Recovery of Cd(II) and Zn(II) from HCl medium using cellulose acetate sponges modified with Cyanex 923

Ma. Elena Páez-Hernández[a], Carlos A. Galán-Vidal[a], I.S. Ibarra[a], Prisciliano Hernández[b], Irma Pérez-Silva[a],*

[a]*Área Académica de Química, Universidad Autónoma del Estado de Hidalgo, Mineral de la Reforma, Hidalgo, Mexico, emails: iperez@uaeh.edu.mx (I. Pérez-Silva), paezh@uaeh.edu.mx (Ma.E. Páez-Hernández), galanv@uaeh.edu.mx (C.A. Galán-Vidal), israel_ibarra@uaeh.edu.mx (I.S. Ibarra)*
[b]*Universidad Politécnica de Francisco I. Madero, Área Académica de Ingeniería en Energía. Domicilio conocido, Tepatepec, Francisco I. Madero, Hidalgo 42660, Mexico, email: phernandez@upfim.edu.mx*

ABSTRACT

In this work, it was studied the recovery of cadmium(II) and zinc(II) from hydrochloric acid solutions by cellulose acetate sponges modified with Cyanex 923® in batch system. Modified sponges (MS) were obtained from a recycled cellulosic man-made material (cigarette butts) that represent a major environmental contamination problem worldwide. MS were characterized using different techniques such as scanning electron microscopy and energy-dispersive X-ray spectroscopy. Some effective parameters on adsorption and recovery of both metals, such as the amount of Cyanex 923 in the test solution, mass of sponges, adsorption time, acidic chloride medium in adsorption, and recovery phase have been evaluated. Adsorption isotherms (Freundlich equation) gave a satisfactory fit of the equilibrium data with a best sorption of 8.90 and 45.43 mg g^{-1} for Cd(II) and Zn(II), respectively. The desorption of both metals occurred with 0.25 mol L^{-1} of HNO$_3$. The proposed method was evaluated with a polluted water from an urban reservoir (dam) doped with heavy metals that are present in hydrometallurgy wastewater.

Keywords: Sponges; Cellulose acetate; Adsorption; zinc; Cadmium

1. Introduction

Any toxic metal may be called heavy metal by the assumption that heaviness and toxicity are inter-related [1]. Heavy metals include lead (Pb), mercury (Hg), arsenic (As), chromium (Cr), copper (Cu), selenium (Se), nickel (Ni), silver (Ag), cadmium (Cd), and zinc (Zn) [2]. These metals contribute to environmental pollution due to natural and anthropogenic causes. Anthropogenic causes are the main sources of emission; these include industrial processes, sites of mining and foundries, combustion by-products, hydrometallurgy, among others.

Cadmium and zinc are potentially hazardous if discharged in large quantities due to high toxicity, which is why they arouse special consideration, and at the same time, they are common in wastewater [3,4]. The concentration of Cd(II) and Zn(II) in samples of unit operation wastewater and treatment system influent are 244 and 188 mg L^{-1}, respectively [5] while the limits of discharge by industrial activities for Cd(II) and Zn(II) are 0.01 and 1 mg L^{-1}, respectively [6].

Zinc is a trace element that is essential for human health, but an excess of Zn can cause stomach cramps, skin irritations, vomiting, nausea, and anemia. On the other hand, cadmium enters the organism primarily via the

* Corresponding author.

alimentary and/or respiratory tract and it may lead to renal toxicity, pancreatic cancer, or enhanced tumor growth [7].

Due to their versatility, long life, and low cost the use of both metals in different industries has increased, which results in an increase of potential sources of contamination, and consequently, in the need to develop effective methods for their recovery. Some used methods include liquid–liquid extraction [8–14], chemical precipitation with hydroxide and sulfide [8], membrane filtration [8], ion exchange [8,15], electrochemical treatment [8,16], and adsorption [8,17,18]. The latter is a flexible, effective, and economic method in which the adsorbent material could, on some occasions, be regenerated [8].

