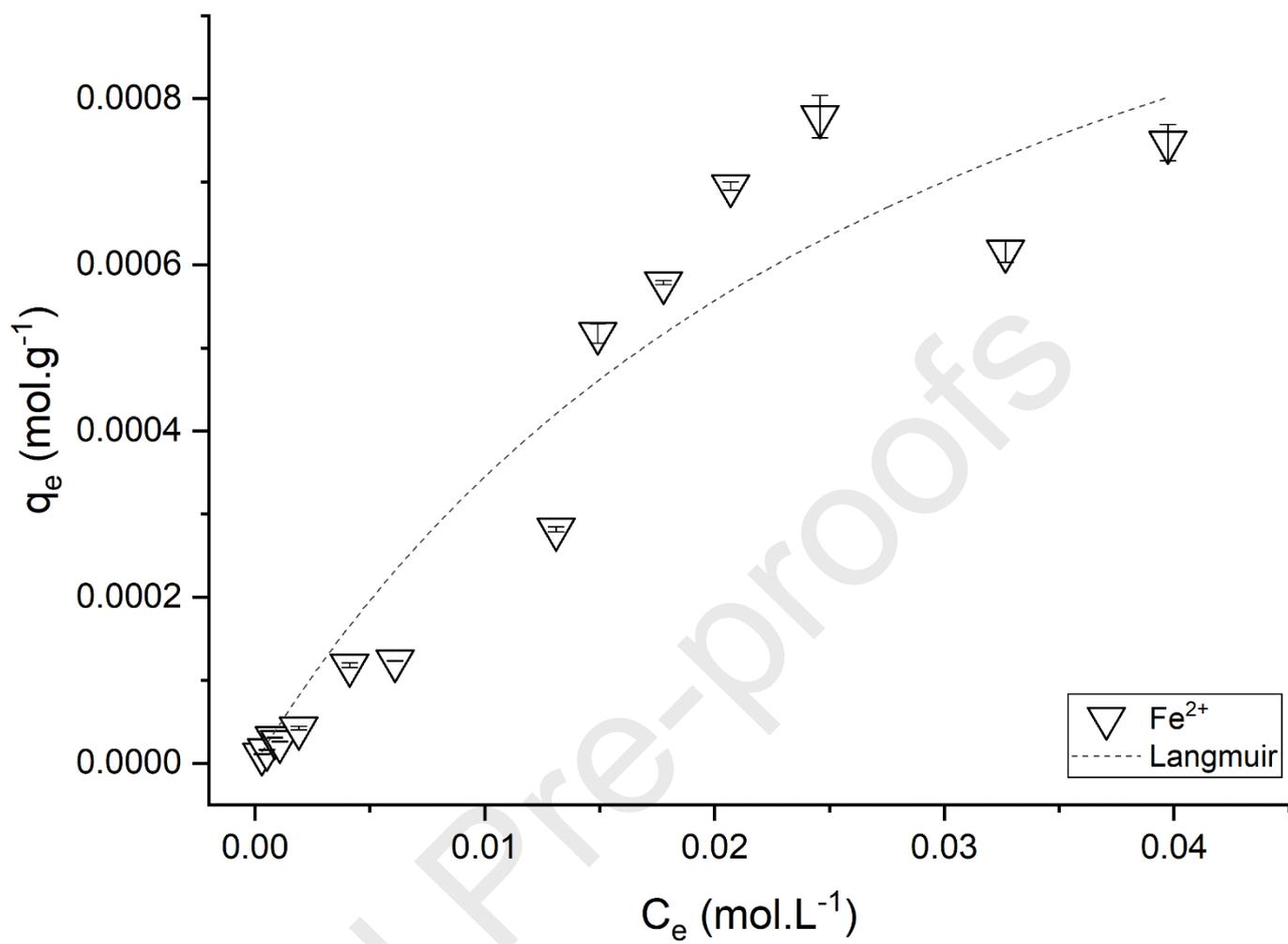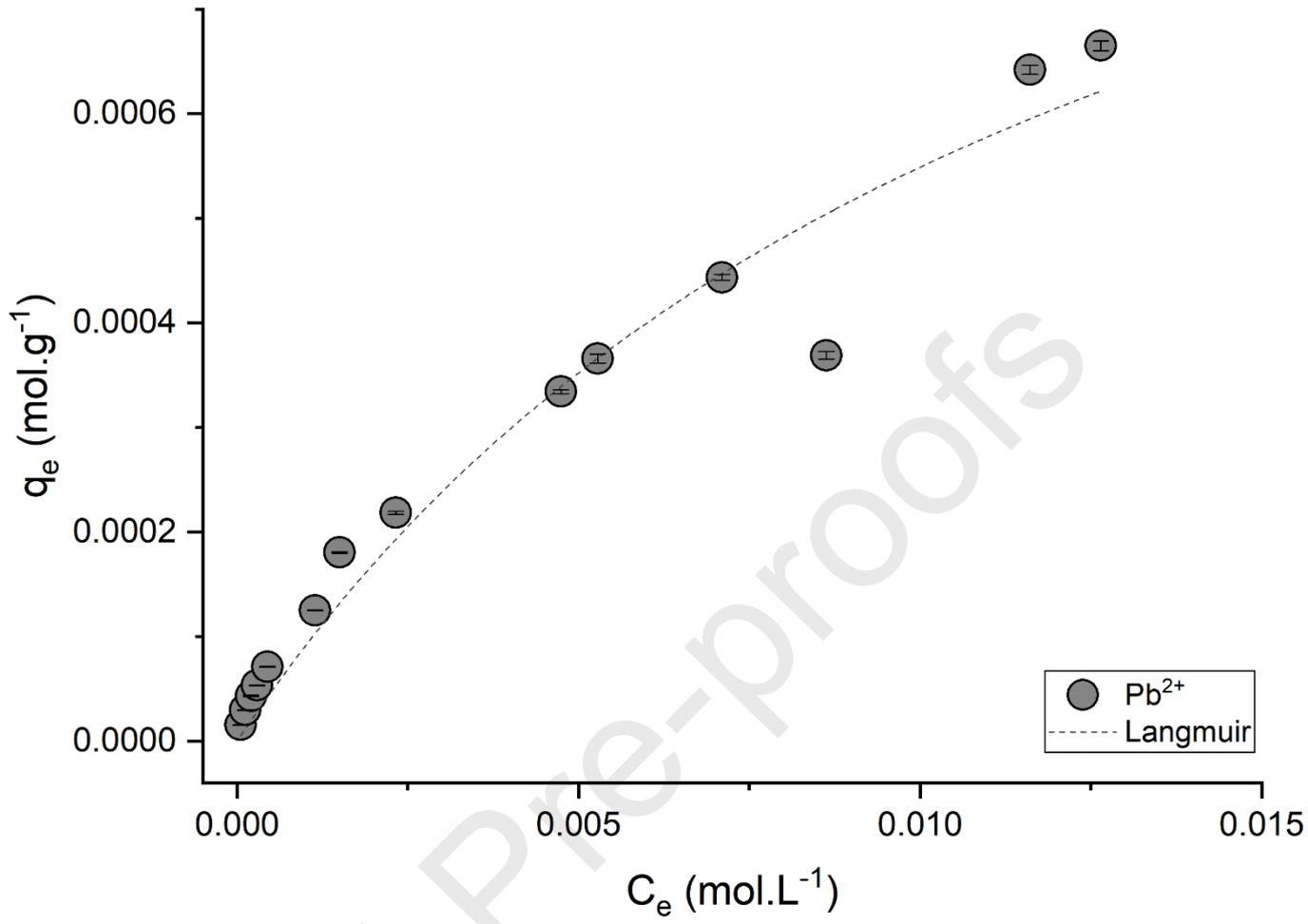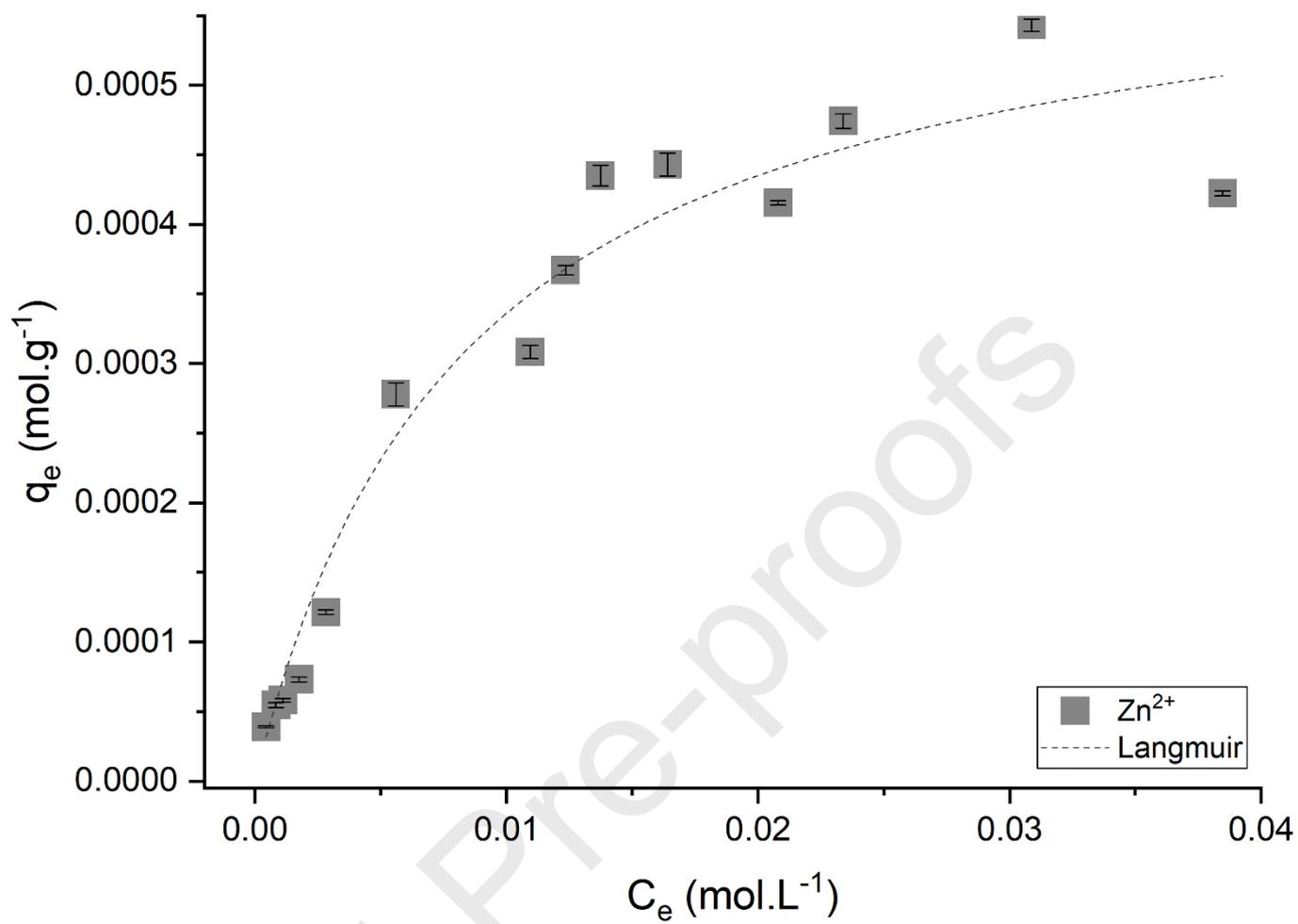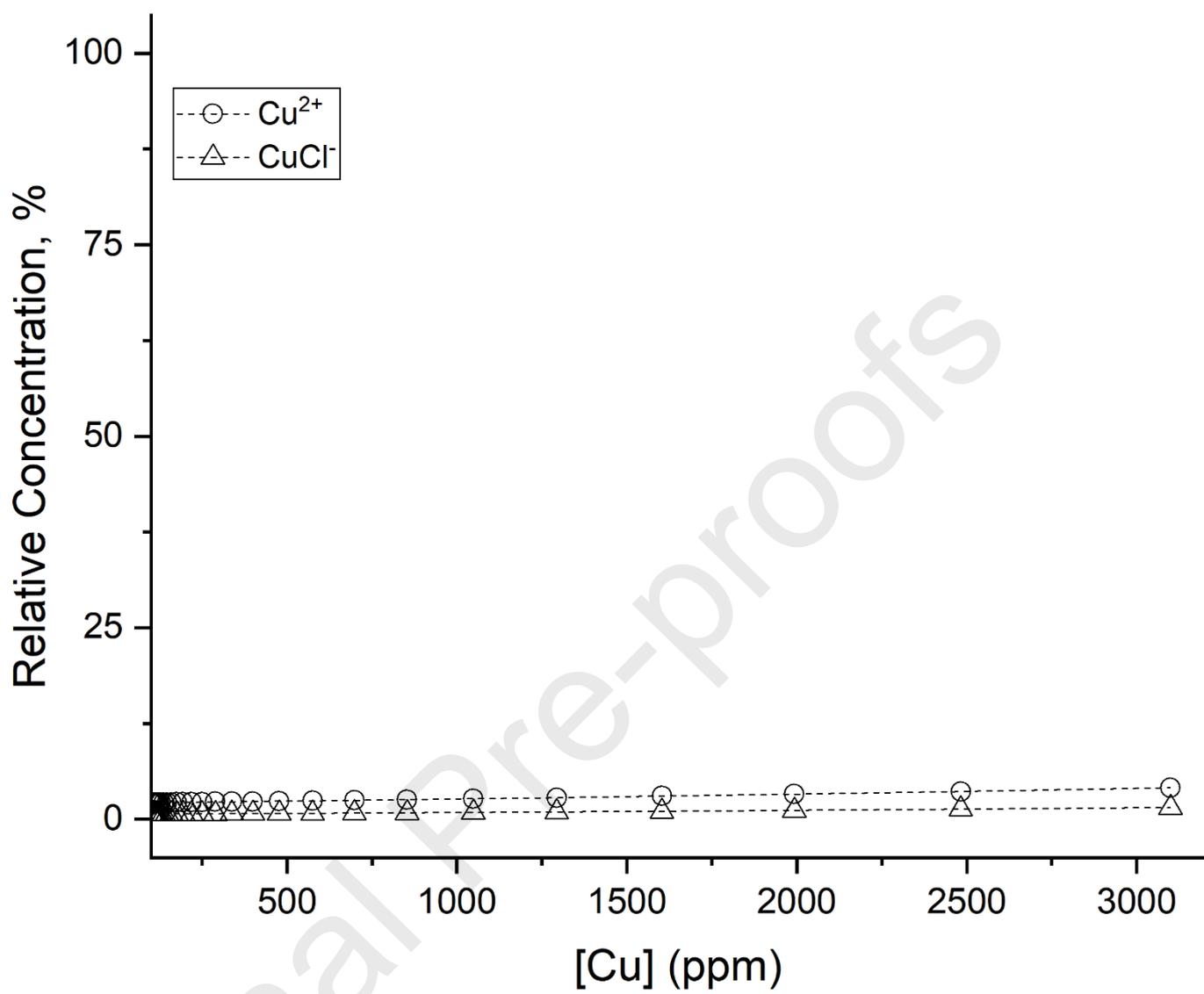
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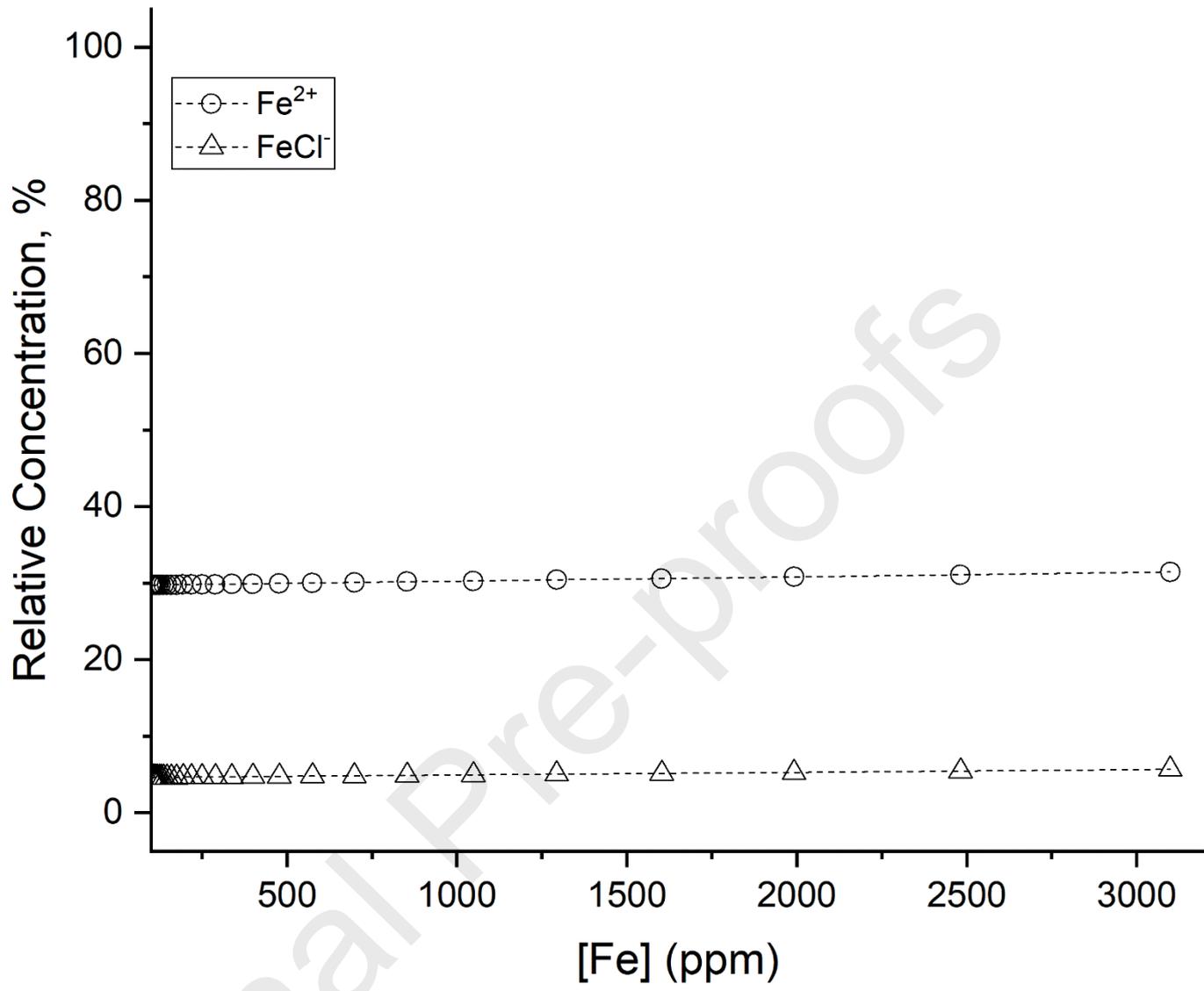
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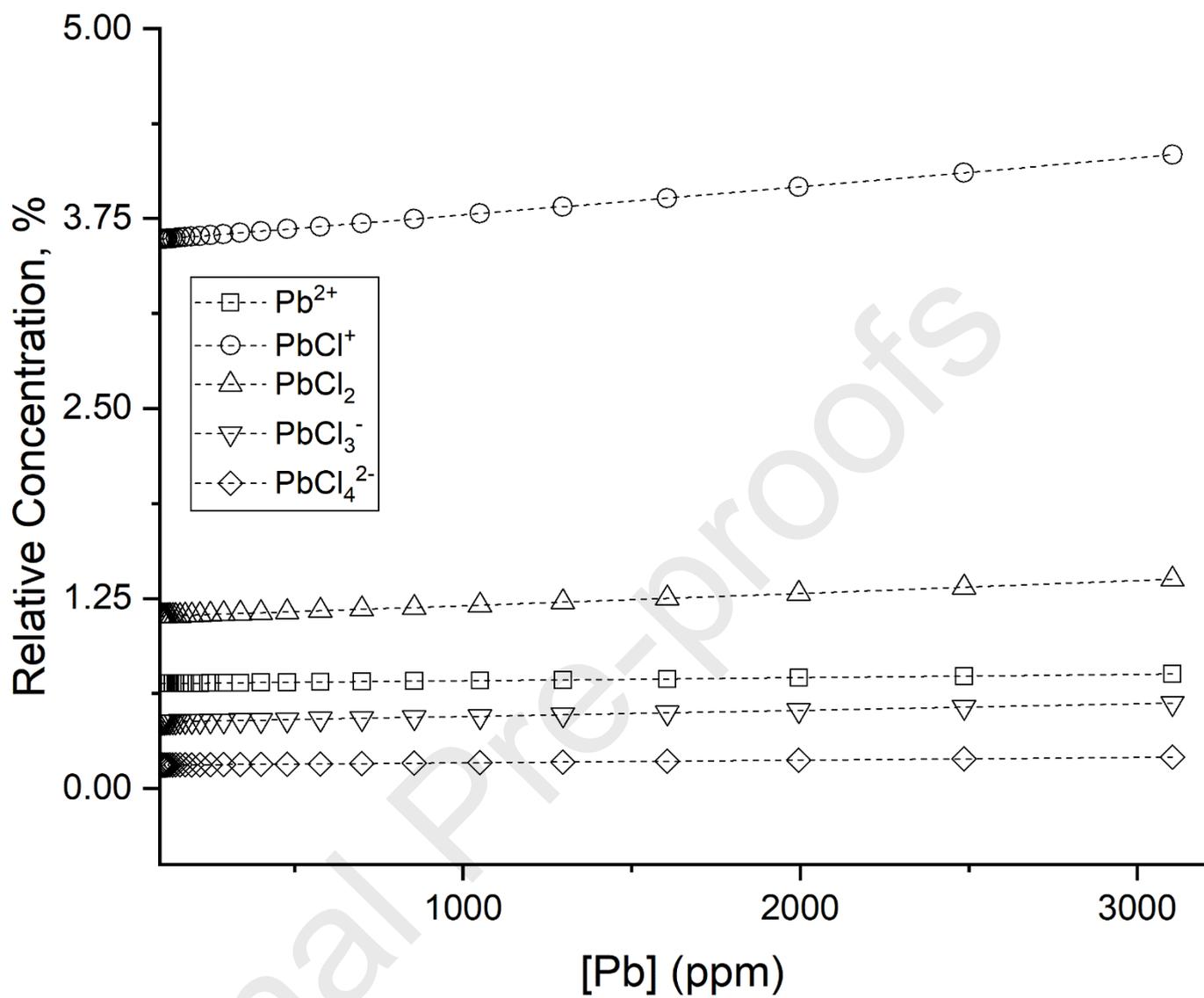
