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# Complexing capacity of electroplating rinsing baths—a twist to the resolution of two ligand families of similar strength

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## Abstract

**Background:** The presence of ligands affects metal behavior when removing metals from wastewaters. So far, most of the attention has been paid to strong ligands; however, experimental observations indicate that also weaker complexing agents may play a key role in the availability of metals in waters and in the success of the treatment to be applied. In particular, we have analyzed wastewaters of an electroplating facility during an 8-h workday. Total metal content (copper, zinc, cadmium, and lead) was determined; ligands were characterized by concentration ( $L_t$ ) and strength (conditional stability constant,  $K'_f$ ). This work focuses on ligands of moderate strength which, as far as we know, have been overlooked in the literature.

**Methods:** A two-moderate-ligand system was used to mimic the wastewaters. N-(2-hydroxyethyl)iminodiacetic acid and nitrilotriacetic acid were used as model ligands. Electrochemical titration data (obtained by square wave anodic stripping voltammetry) were analyzed combining the Scatchard linearization method with a standard non-linear curve fitting function to focus on the resolution of two ligand families of similar strength. Correctness was tested both for the analytical procedure and data analysis.

**Results:** Most significant changes in metal concentration were related to zinc and lead that increased along the workday. Copper and cadmium contents were negligible. The model system and wastewater samples were successfully characterized by this methodology. Two ligand families of constants  $K'_f_1 (4.07 \pm 0.69) \times 10^5$  and  $K'_f_2 (5.56 \pm 0.78) \times 10^5$  were discriminated in the micromolar range using zinc in the titration of the wastewater sample.

**Conclusions:** A combined strategy involving electrochemical techniques, the Scatchard linearization, and a non-linear curve fitting function was successfully applied to the model system, within experimental error. Our main goal was to characterize two moderate ligand families of similar strength in the wastewater samples by means of the same strategy, a task that so far has not been described. The combined strategy used in this particular case may be of interest for different environmental matrixes.

**Keywords:** Complexing capacity, Moderate ligands, Electroplating bath, Zinc, Cadmium

## Background

The development of industrial activities has intensified concerns about environmental pollution issues. Metal-finishing industries constitute a highly sensitive sector that is responsible for important metal emissions to the environment. Due to ever increasing regulatory driving forces, more stringent and usually more expensive treatment

methodologies must be used to achieve lower metal releases to the environment. This issue has forced many industries to pursue “greener” technologies (Baral and Engelken 2002) and to develop better treatment methods.

Electroplating is a widely used technique to protect metal pieces from corrosion. There are different types of electroplating systems. Chromium electroplating and anodizing tanks are among the largest sources of chromium emissions in the USA. However, the use of zinc in electroplating baths is also widespread. The monitoring of additives in electrolytic baths is a fundamental task for proper coatings.

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Benzylideneacetone (BDA), benzoic acid (BA), and polyethylene glycol 400 (PEG400) are easily found among the additives used in zinc baths (Barriola et al. 2012). Many of these additives can act as metal ligands affecting the efficiency of the recovery and/or wastewater treatment processes. Spent plating baths and some rinsing solutions use conventional treatment methods based on alkaline precipitation, but these processes generate large amounts of hazardous plating sludge that require dumping sites.

When dealing with more diluted solutions, biotreatments mediated by micro-organisms are simple and usually compatible with the development of inexpensive technologies without causing environmental damage. Kumar et al. (2012) reported a 73.21, 68.35, and 70.21 % removal of Cr(VI), Zn(II), and Ni(II) from electroplating industrial wastewater, respectively. They also mentioned that biosorption of metals from wastewater samples was lower compared to a synthetic sample. This fact can be explained since industrial wastewaters usually contain non-negligible amounts of different anions (ligands) that influence the biosorption processes.

In the presence of ligands, metals are capable of bonding to form metal complexes of variable strength, keeping metals in solution and affecting metal availability when treatments are to be applied. Aristilde et al. (2012) claim that weak ligands can enhance the bioavailability of trace metals to phytoplankton in the presence of strong chelating agents. Given the apparent lack of specificity of the underlying mechanism, Aristilde expected that this effect could be widely observed in several essential metals and many micro-organisms in the presence of many types of ligands. These observations indicate that not only strong ligands are important, but also that weak complexing agents may play a key role in metal availability in natural waters.