Synthetic polymers have attracted attention for their use in water treatment in the last decades; however, the industry faces two major problems: the use of non-renewable chemicals to manufacture commodity polymers and the ultimate fate of waste materials [19]. For this reason, biodegradable polymeric materials have attracted a lot of attention because of current interest in sustainability, recyclability, and environmental responsibility [20]; some examples are chitin, starch, polyhydroxyalkanoates, polylactide, polycaprolactone, collagen, and cellulose [21].

Cellulose is one of the most abundant naturally occurring polymers on earth, it is insoluble in water and in most used organic solvents due to strong inter and intra-molecular hydrogen bonding between the individual chains [22]. Cellulose has a low heavy metal adsorption capacity, but a chemical modification can be carried out to achieve adequate structural durability and efficient adsorption capacity [23], the chemical, and/or mechanical treatment of cellulose can produce some materials as fibers and sponges [24,25]. Modified sponges have cavities where different substances can get trapped with high porosity, compressibility, and adsorption capacity [26,27]. Some uses of the modified sponges are water treatment to produce ultrapure water [28,29] and as adsorbents in pre-concentration processes for the quantification of azo dye [30].

When the adsorbent cellulose base is obtained from a recycled cellulosic man-made material, this adds additional value to the final product and it can contribute to solving environmental problems. An example of this type of material is the cigarette filters that are made of cellulose acetate from which cellulose can be obtained through the deacetylation process [31].

Around 9 trillion filtered cigarettes that are expected consumed by 2025 pose a serious toxic waste disposal problem causing an environmental risk due to toxic effects on living organisms and their durability in natural environments [32]. A solution to this problem is having recycling technology to achieve the sustainable use of cigarette waste. Researchers have developed different methods to recycle cigarette butt as incineration, adsorbents, biofilm, activated carbons, fibers for the reduction of polluted gases, and treatment of wastewater [33] for the remotion of different pollutants as lead, chrome [34], arsenic [35], and erythrosine dyes [36].

In this work, the obtained cellulose acetate from cigarette butt was used to prepare new cellulose acetate sponges modified with Cyanex 923. The sponges were used for the recovery of cadmium and zinc from an HCl medium due to the increase of acid in the hydrometallurgy for the high efficiency of the chloride in leaching processes, the solution power of oxides, hydroxides, and carbonates, the construction of resistant materials and the success of the different operations of the process [37,38]. The parameters that affect the adsorption and recovery of both metals were evaluated in a batch system.

2. Materials and methods

2.1. Reagents

Cigarette butts were collected in a local community. Denatured ethanol (96% v/v) and sodium hypochlorite (4.5% p/v) were purchased in a drugstore and a supermarket, respectively. Potassium hydroxide was J.T. Baker (ACS grade, Mexico) and acetic acid was Mallinckrodt (ACS grade, Mexico). Cd(II) and Zn(II) solution standards for inductively coupled plasma-direct current plasma (ICP/DCP) were Fluka (USA) HNO_3 70% and HCl 37% were obtained from Aldrich (ACS grade, USA). The ion carrier trialkyl phosphine oxides (Cyanex 923) was supplied from Cytec Industries Inc., (Mexico). Water was purified through a MilliQ Plus system (Millipore); the water resistivity being >18.2 MΩ cm.

2.2. Preparation of modified cellulose sponges

Tipping and wrapping paper and tobacco were removed from cigarette butts. About 14 g of cigarette butts were cut and treated for 1 h at a time with 200 mL of ethanol and 1.5% (v/v) sodium hypochlorite solution, washing between each solution with deionized water, in order to remove the compounds present in the filter after its use. Clean cigarette filters (0.5 g) were dissolved in 15 mL glacial acetic acid. The cellulose acetate sponges were prepared according to the immersion–precipitation method [30], the solution of cigarette filters in glacial acetic acid was added to 50 mL of deionized water at constant stirring and room temperature, resulting in the formation of sponges (SP) for precipitation. The SP were filtered and rinsed with deionized water several times to remove the excess of the acetic acid. The washed SP were poured in 50 mL of KOH 2 M solution for 24 h under constant stirring to alkalize the material. Filtering–washing procedure was repeated until excess base is removed (pH < 8), later 4 g of wet SP (~87% of humidity) were added to 200 mL of Cyanex 923 solution at different concentrations (casting solutions) for 15 h. After this period, filtering–washing procedure was repeated until removing the extra Cyanex 923 to obtain the modified sponges (MS).