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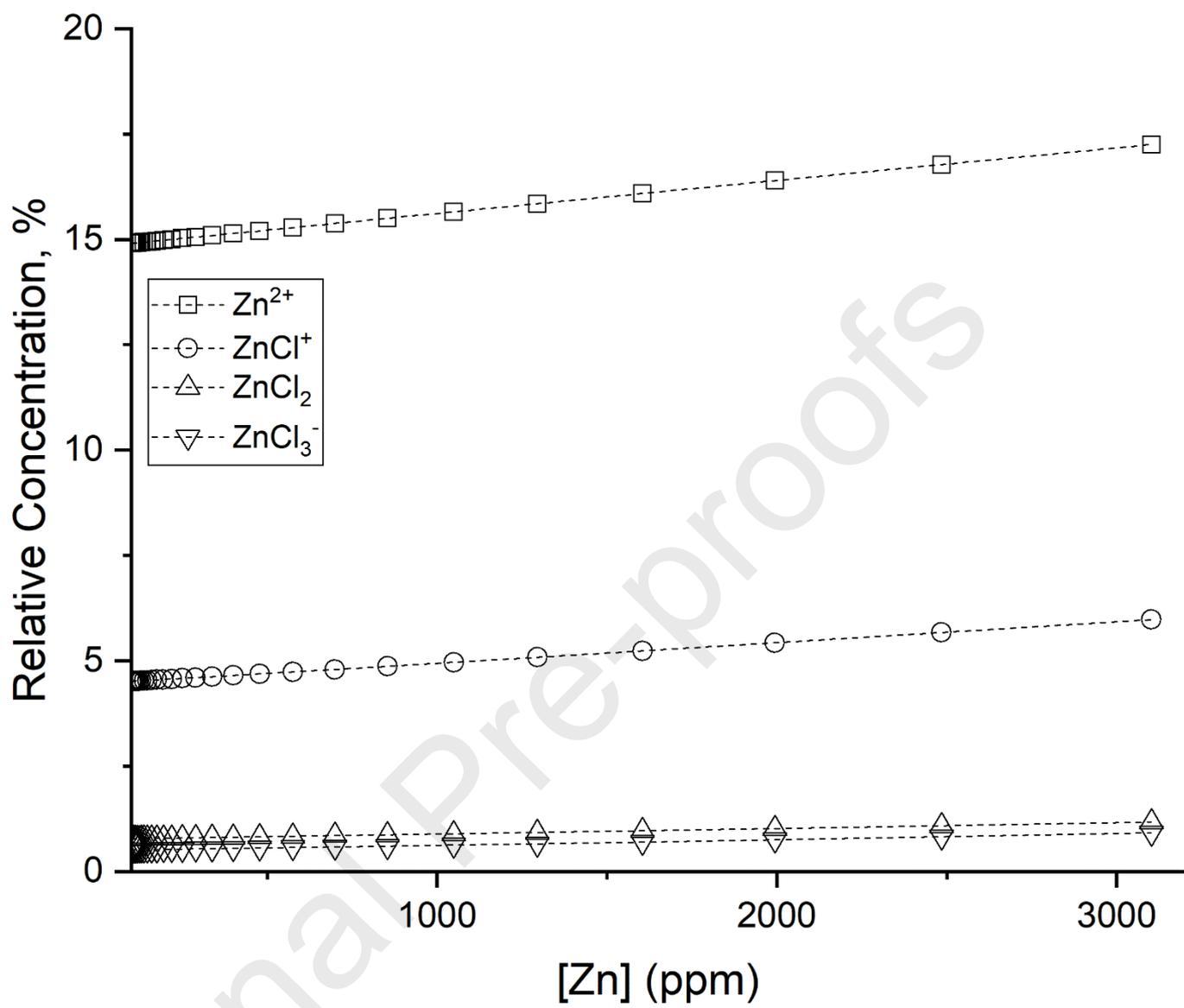
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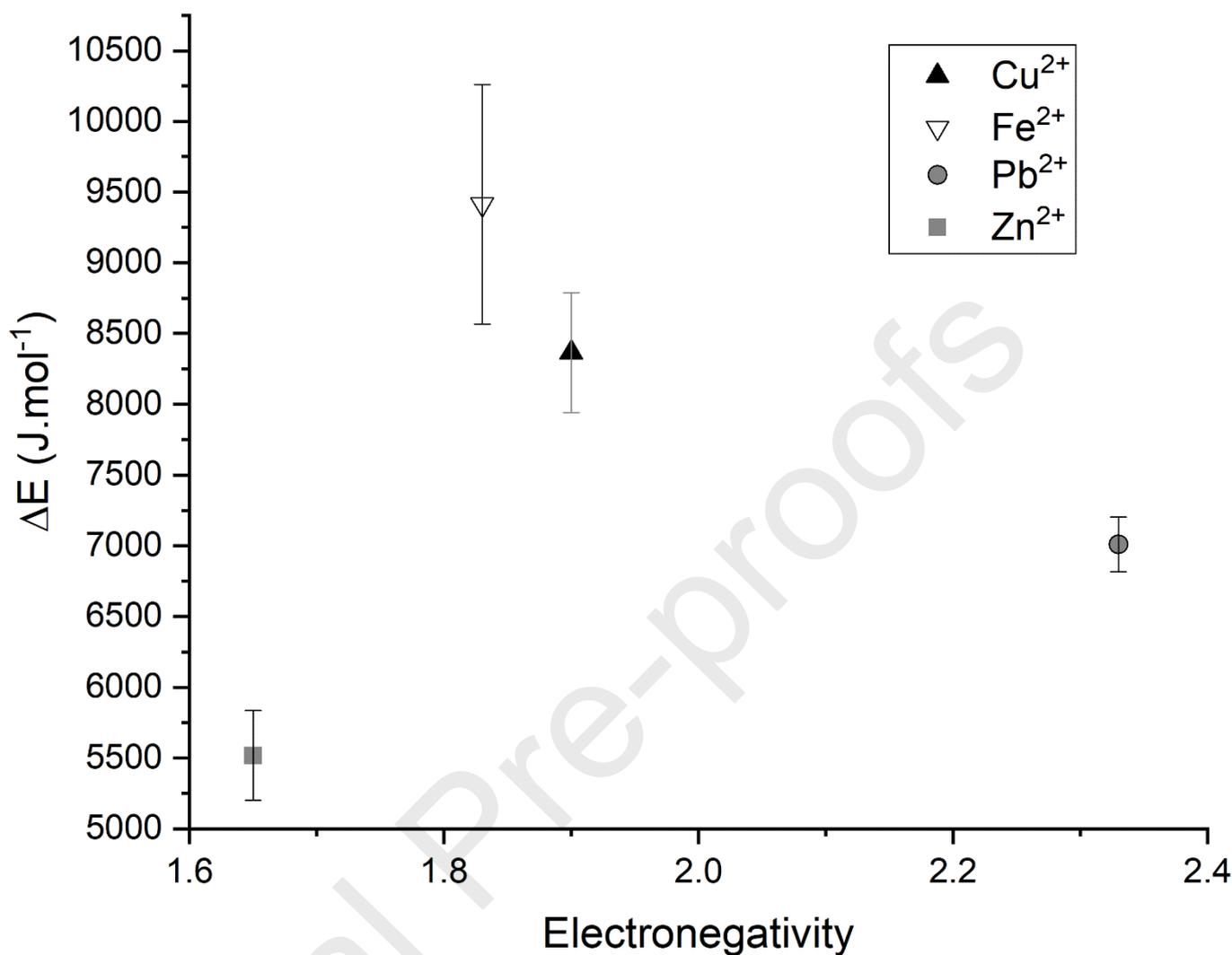
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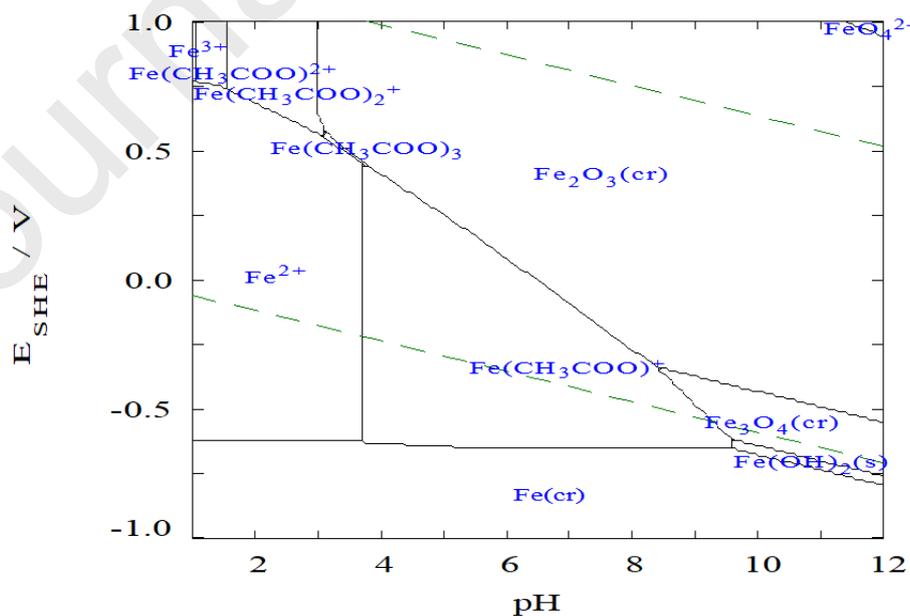