The aim of the present work is to evaluate metal loading and complexing capacity (CC) in wastewaters of an electroplating facility. Samples from a second rinsing bath (SRB) were taken every hour during an 8-h workday. They were analyzed to focus on ligands of moderate strength, which from our point of view have been overlooked in the literature. We consider that they may play an important role in metal availability and in the success of the treatment to be applied. A model system with two ligands of similar strength was used to discriminate between both ligands. For this, a non-linear curve fitting function was applied to the experimental data using a home computer. The same methodology was successfully used to evaluate the CC toward Zn in the SRB samples.

## Methods

### SRB sampling and determination of total metal concentration

It is a general practice that once the electroplating process is finished, each electroplated piece is rinsed by

consecutive immersion in two big pools. Effluents from the second pool, the SRB, may be ca. 20 m<sup>3</sup> per day (Olivera and Mijangos, 2001) and typically contain metal ions (for example chromium, nickel, cadmium, and zinc) and organic substances such as polyelectrolytes, surfactants, etc. included in the galvanic process. Depending on a variety of parameters such as metal content and pH, these wastewaters should be treated if they do not meet the criteria for disposal (Argentina, Decree PEN 999/92). Eight SRB samples were taken during one workday, in 1-h intervals. Each sample was filtered through a 0.45- $\mu$ m pore diameter cellulose membrane to avoid the presence of suspended solids, then divided into fractions A and B and stored at -4 °C.

For total metal content determination by square wave anodic stripping voltammetry (SWASV), aliquots of A fractions were previously conditioned to approximately pH 1 adding HNO<sub>3</sub> (concentrated, Merck), transferred to PTFE bottles, and exposed to UV radiation for at least 12 h for organic matter oxidation (Campos et al. 2001). Applied voltage in the preconcentration step was -1.1 V for 60 s (Zn[II]) and -0.75 V for 120 s (Cd[II]); the scan range was from -1.2 to -0.10 V for Zn(II) and from -0.8 to -0.25 V for Cd(II). Instrument settings common to both metal determinations were equilibration time 5 s, step potential 5.1 mV, and pulse amplitude 19.95 mV.

### Complexing capacity of the SRB: sample conditioning and ASV-monitored titration

B fractions were used to determine complexing capacity (CC). Due to the effect of pH on metal-ligand interactions, it is paramount that the solutions are buffered in a narrow pH range. The choice of the buffer should also consider the absence of interactions between the metal and the buffer components which may modify the metal-ligand equilibrium in the sample. Ceretti et al. (2006) demonstrated that buffer HEPES is suitable for Cd(II) speciation studies. However, the behavior of Zn(II) toward HEPES has not been reported so far.

In the present study, CC was determined from SWASV-monitored titration data. Instrument settings have been described in the previous section.

In the titration, Me' (Me<sup>2+</sup> peak current) was measured after increasing additions of the Me<sup>2+</sup> standard solution. After every metal spike, solutions were stirred for equilibration, and N<sub>2</sub> was bubbled to deoxygenate. A titration curve (Me' vs. added Me<sup>2+</sup> concentration) was plotted for each dataset.

We consider that another relevant aspect in CC determination is the fact that ligands must be "free" to interact with the metal ions added during the ASV-monitored titration. For this purpose, ligands need to be released from the metal complexes existing in the sample. Sixty milliliters of each sample was supplemented with

HEPES and  $\text{KNO}_3$  (final concentration 0.05 M in each compound), equilibrated with 0.2 g Chelex 100 for 4 h in an orbital shaker (25 °C, 200 rpm), and filtered through a 0.45- $\mu\text{M}$  pore diameter cellulose membrane. Chelex 100 is a cationic resin that has proved effective for metal removal including cadmium and zinc (Manouchehri and Bermond 2006, Leung et al. 2008 and Ceretti et al. 2010). The amount of resin to be employed was calculated considering wet resin capacity and total metal content. The effectiveness of the resin treatment was verified by total metal concentration determined through SWASV on sample 8 (S8), collected at the end of the workday, before and after Chelex 100 treatment. Results showed that more than 99 % zinc and lead had been removed.

Model solutions containing a mixture of HIDA and NTA (two-ligand-model system) were also evaluated for CC by SWASV.