The MS morphology was analyzed using scanning electron microscopy (SEM) (JEOL JSM-63000 microscope). The estimate of phosphorous atomic percentage immobilized was determined by energy-dispersive X-ray spectroscopy (EDX) in a SEM, JEOL JSM-5600LV model.

2.3. Metal adsorption–desorption general procedure

10 mL of binary solution of Cd(II) and Zn(II) with initial concentrations of 10 mg L^{-1} for each metal (amount used in evaluation of other sorbents [39–41]) in HCl were shaken

with different amount of MS. The total metal adsorbed was calculated according to Eq. (1):

$$q_A = \frac{(C_0 - C_{AS}) \times V}{At.Wt._M \times m_{MS}}$$ (1)

where q_A is the amount of metal adsorbed (mmol kg^{-1}), C_0 and C_{AS} is the Cd(II) and Zn(II) concentration (mg L^{-1}) in the solution before and after the sorption respectively; V is the aqueous solution volume (L), At.Wt.$_M$ is metal atomic weight, and m_{MS} is the amount of modified sponges (kg).

The percentage of adsorption of each metal (%E_{Ads}) was calculated according to Eq. (2) where C_0 is the concentration of each metal in the initial solution:

$$\%E_{Ads} = \left(\frac{C_0 - C_{AS}}{C_0}\right)100$$ (2)

For the total desorption of cadmium(II) and zinc(II), MS used in the sorption was shaken with 10 mL of a recovery solution for 1 h. The capacity of desorption (q_D) of both metals was calculated according to Eq. (3):

$$q_D = \frac{C_{AD} \times V}{At.Wt._M \times m_{MS}}$$ (3)

where C_{AD} is the concentration of each metal in the recovery solution after the desorption (mg L^{-1}).

All the experiments (sorption and desorption) were performed three times and the concentration of the metals was determined by means of a flame atomic absorption spectrometer (VARIAN SpectrAA-880).

2.4. Adsorption isotherm

The adsorption of Zn(II) and Cd(II) was recorded in the range of 20–160 mg L^{-1} of metal ions in 1.5 M of HCl.

1.5 g MS prepared with 0.05% (w/v) of Cyanex 923 in casting solution (0.1 g$_{Cy\,923}$/g$_{SP}$) shaken at room temperature until the equilibrium was reached. Adsorption isotherm data were fitted to Langmuir, Freundlich, and Dubinin–Radushkevich model since they are the most used to describe the adsorption for wastewater treatment applications [42]. Table 1 shows linear forms of the isotherm used.

It is necessary for an error function to be defined in order to be able to evaluate the fit of the isotherm. For this reason, isotherms were evaluated by chi-square test (χ^2), a statistic to assess the fit of a regression. The data came from an experiment in which the fitted model is true, it is based on observed and expected observations according to Eq. (4) [48]:

$$\chi^2 = \sum \frac{(q_{ex} - q_{e,m})^2}{q_{e,m}}$$ (4)

where $q_{e,m}$ is the equilibrium capacity (mg g^{-1}) obtained from the model and q_{ex} is experimental data is the concentration of each metal in the solution after the desorption process (mg L^{-1}).