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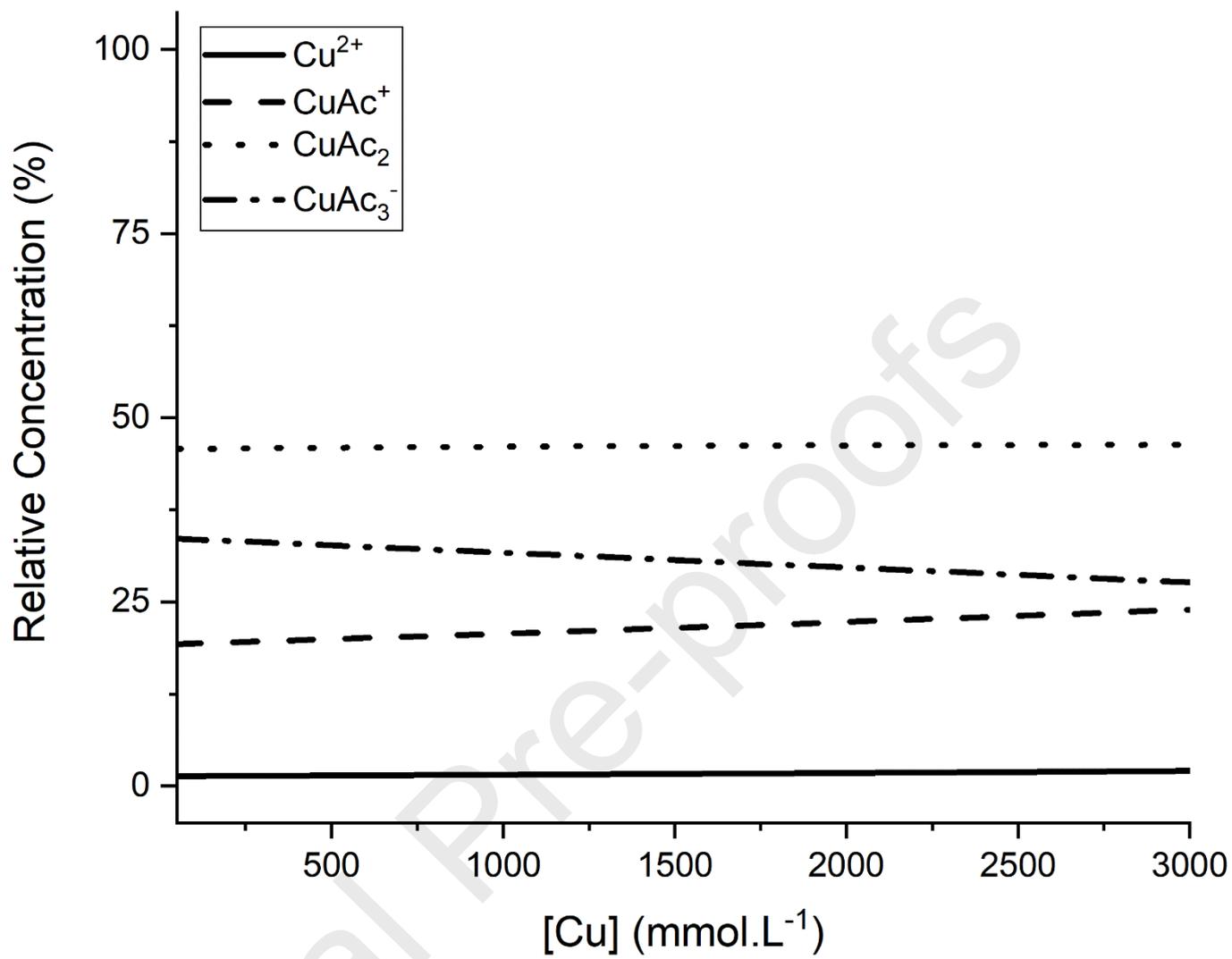
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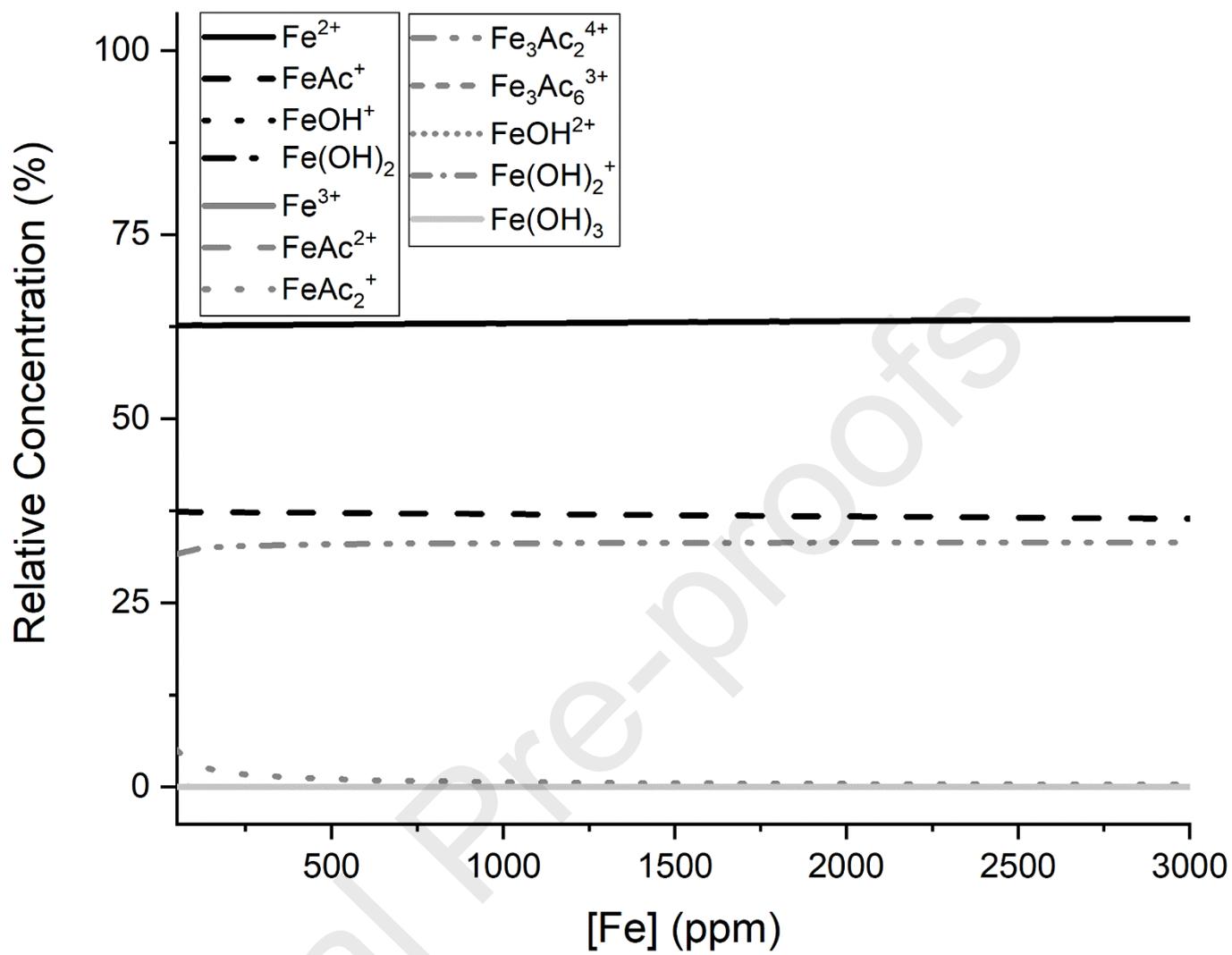
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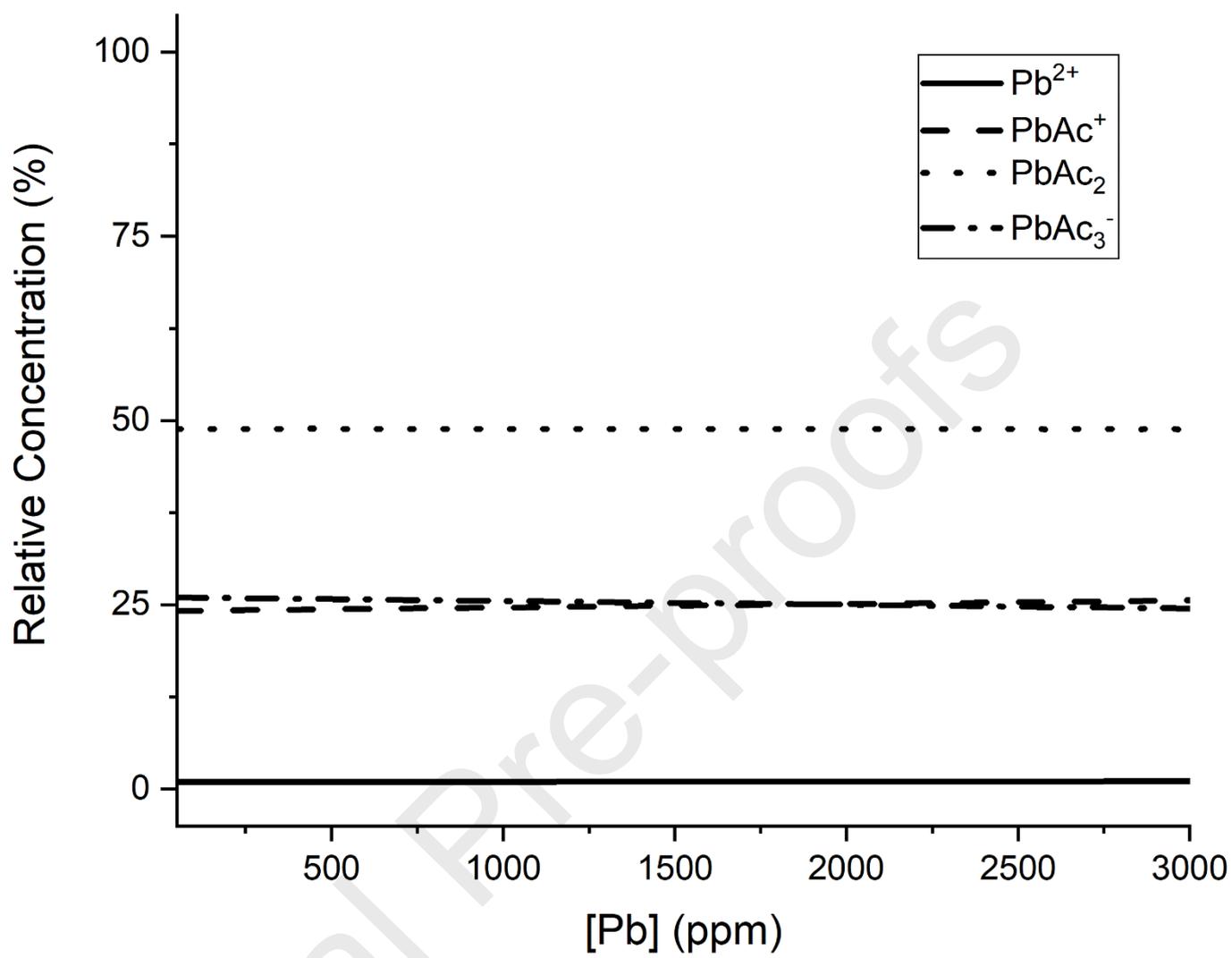
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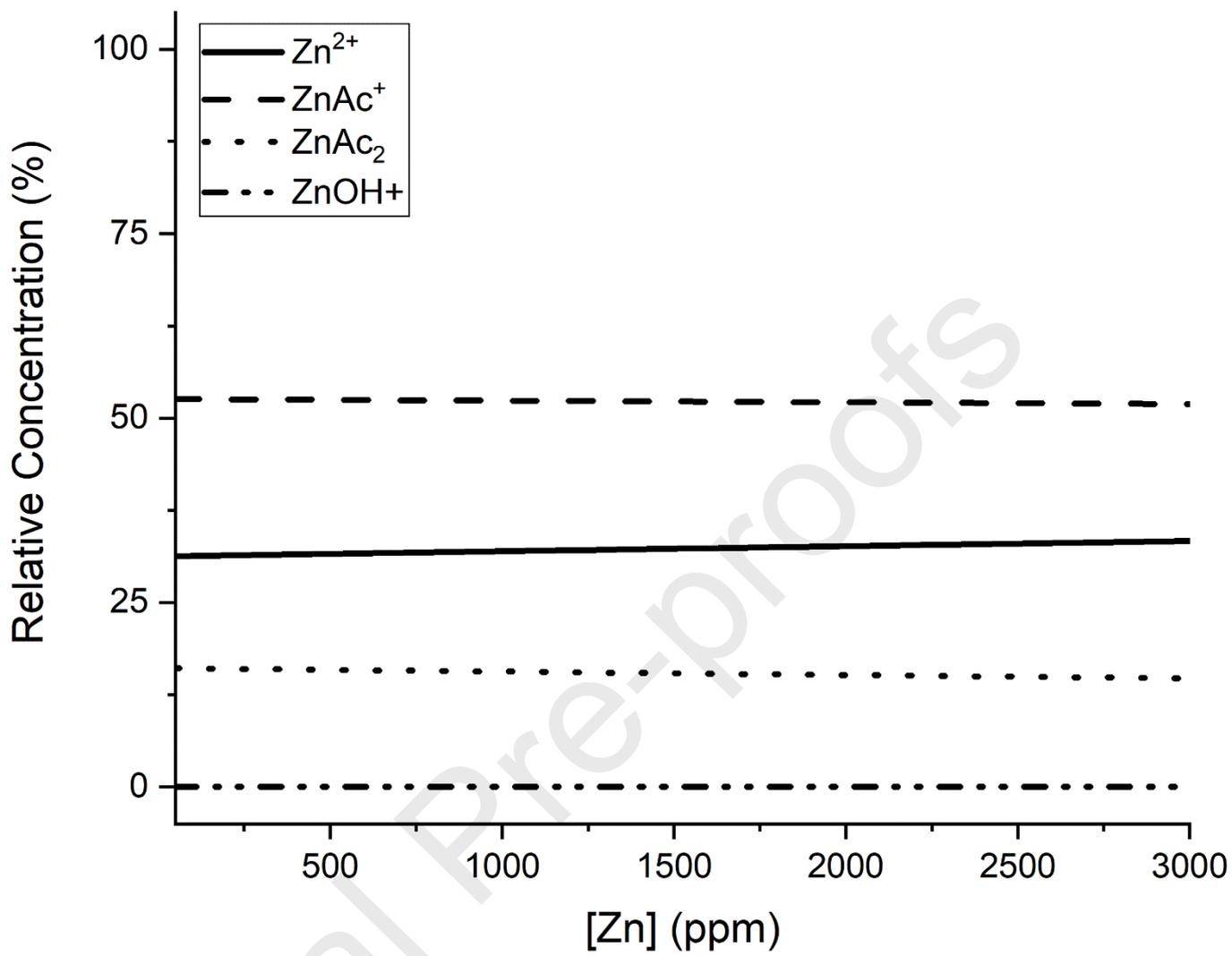