## Results and discussion

### The problem—temporal characterization of a SRB

Samples of SRB were taken every hour during an 8-h workday to measure pH, copper, cadmium, lead, and zinc content. Since samples were rinsing waters of a metal-finishing process, pH, metal, and ligand content were expected to increase during the workday. The most significant changes in metal concentration were related to zinc and lead (Fig. 1). Metal concentrations were low, but they did not meet the criteria set out in legislation for direct disposal and thus wastewater treatment becomes a necessity. Copper and cadmium contents were negligible ( $\text{Cu} < 0.09$  ppm and  $\text{Cd} < 0.06$  ppm).

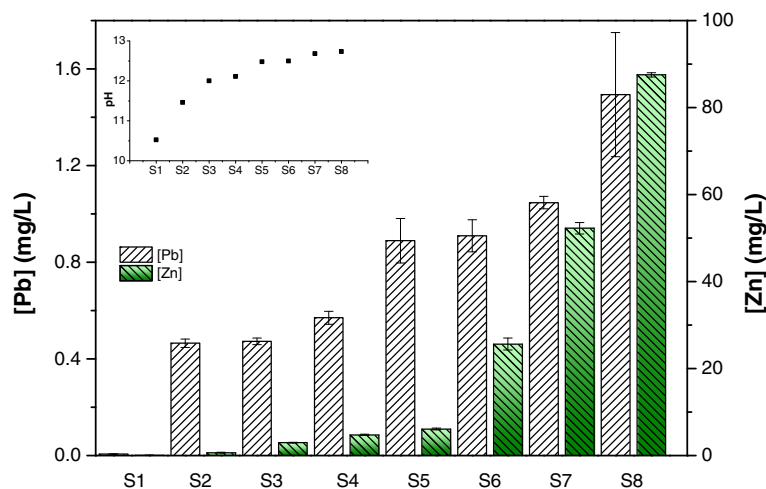
Metal-ligand interactions can be characterized through determining total ligand concentration (Lt) and the conditional stability constant ( $K'f$ ). Both parameters are referred to as complexing capacity (CC). Determination of

Lt and  $K'f$  (which depends on the specific metal) can be achieved with a variety of techniques (Pesavento et al. 2009), among which SWASV is one of the most used.

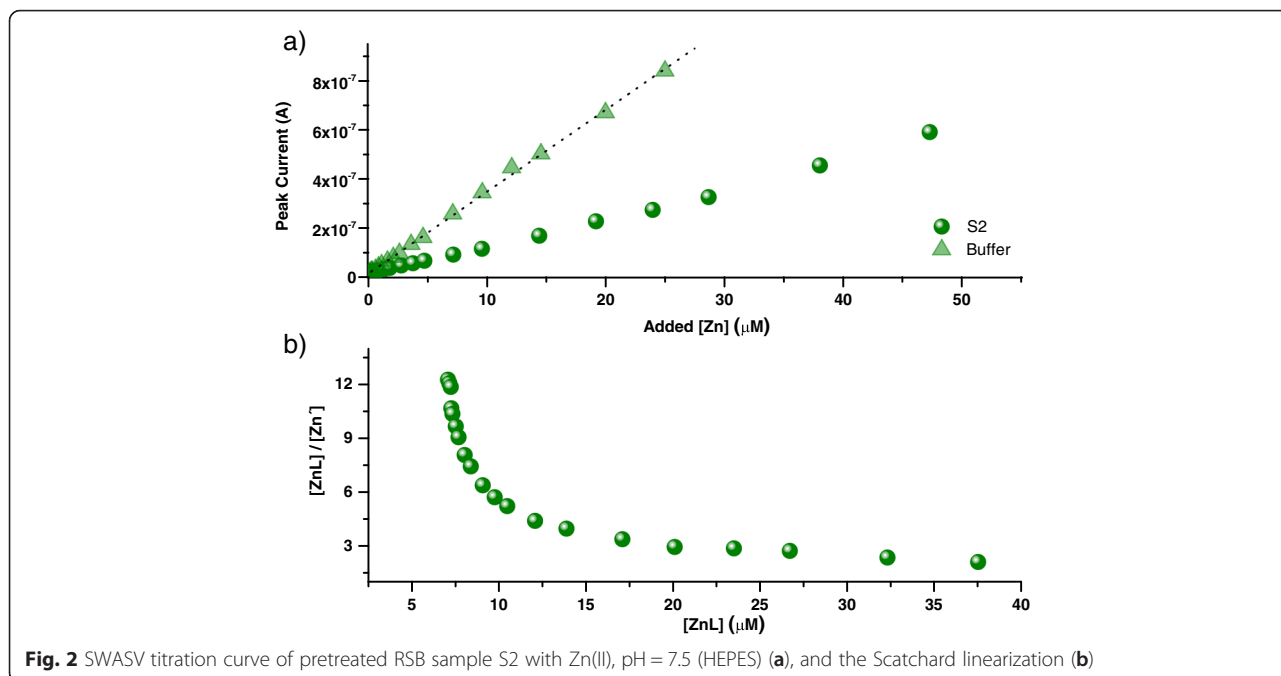
Pretreated B fractions of SRB were titrated using Zn in an ASV-monitored titration to evaluate CC. As an example, Fig. 2a shows the titration curve of sample S2 denoting the presence of complexing substances. On the other hand, the titration curve of buffer HEPES confirmed that there were no interactions between Zn and HEPES. In the final portion of the titration curve, the slope is similar to that of the buffer solution alone. The linear behavior of the final portion reflects Zn(II) excess.