3. Results and discussion

3.1. Evaluation of the extractant concentration

The effect of the extractant amount on the modification process was investigated. Different concentrations in the casting solution were tested and shown in Table 2. It is also shown the relationship between the grams of Cyanex 923 and the grams of sponges mixed during the modification process described in the experimental part. The results have shown that the percentage of phosphorous in the MS increased according to the extractant concentration in the casting solution increasing the metal adsorption capacity [49]. Considering all this, 0.1 g$_{Cy\,923}$/g$_{SP}$ was found to be more effective in separating those metal ions.

Table 1
Linear forms of different isotherms used in this work [43–47]

Isotherm	Linear form	Fundament	Parameter
Langmuir	$\dfrac{C_e}{q_e} = \dfrac{1}{q_{max}K_L} + \dfrac{C_e}{q_{max}}$	Adsorption only occur in identical and localized sites, homogeneous form, and in monolayer	q_e = amount adsorbed (mg g^{-1}) C_e = equilibrium concentration of adsorbate (mg L^{-1}) q_{max} = maximum adsorption capacity (mg g^{-1}) K_L = Langmuir constant of adsorption
Freundlich	$\log q_e = \log K_f + \dfrac{1}{n}\ln C_e$	Describe non-ideal and reversible process and over a heterogeneous surface	K_f = adsorption capacity (mg g^{-1}) n = adsorption intensity
Dubinin–Radushkevich	$\ln q_e = \ln q_{max} - \beta\varepsilon^2$ $\varepsilon = RT\ln\left(1 + \dfrac{1}{C_e}\right)$ $E = \dfrac{1}{\sqrt{2B}}$	It is applied to distinguish the physical and chemistry adsorption (heterogeneous surface)	ε = Polany potential β = Dubinin–Radushkevich constant R = gas constant (8.1 J mol^{-1} K^{-1}) E = adsorption energy

Table 2
Effect of variation of the concentration of Cyanex 923 used for obtained the modified sponges (MS)

Cyanex 923 in casting solution (%w/v)	$g_{Cy\,923}/g_{SP}$	%P^a (SEM)	$q_{A_{Cd(II)}}{}^b$ (mmol kg^{-1})	$q_{A_{Zn(II)}}{}^b$ (mmol kg^{-1})
0.00	0.000	0.00 (0.00)	0.07 (9.17)	0.09 (4.94)
0.05	0.025	1.01 (2.80)	0.70 (2.09)	1.16 (4.25)
0.10	0.050	1.20 (0.59)	0.71 (8.15)	1.34 (3.87)
0.20	0.100	1.46 (4.84)	0.82 (2.85)	1.51 (4.38)
0.40	0.200	2.23 (5.07)	0.85 (0.15)	1.59 (0.39)

[a]Percentage of atoms of phosphorous;
[b]Experimental conditions: 10 mg L^{-1} of each metal ion in aqueous solution in 2 M of HCl; 2 g of MS. Values were obtained after 2 h counted from the start of the experiment;
In all the cases percentage of relative standard deviation in parenthesis

The morphology of the MS was examined by SEM. Fig. 1 shows that the surface of the sponge has different size cavities (1.05 μm, n = 8) distributed in the entire surface, which allowed having a great adsorption area and a better interaction between the metals and the surface.

### 3.2. Evaluation of the effect of the MS mass on the metal adsorption

Fig. 2 shows the effect of the MS amount in the adsorption percentage of Cd(II) (Fig. 2a) and Zn(II) (Fig. 2b). An increase in the MS dosage resulted in an increase in adsorption percentage of metal ions due to the increase of amount of Cyanex 923 in the system; however, from 1.5 g_{MS} the adsorption percentage is constant for both metals, for this reason, this is the mass used in the following experiments.

3.3. Evaluation of the effect of HCl concentration

Different chemical species of Cd(II) and Zn(II) are present in the aqueous phase at varying HCl concentration, for this reason, it is necessary to do an evaluation of the effect of HCl concentration. At low HCl concentrations

Fig. 1. SEM image of the MS prepared with 0.1 $g_{Cy\,923}/g_{SP}$ in casting solution.

cadmium and zinc exist as M^{2+} and MCl$^+$ [50,51] but with an increase of HCl concentration, MCl$_2$ can be formed and this, in turn, increase the amount of solvated neutral complex to make the adsorption easier (Fig. 3). This allowed to use 1.5 mol L^{-1} as the optimal concentration for subsequent recovery experiments with which, in addition, more accurate results are obtained.