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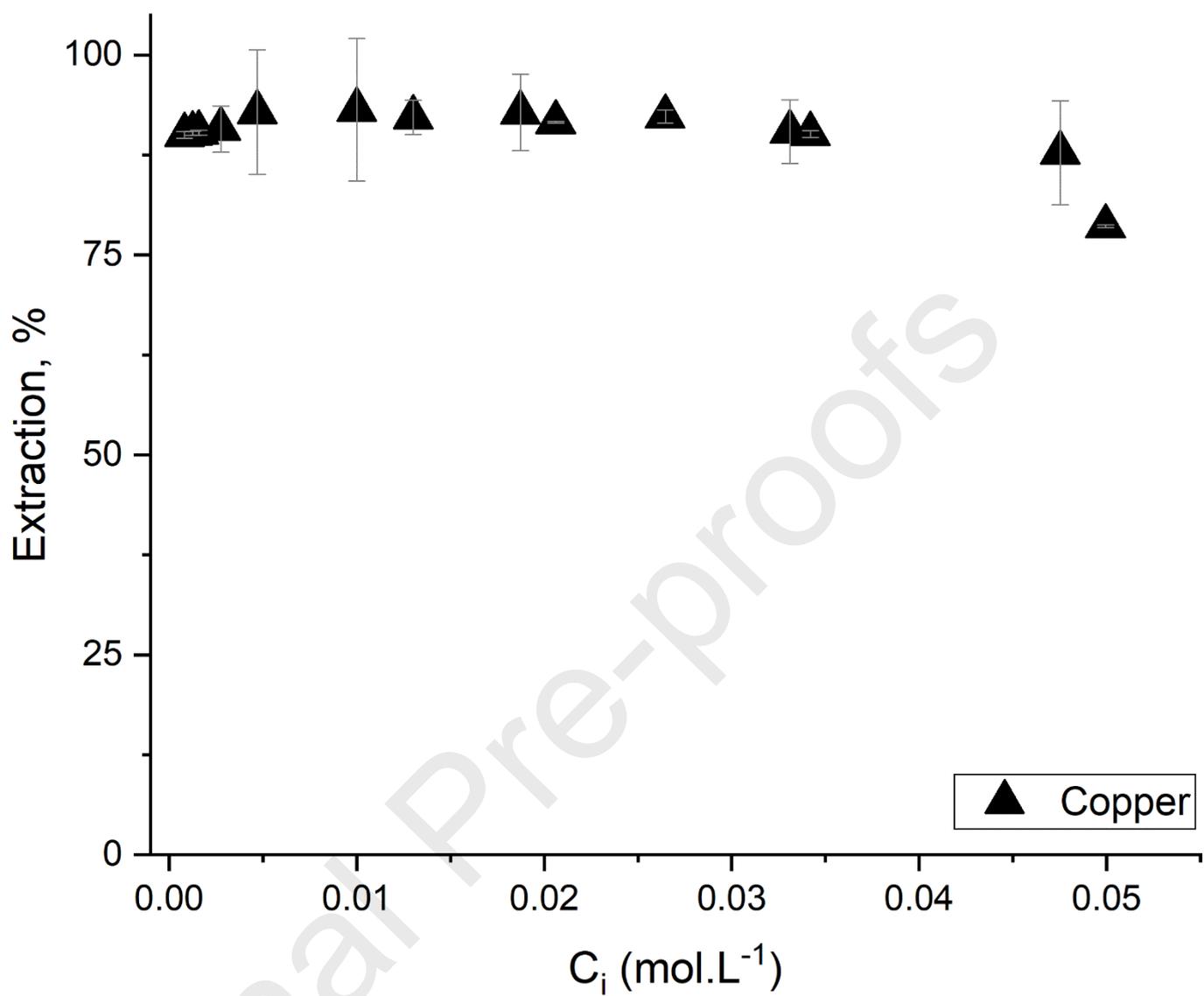
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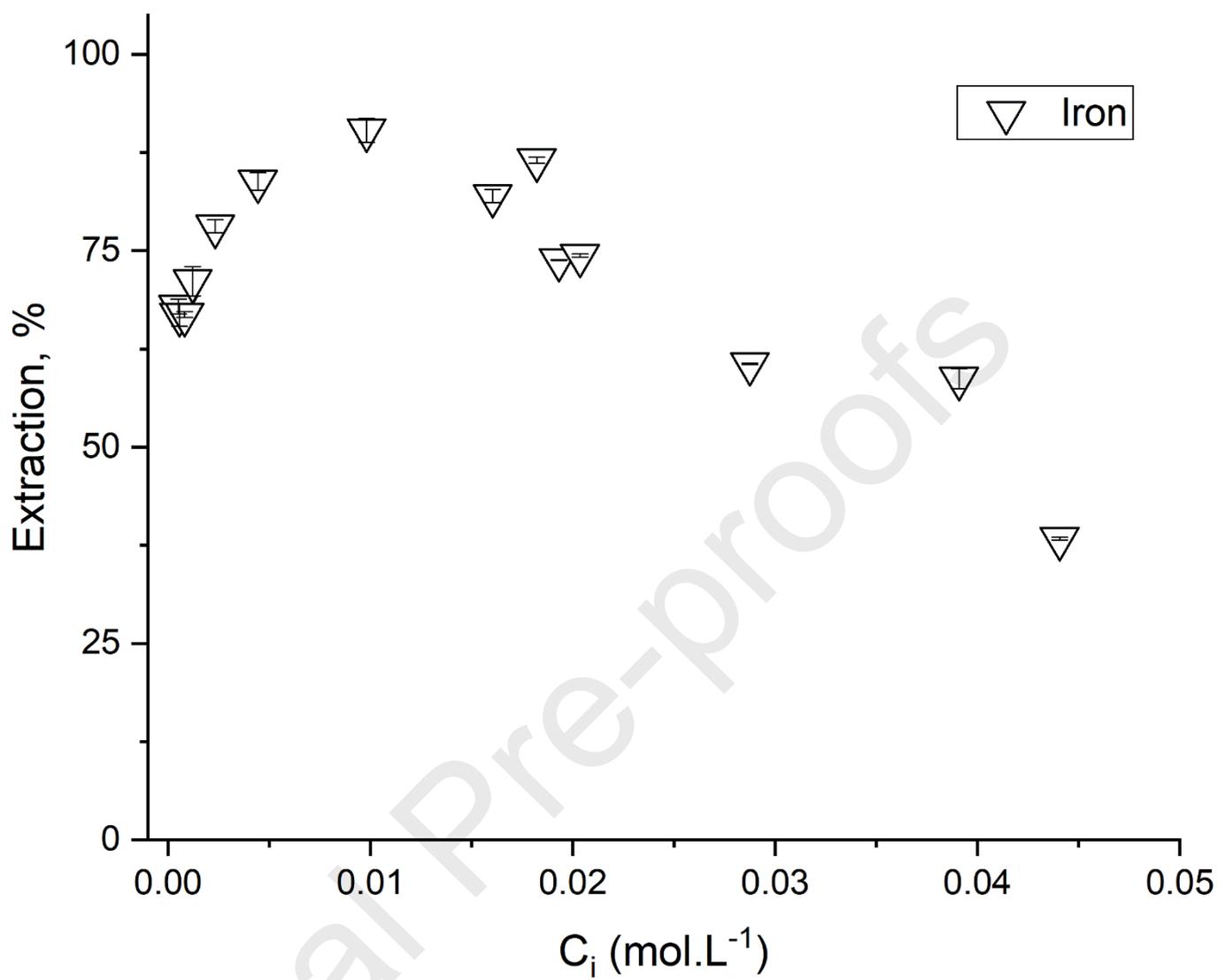
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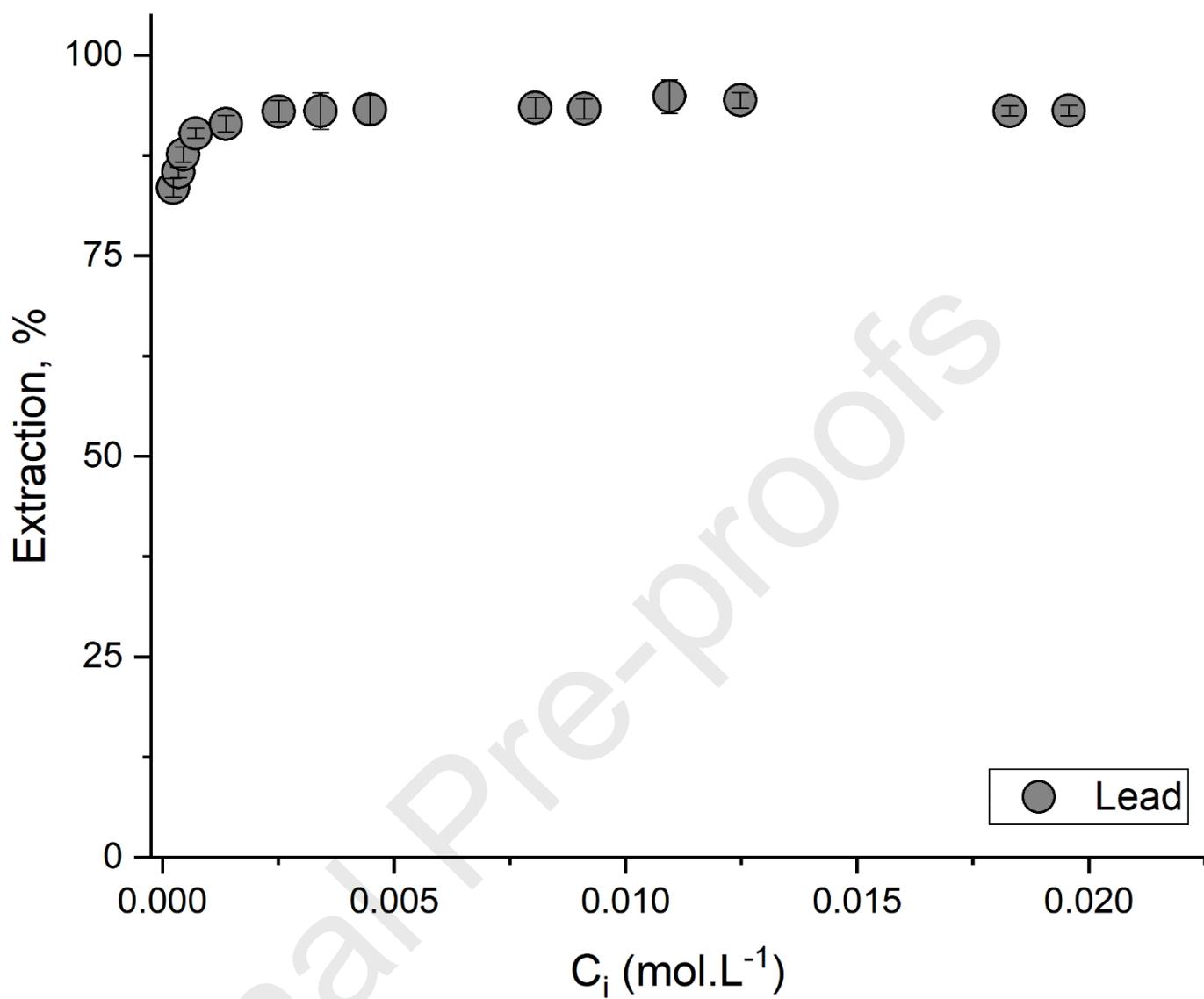