The titrations were performed at  $\text{pH} = 7.5$  (buffer HEPES) to obtain information on zinc speciation at this pH. This is an intermediate value in the wastewater disposal range. It is a common practice to perform the Ruzic and/or Scatchard linearization with the experimental datasets of the titration curves to better estimate Lt and  $K'f$  (Oldham et al. 2014, Abdelraheem et al. 2013, Bundy et al. 2013). For each sample, Lt and  $K'f$  were determined from the slopes of the Ruzic (1982) and Scatchard (1949) linearizations, respectively. Figure 2b shows the Scatchard linearization for sample S2. Two different slopes were clearly seen, indicating the presence of two ligand families in the SRB.

The results in Table 1 show that the classical titration data treatment using the Scatchard and Ruzic linearizations suggests that there are two ligand families. Lt increased along the workday (from micromolar to millimolar) and  $K'f$  values stayed in the range  $10^5$ – $10^7$ , representing ligands of moderate strength. However, a closer look showed that for the two families detected in most of the samples,  $K'f$  differed in ca. by one order of magnitude. Also, odd fluctuations were observed in  $K'f$  and Lt values. Even in one sample, the definition of the



**Fig. 1** Metal content (zinc and lead) and pH evolution for the eight SRB samples during a workday



**Fig. 2** SWASV titration curve of pretreated RSB sample S2 with Zn(II), pH = 7.5 (HEPES) (a), and the Scatchard linearization (b)

second slope corresponding to the weaker family was too poor to be considered. Following Scarponi et al. (1996), it is not possible to distinguish between two families of similar strength.

**Searching for answers—the use of model systems**

To shed light on the resolution of two ligand families of similar strength, HIDA and NTA were selected for an electrochemical characterization of both K’f and Lt using Cd as titrant. Both ligands used as models form moderate complexes with Cd (Martell and Smith 2010), with K’f values less than two orders apart.

In previous research (Ceretti et al. 2006, 2010), the Scatchard and Ruzic linearizations were applied to the titration data obtained from solutions containing HIDA

or NTA as “one ligand model systems” within the operational titration window (K’f x Lt) to estimate K’f and Lt of the Cd(II) complexes. In this work, both parameters K’f and Lt were calculated using Eq. 1 in the non-linear curve fitting function of OriginLab (Origin Pro 7.5).

$$K_f' \cdot [Me']^2 + [1 + K'(L_t - [Me_t])] \cdot [Me'] - [Me_t] = 0 \tag{1}$$

In the case of the Cd-HIDA, fitting of Lt resulted in 3.86 ± 0.17 μM, and K’f was (9.37 ± 0.46) × 10<sup>5</sup>. Taking into account that the actual concentration of the solution was 3.75 μM and K’f was 1.38 × 10<sup>6</sup> (calculated from literature data, pH = 7.5), the agreement between expected and fitted values was good.

Cd-NTA complex was previously characterized using an ASV-monitored titration (Ceretti et al. 2006). This complex exhibits an electrochemically labile behavior that is seen as a shift of Cd(II) peak potential as Cd(II) concentration increases (Van Leeuwen et al. 1989). The Ruzic and Scatchard linearizations as well as the Origin fitting results for Lt—3.78 ± 0.04 and 3.61 ± 0.10 μM, respectively—were in good agreement with the actual NTA concentration. K’f for NTA-Cd was 6.24 × 10<sup>7</sup>. In this case, the experimental values were (7.91 ± 0.26) × 10<sup>6</sup> (Ruzic and Scatchard approach) and (5.29 ± 0.65) × 10<sup>6</sup> (non-linear curve fitting), probably due to the labile behavior previously described (Van Leeuwen et al. 1989).