Considering this, the metal transport is according to the next reaction (Eq. (5)), where M represents the metal (Zn or Cd), L is the extractant, and n = 0, 1, 2 [52–54]:

$$M_{aq}^{2+} + (2+n)Cl_{aq}^{-} + nH_{aq}^{+} + qL_{org} \leftrightarrow H_nMCl_{(2+n)}qL_{org} \qquad (5)$$
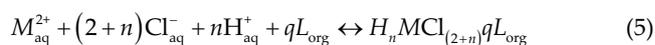
3.4. Adsorption isotherms

Information on distribution of metal ions between the liquid phase and the solid phase allowed to understand the adsorption process. In this case, isotherm models such as Langmuir, Freundlich, and Dubinin–Radushkevish were used to describe the adsorption. First, to find the time in which the extraction reached the equilibrium, experiments were carried out at different contact times (0.25 and 7 h). The minimum contact time was found to be 5 h for both metals. However, prolonged times had not an adverse effect on the extraction of Cd(II) and Zn(II) according to Table 3.

Table 4 shows that the adsorption energy obtained for Cd(II) (7.86 kJ mol^{-1}) and Zn(II) (7.11 kJ mol^{-1}) suggesting that the adsorption of both metals was by physisorption. The R^2 values Freundlich isotherm fit the sorption data in both cases; this indicated that there is the formation of a multilayer and a heterogeneous surface according to n [43–45].

According to Freundlich isotherm, the maximum adsorption capacity [46] for cadmium (8.90 mg g^{-1}) is lower than the adsorption capacity for zinc (45.43 mg g^{-1}); this is an advantage as cadmium is much less abundant in the earth's crust than zinc.