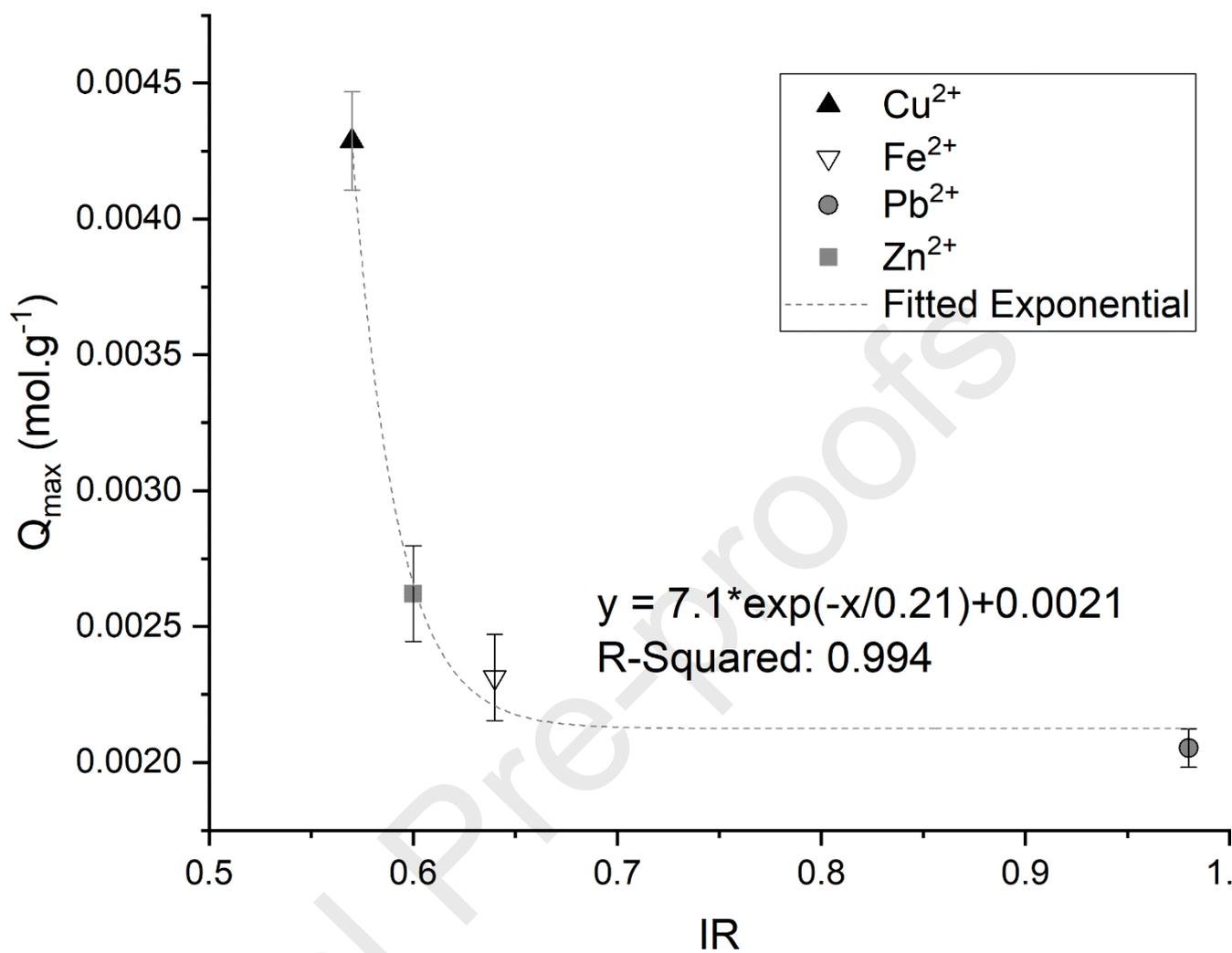[97]
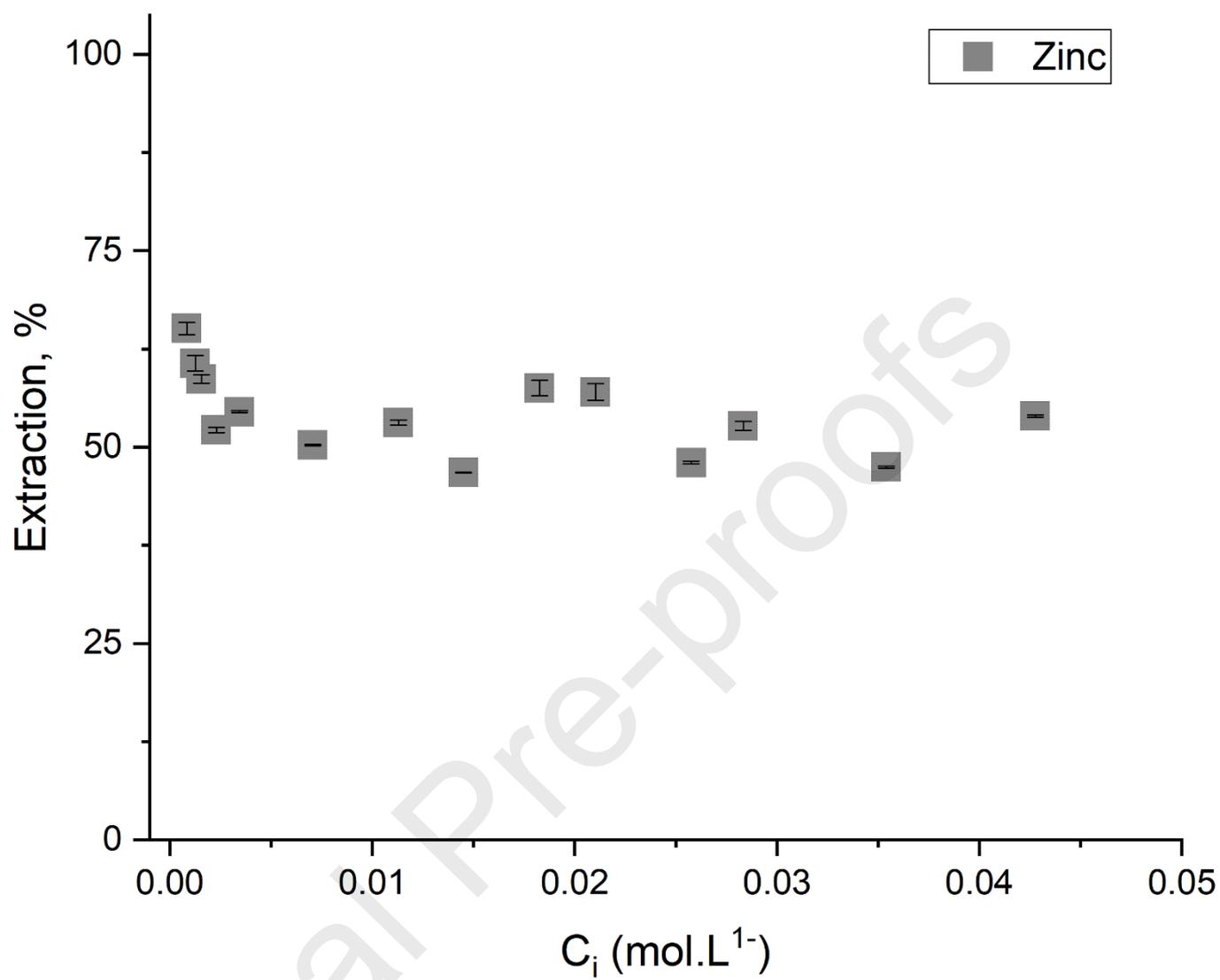
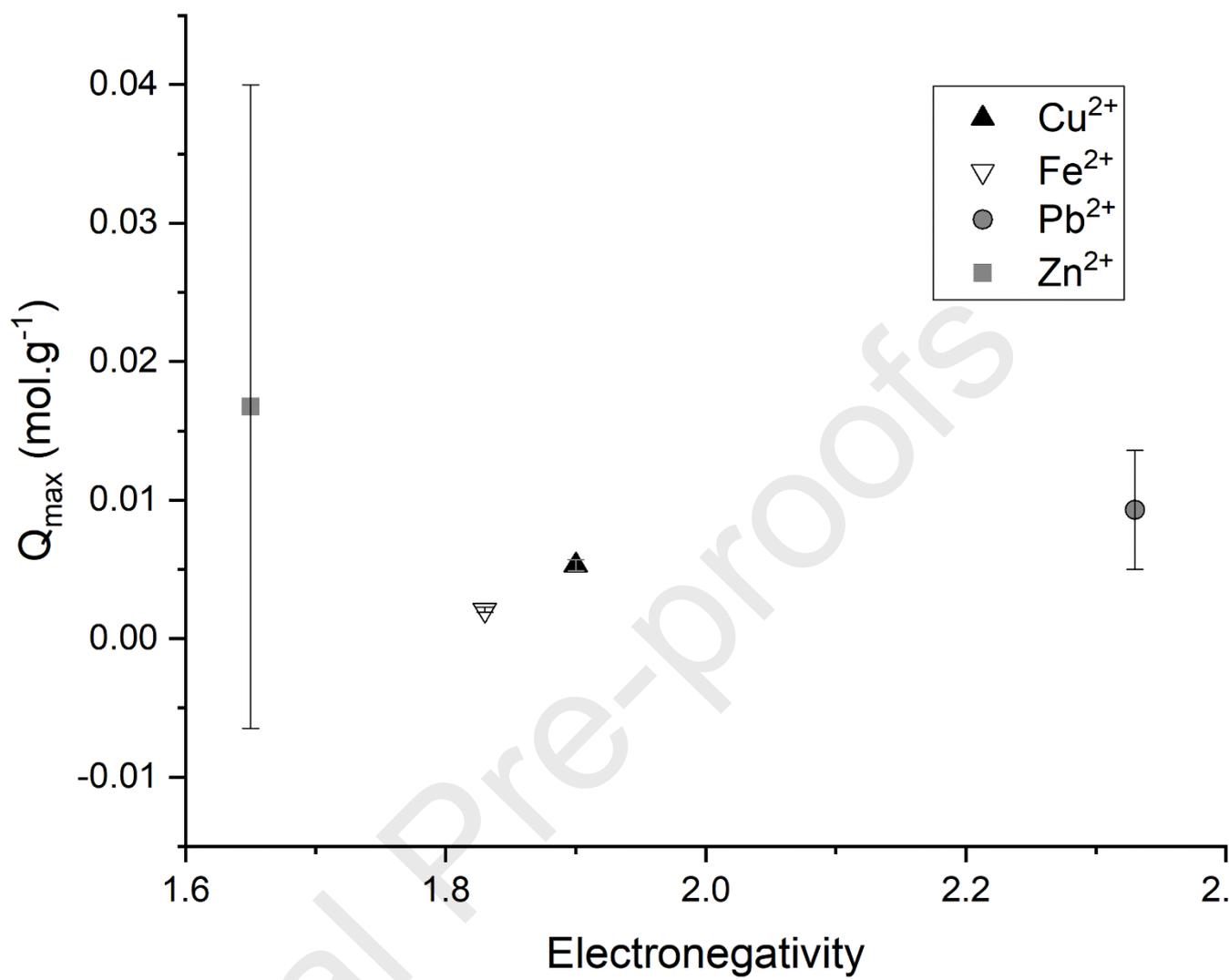[98]
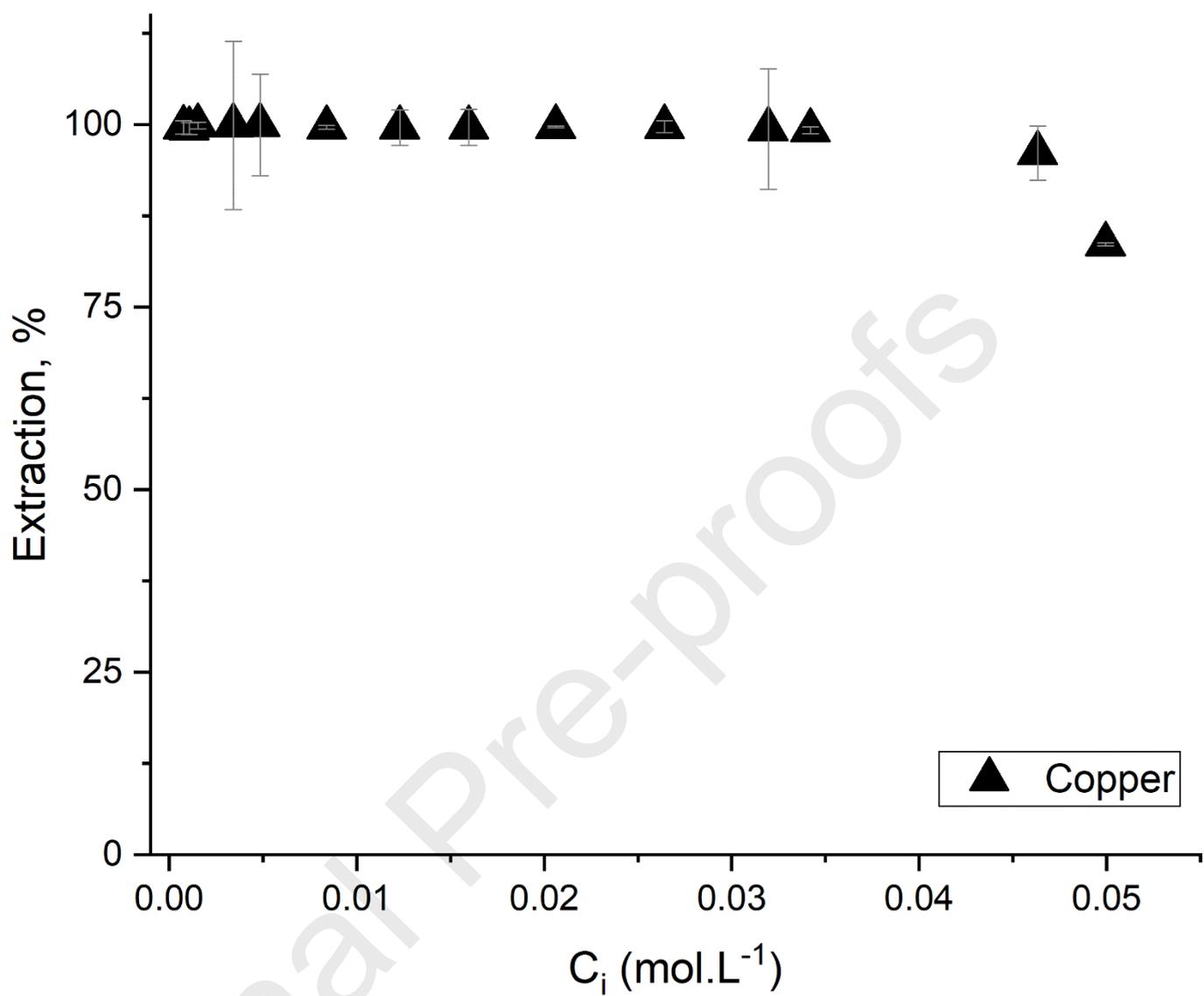
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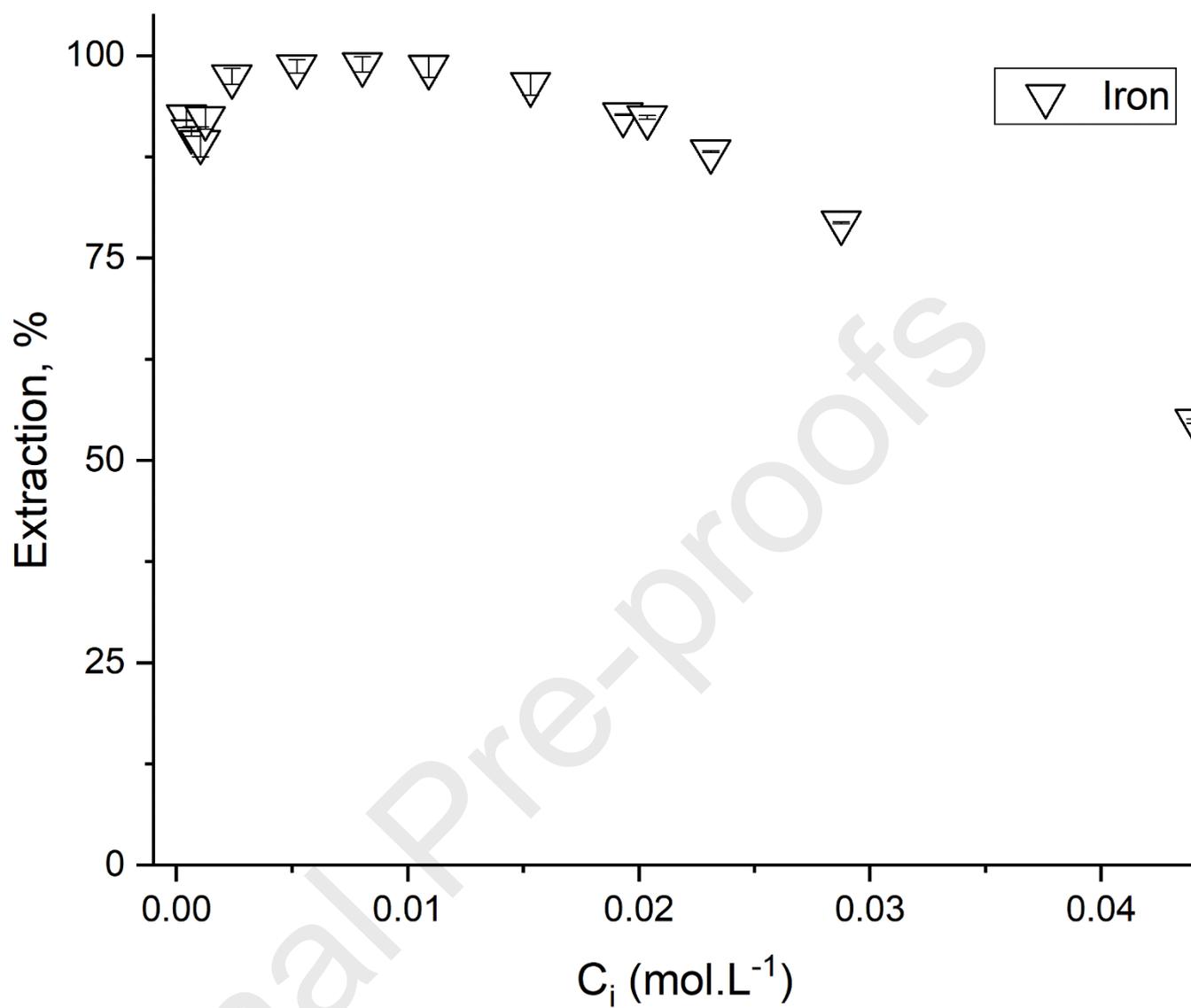
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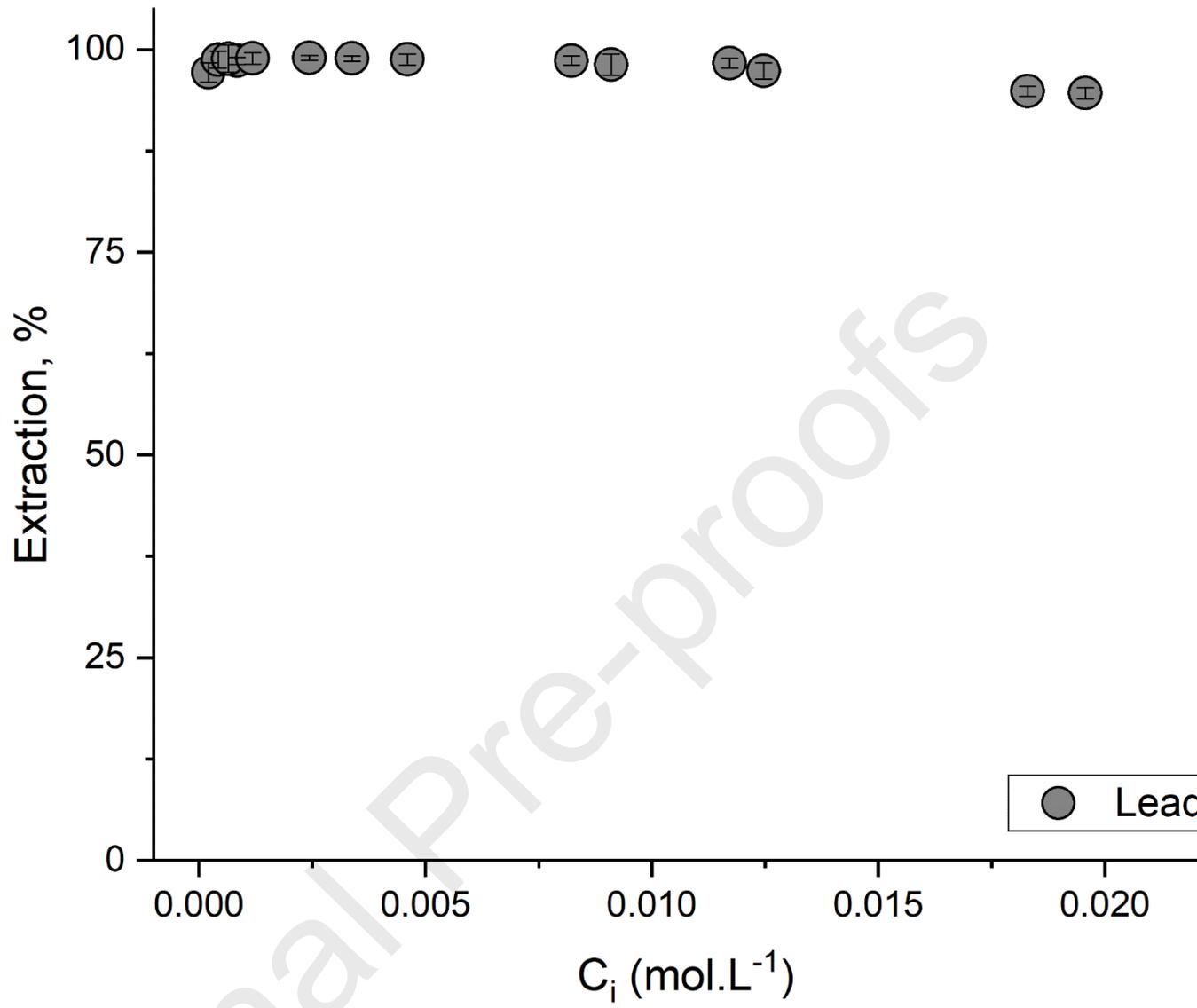