The experimental titration curve for a solution containing two ligand families (2.99 μM HIDA and 0.89 μM NTA) and the corresponding Scatchard

**Table 1** K’f and ligand concentration of second rinsing bath samples

SRB use, hs	Family 1		Family 2	
	K’f	Lt (μM)	K’f	Lt (μM)
0	3.29 × 10 <sup>5</sup>	5.52	6.11 × 10 <sup>6</sup>	1.81
1	3.43 × 10 <sup>6</sup>	42.45	4.46 × 10 <sup>7</sup>	21.05
2	9.59 × 10 <sup>4</sup>	313.00	6.67 × 10 <sup>6</sup>	595.50
3	5.74 × 10 <sup>6</sup>	298.00	2.49 × 10 <sup>7</sup>	217.50
4	5.17 × 10 <sup>5</sup>	730.00	1.09 × 10 <sup>7</sup>	263.20
5	2.44 × 10 <sup>6</sup>	937.34	3.09 × 10 <sup>7</sup>	462.77
6	*	*	1.10 × 10 <sup>7</sup>	502.80
7	3.58 × 10 <sup>6</sup>	2874.5	3.68 × 10 <sup>7</sup>	1983.50

K’f and Lt were obtained from the Ruzic and Scatchard plots, respectively  
 \*Poor definition of the second slope

linearizations are also shown in Fig. 2. In spite of the fact that HIDA and NTA are moderate ligands with similar strength, the Scatchard plot clearly shows a change in the slope, indicating that two different ligands are present. Results of  $K_f$  and  $L_t$  obtained by the Ruzic and Scatchard linearizations and non-linear curve fitting are summarized in Table 2. The titration curve for two 1:1 complexes of Cd(II) with two ligands is described by Eq. 2.

$$[Cd]_t = [Cd'] + \frac{K_1' \cdot L_{t1} \cdot [Cd']}{1 + K_1' \cdot [Cd']} + \frac{K_2' \cdot L_{t2} \cdot [Cd']}{1 + K_2' \cdot [Cd']} \quad (2)$$

$K_f$  values for both Cd-HIDA and Cd-NTA are in agreement in any procedure. However, the Ruzic and Scatchard linearizations always yield higher ligand concentrations. This trend was also observed in all titrations performed with different proportions of ligand concentrations keeping the same total value (nearly 4  $\mu$ M). Thus, the non-linear curve fitting function gives a better description of a mixture of two 1:1 complexes of one metal, which renders a better characterization regarding  $L_t$  for the ligand families with no meaningful variation in  $K_f$ . However, it is necessary to decide the number of existing ligand families before applying a non-linear curve fitting to a general case. We suggest analyzing the titration data using the Scatchard linearization and then applying non-linear curve fitting to get the best quantitative description of the sample through  $K_f$  and  $L_t$ .

### Dealing with ligands in the SRB

Since Zn(II) is the most concentrated metal in the SRB (in the millimolar range), all B fractions were characterized for  $L_t$  and  $K_f$  using Zn(II) as titrant in the ASV-monitored titration.

Data of all fractions were first evaluated with the Scatchard linearization in order to assess the presence of one or two ligand families. All fractions showed two clearly different slopes. Therefore, the titration curve equation applied in the non-linear curve fitting function

**Table 2**  $K_f$  and ligand concentration values obtained from the model system containing HIDA and NTA

Ligand	Expected values	Experimental values	
		Ruzic and Scatchard linearizations	Non-linear curve fitting
HIDA	$K_f = 1.38 \times 10^{6a}$	$(4.49 \pm 0.95) \times 10^5$	$2.81 \times 10^5$
	$L_t = 2.99 \mu\text{M}$	$4.54 \pm 0.32 \mu\text{M}$	$3.06 \pm 0.21 \mu\text{M}$
NTA	$K_f = 6.24 \times 10^{7a}$	$(3.31 \pm 0.97) \times 10^6$	$6.01 \times 10^6$
	$L_t = 0.89 \mu\text{M}$	$1.78 \pm 0.12 \mu\text{M}$	$1.05 \pm 0.31 \mu\text{M}$

Comparison of results obtained from the titration curve of solutions containing HIDA and NTA as model ligands, evaluated with linearization and non-linear fitting procedures. Cd(II) was used as titrant agent (it forms 1:1 complexes with both ligands)