On the other hand, sponge without modification indicated physisorption for both metals and the existence of monolayer at the outer surface of the adsorbent [44]. The maximum adsorption capacity of SP (0.801 and 0.018 mg g^{-1} for Cd(II) and Zn(II), respectively) was less than the maximum capacity of MS, this is to confirm that the adsorption characteristics of the sponges improve with
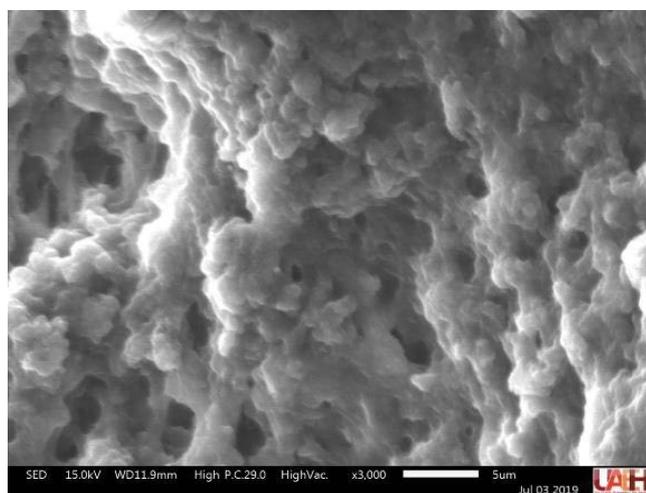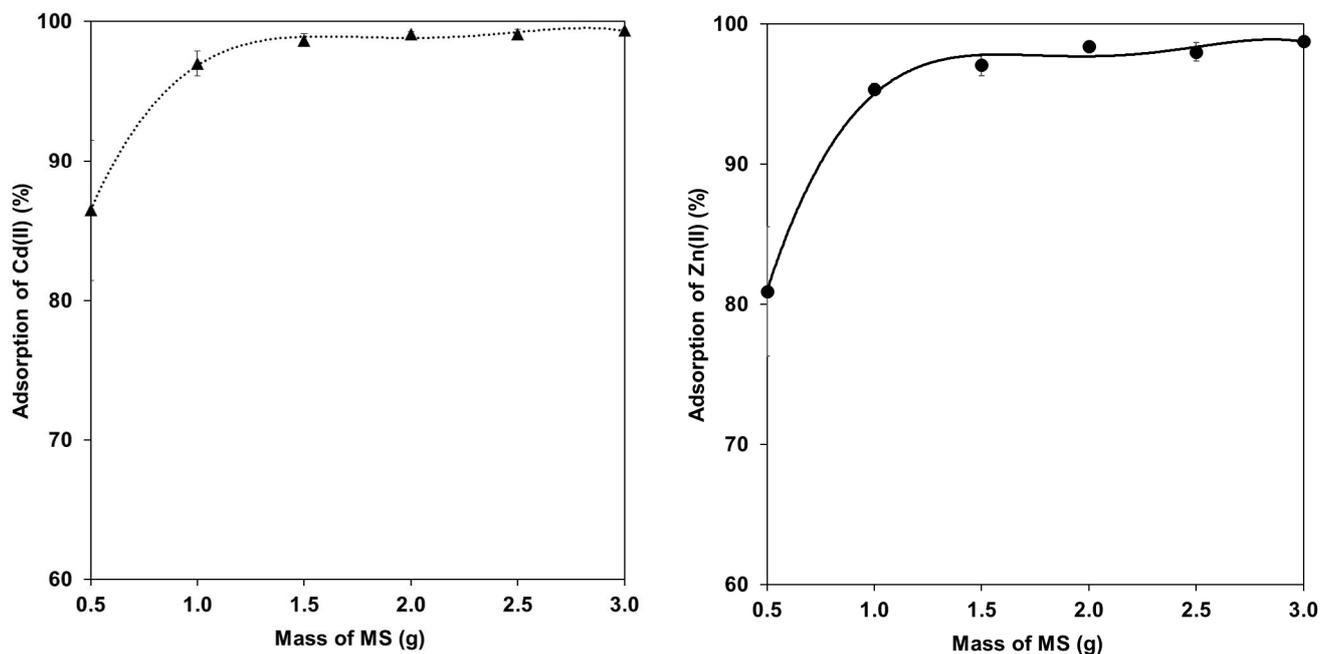
Fig. 2. Effect of variation of the weight of MS in the adsorption percentage. Experimental conditions: 10 mg L^{-1} of each metal ion in aqueous solution in 2 M of HCl, MS prepared with 0.1 g $_{Cy\ 923}$/g$_{SP}$ in casting solution. Values were obtained after 2 h counted from the start of the experiment. Relative standard deviation between 0.1 and 5.8.
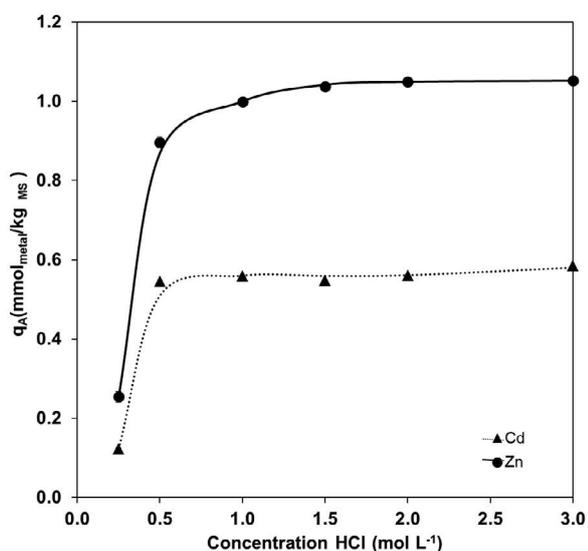

Fig. 3. Effect of variation of the HCl concentration in the absorption capacity. Experimental conditions: 10 mg L^{-1} of each metal ion in aqueous solution, 1.5 g MS prepared with 0.1 g$_{Cy\ 923}$/g$_{SP}$ in casting solution. Values were obtained after 2 h counted from the start of the experiment. Relative standard deviation between 0.2 and 5.5.