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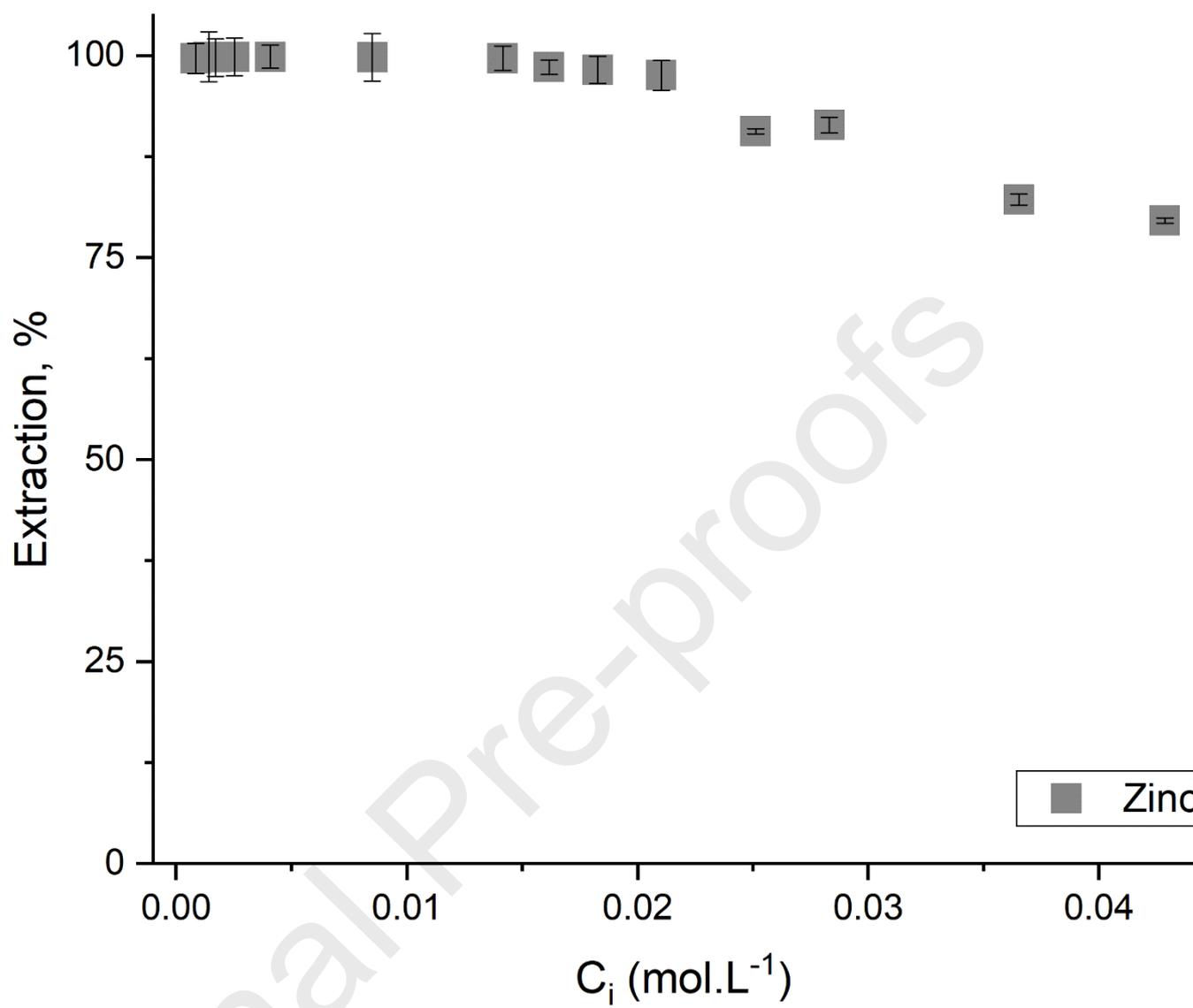
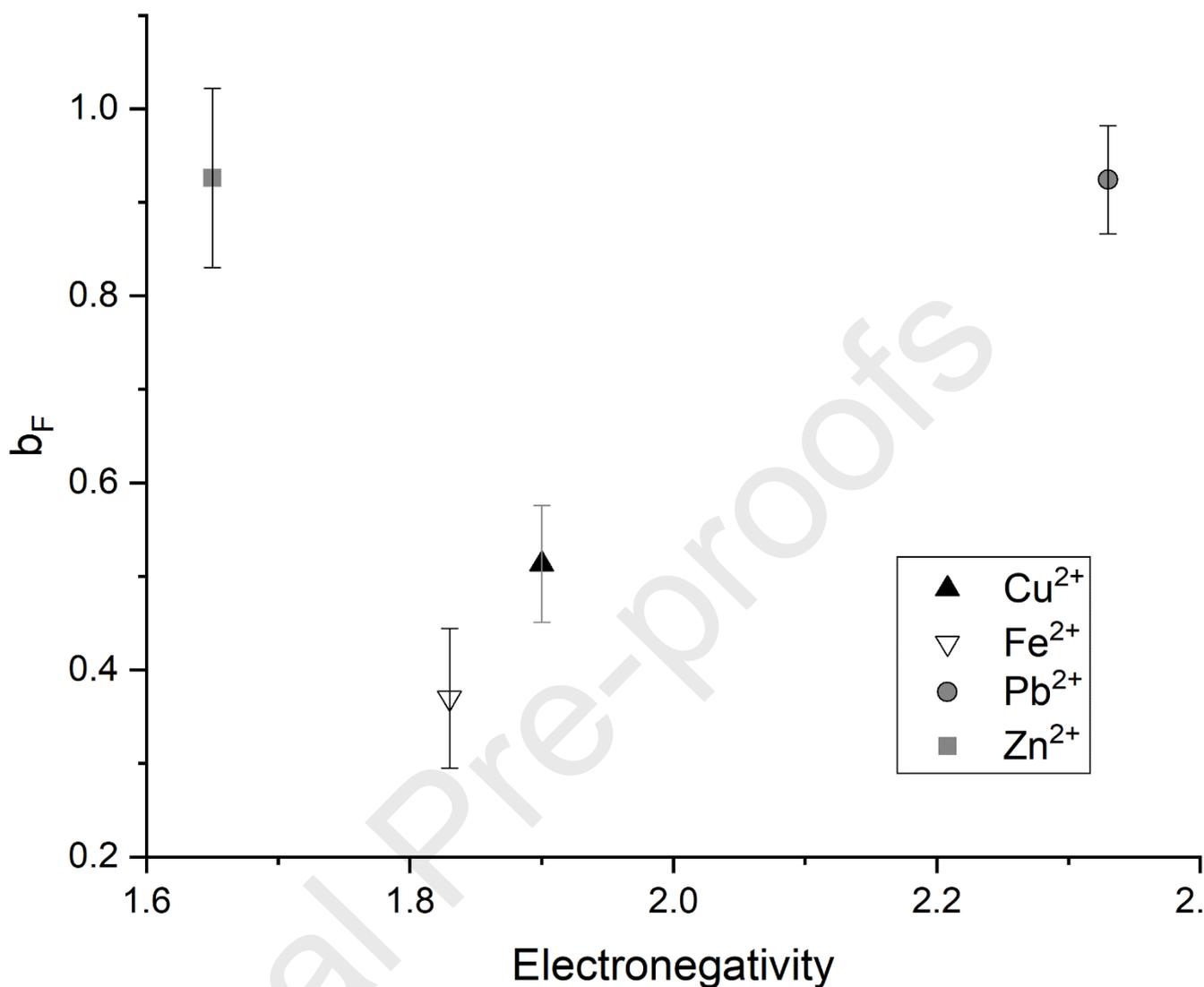[102]
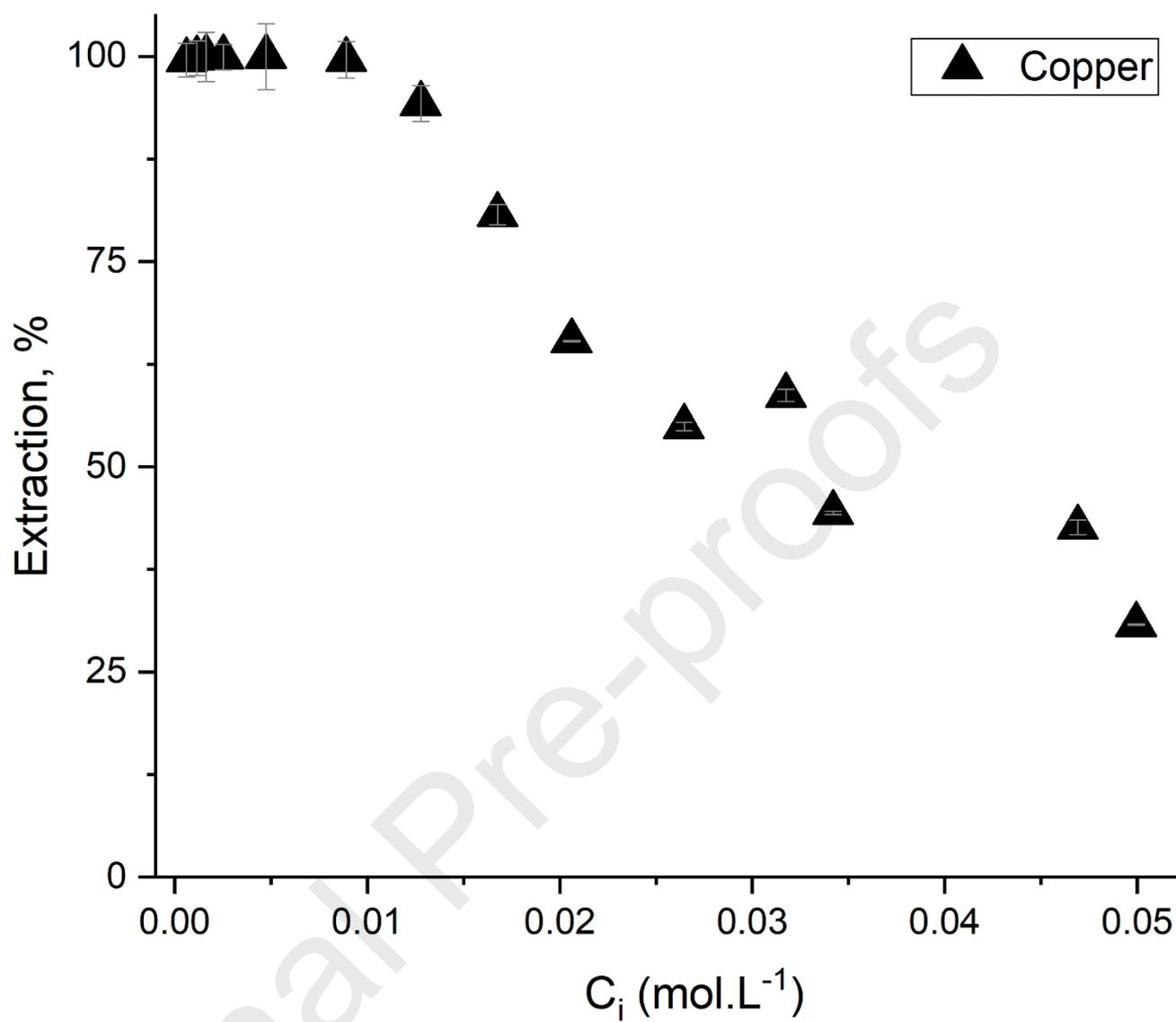
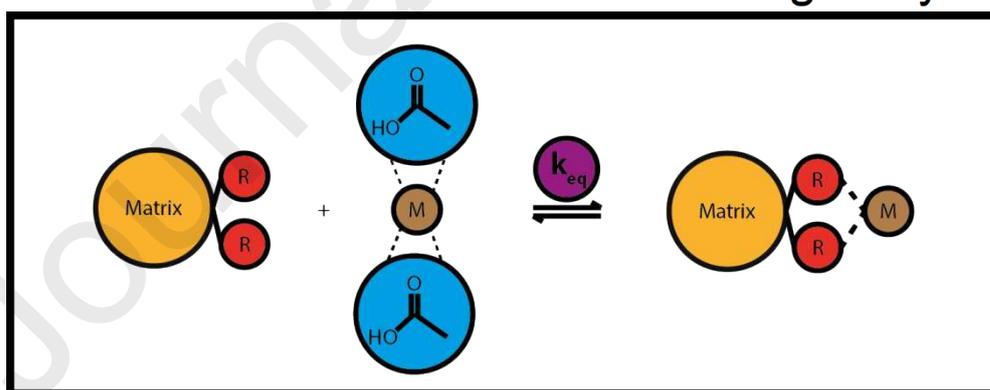[103]
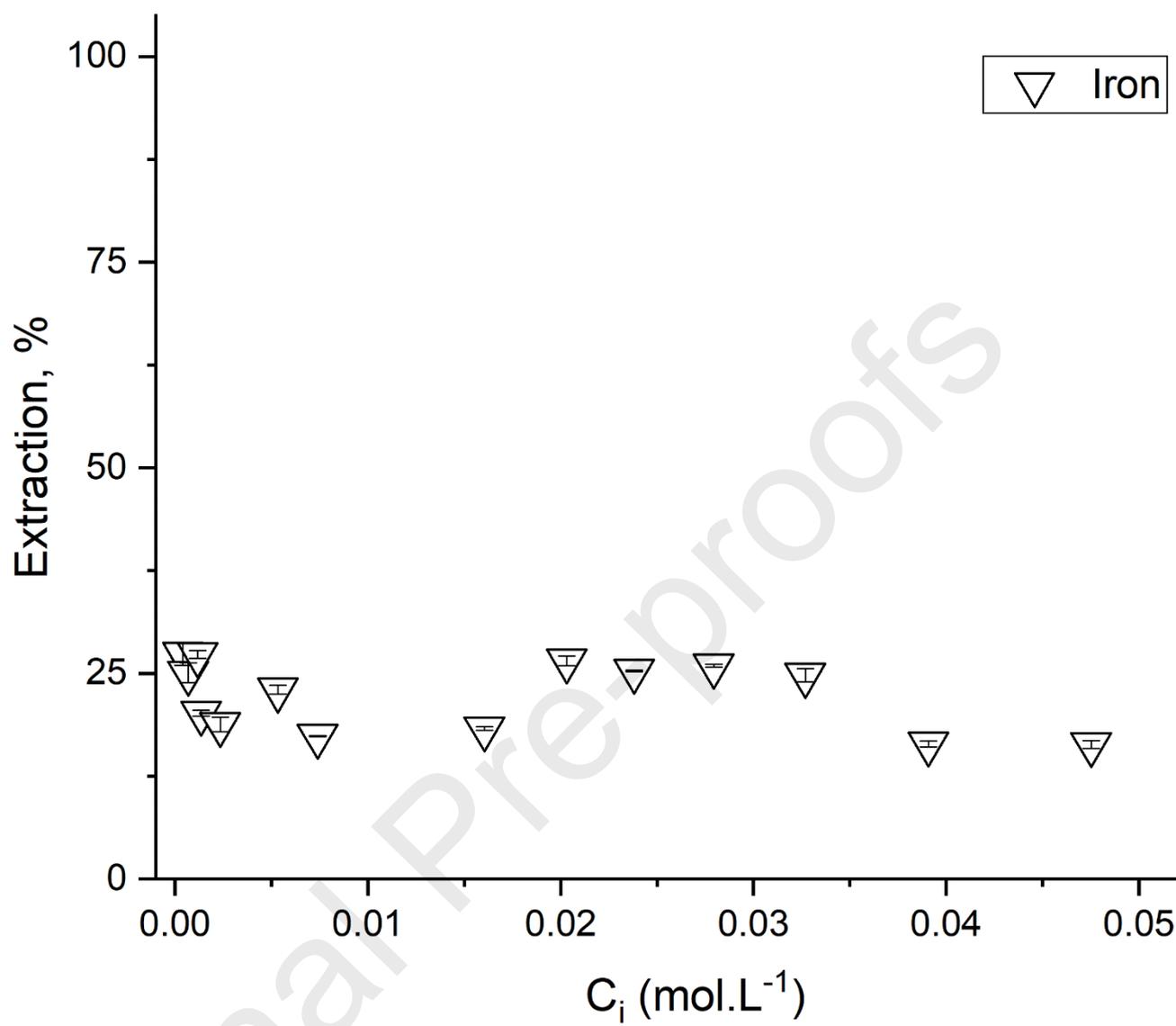
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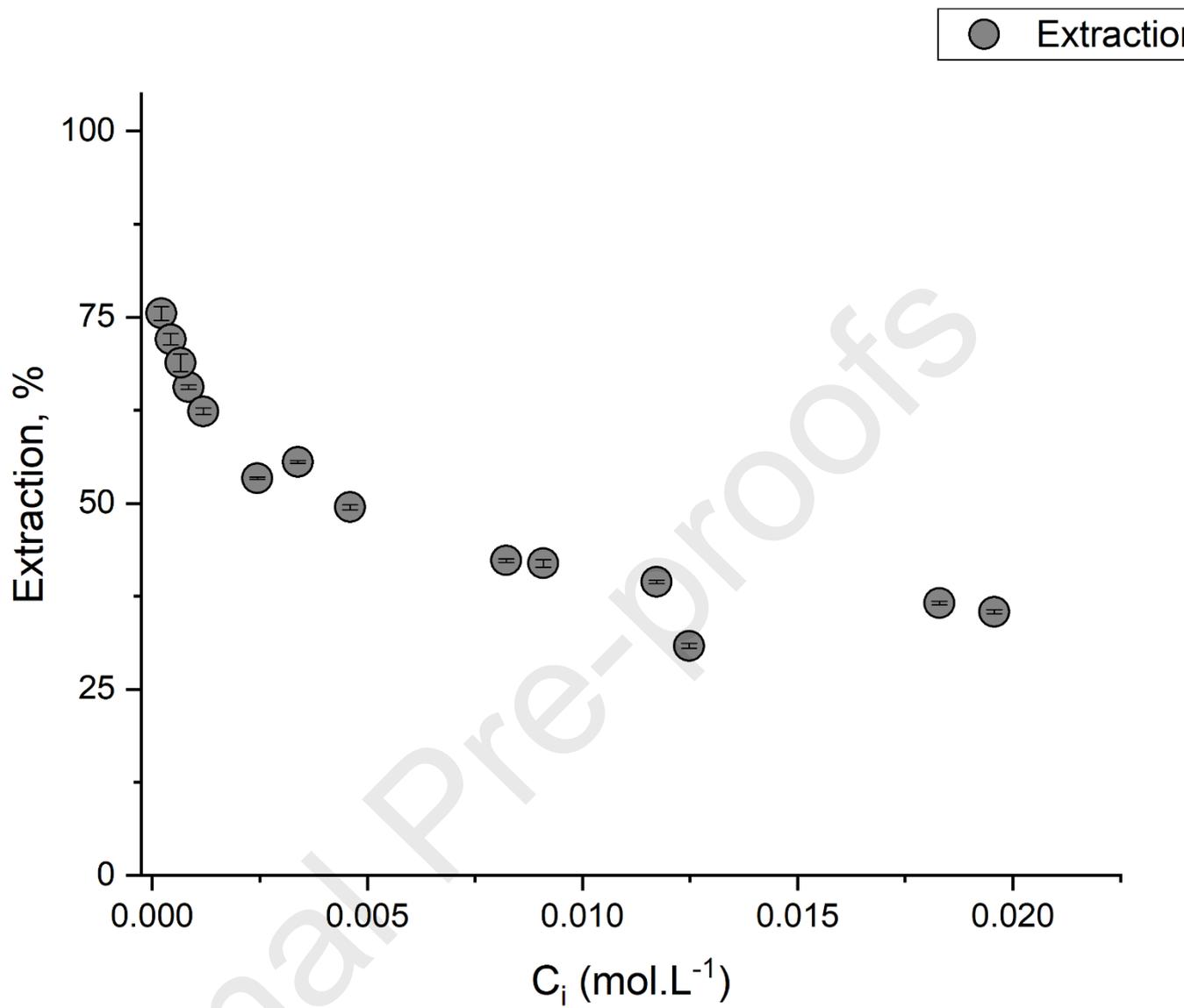