<sup>a</sup>Calculated from Martell and Smith (2010)

procedure was Eq. 2. The different SRB fractions were described by two ligand families  $K_f1$ ,  $(4.07 \pm 0.69) \times 10^6$  and  $K_f2$ ,  $(5.56 \pm 0.78) \times 10^5$ . Ligand concentrations along the workday are shown in Fig. 3. As expected, both ligand families increased their concentration from the micromolar to the millimolar range. In this study, ligand concentration was higher for the stronger ligand family. The chemical environment of Zn(II) in the SRB changed along the workday. At the beginning, Zn(II) was partially complexed by the ligands, then became fully complexed, and finally, ligands exceeded Zn(II) concentration. In this scenario, attention should be paid to Zn(II) and ligand concentration for a successful treatment prior to disposal.

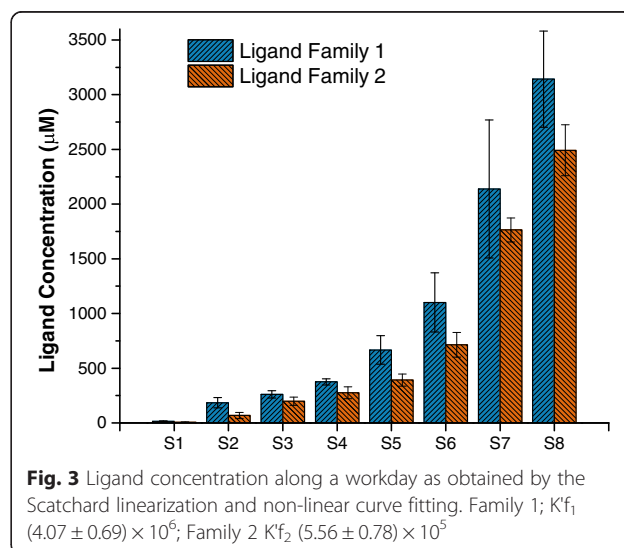
## Experimental

### Chemicals and reagents

Chelex 100 (sodium form, 100–200 mesh, biotechnological grade, wet capacity 40 meq/mL) was obtained from Bio-Rad Laboratories, Inc.  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  standard solutions were prepared from a certified 1000 ppm solution (Merck Certipur).  $\text{NaNO}_3$  (Aldrich, 99.99 + %) was used as supporting electrolyte. HEPES (Aldrich) (N-[2-hydroxyethyl]piperazine-N'-[2-ethansulfonic acid],  $\text{pK}_a = 7.5$ ) was used in the preparation of 0.05 M buffer solutions, also containing 0.05 M  $\text{NaNO}_3$ . pH was adjusted with HCl (Merck). HIDA (N-(2-hydroxyethyl)iminodiacetic acid, Sigma) and NTA (nitrilotriacetic acid, Sigma) were used as model ligands. Water ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) was obtained from Millipore Simplicity equipment.

### Instruments

SWASV measurements were performed with an Autolab PGSTAT10 (EcoChemie, software GPES version 4.9) and a Metrohm 663 VA polarographic stand (hanging mercury drop electrode mode). All potentials were measured against a Ag/AgCl reference electrode (3 M KCl).



**Fig. 3** Ligand concentration along a workday as obtained by the Scatchard linearization and non-linear curve fitting. Family 1;  $K_f1$   $(4.07 \pm 0.69) \times 10^6$ ; Family 2  $K_f2$   $(5.56 \pm 0.78) \times 10^5$

## Conclusions

Zinc, lead, cadmium, and copper were detected in the SRB samples. The most important changes in metal concentration were related to zinc and lead, which increased along the working day.

A combined strategy involving electrochemical techniques (SWASV), the Scatchard linearization, and a non-linear curve fitting function was applied to a model system of two ligand families of similar strength. The number of ligand families, the concentration ( $L_t$ ), and the strength of the metal-ligand interaction ( $K'f$ ) were successfully determined within experimental error. The same strategy was applied to characterize the complexing capacity of the SRB using Zn(II) as a representative metal of this electroplating process.

## Competing interests

The authors declare no competing interests.

## Authors' contributions

GLS performed the entire experimental work, data analysis and contributed to the draft version of the manuscript. Supervision of experimental work, analysis of results and writing of all versions of this manuscript was done by AZ and SAR. All authors read and approved the final manuscript.

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