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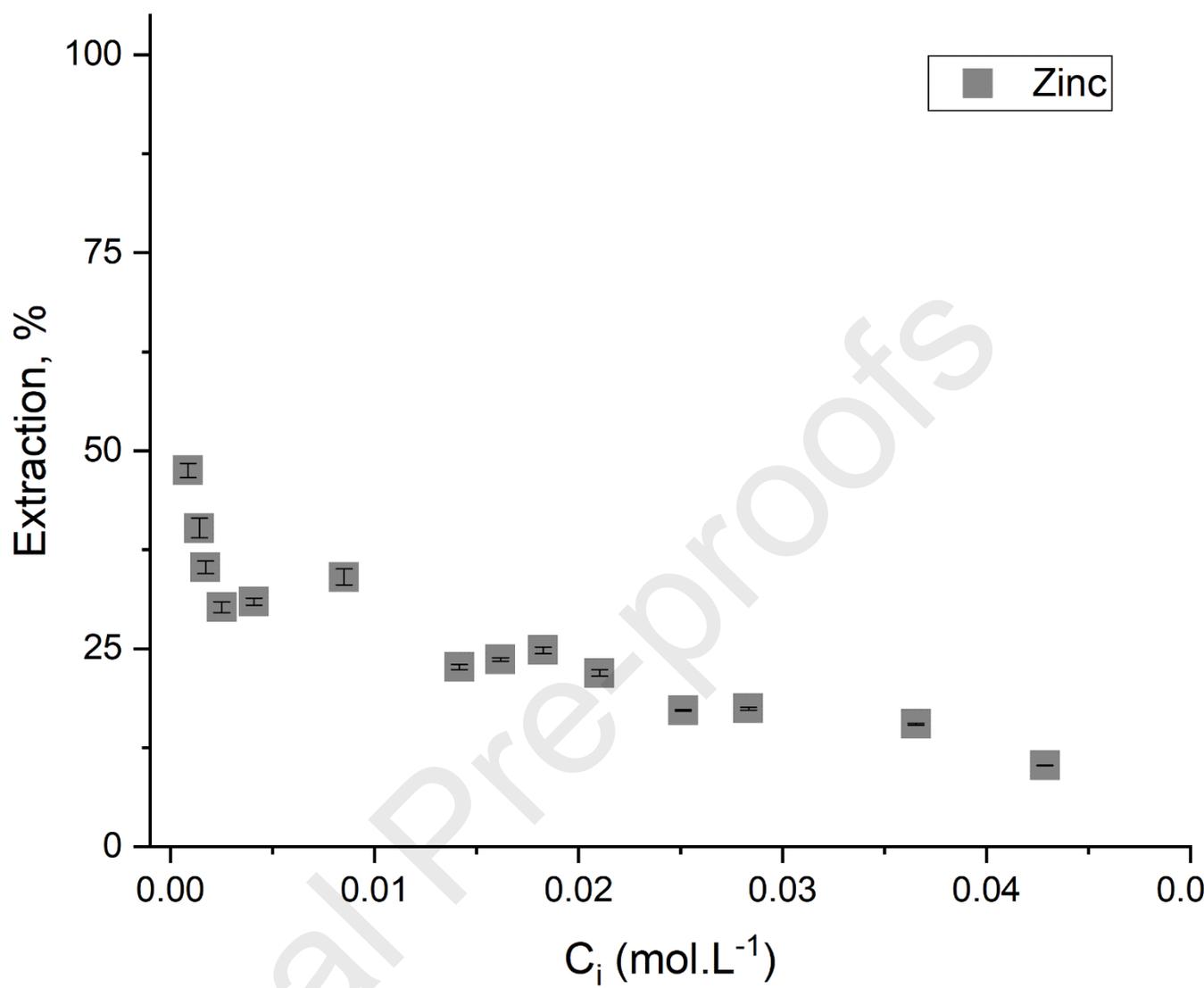
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6   Highlights

- Copper undergoes homogeneous ion-exchange binding to both MTS9301 and C107E
- Iron(II) extraction was the lowest of all measured and modelled extraction values
- Lead displays the most heterogeneous binding with respect to C107E with low binding energies
- C107E was ineffective for the extraction of zinc from within acetate media

[111]

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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