Table 3
Effect of the contact time in the adsorption of both metals[a]

Contact time (h)	$q_{Cd(II)}{}^{b}$ (mmol kg^{-1})	$q_{Zn(II)}{}^{b}$ (mmol kg^{-1})
0.25	0.55 (0.56)	0.25 (4.99)
0.50	0.55 (0.21)	0.90 (1.52)
1.00	0.55 (0.80)	1.00 (0.49)
2.00	0.56 (0.27)	1.04 (0.26)
5.00	0.55 (0.14)	1.05 (0.80)
7.00	0.55 (0.13)	1.05 (0.29)

[a]Experimental conditions: 10 mg L^{-1} of each metal ion in aqueous solution in 1.5 M of HCl; 1.5 g MS prepared with 0.1 g$_{Cy\ 923}$/g$_{SP}$ in casting solution;
[b]Percentage of relative standard deviation in parenthesis.

the presence of the extractant. In all the cases, high values of chi-square were obtained, showing a satisfactory fit of experimental data.

The adsorption capacity of the MS obtained is reasonable for adsorption of Cd(II) and Zn(II), it is within the values obtained for this type of materials (Table 5) which make it competitive for the removal of cadmium(II) and zinc(II).

3.5. Evaluation of the stripping phase in the recovery of Cd(II) and Zn(II)

The possibility of desorbing the metals from the MS is an important criterion to use this material as it makes recycling the metals possible. For this reason, different stripping phases that remove the metals through the destabilization of the chloro-complex were evaluated [52].

Solvating extractants can extract mineral acids because they share a pair of electrons through a donor atom; taking advantage of this, different acids were evaluated to desorb both metals [64].

Table 4
Isotherm parameters obtained by linear methods for adsorption of Cd(II) and Zn(II) onto sponge without modified and modified sponge

Isotherm	Parameter	Sponge without modified		Modified sponge	
		Cd(II)	Zn(II)	Cd(II)	Zn(II)
Langmuir	Q_0 (mg g^{-1})	0.801	0.018	0.20	2.918
	K_L (L mg^{-1})	0.001	0.071	0.25	0.005
	R^2	0.935	0.974	0.992	0.934
	χ^2	0.084	0.001	0.979	0.059
Freundlich	K_F (mg g^{-1})	0.004	0.003	8.900	45.430
	n_0	1.627	1.444	8.650	1.280
	R^2	0.615	0.692	0.995	0.944
	χ^2	1.509	0.095	0.0003	0.039
Dubinin–Radushkevich	β (mol J^{-2})	–0.010	–0.010	–0.008	–0.010
	E (kJ mol^{-1})	7.04	7.00	7.86	7.11
	R^2	0.999	0.997	0.993	0.999

[a]Experimental conditions: 10 mg L^{-1} of each metal ion in aqueous solution in 1.5 M of HCl; 1.5 g MS prepared with 0.1 $g_{Cy\ 923}/g_{SP}$ in casting solution.

The results of Fig. 4 show that its efficiency follows the order: $HNO_3 > H_2SO_4 > H_3PO_4 > H_2O$, indicating that desorption in water is lower than in an acid medium, probably due to the different hydration energies of the compounds and its readily dehydration [65]. This behavior was previously observed by Arias et al. [66] and El-Hefny et al. [67]. Considering this, HNO_3 was used for subsequent studies.

3.6. Evaluation of stripping phase concentration

The effects of HNO_3 concentration (0.1–1.0 mol L^{-1}) on the recovery of Cd(II) and Zn(II) were investigated and the results are shown in Table 6. From the obtained results, it seems that recovery capacity is similar in all cases, but data confirm a better reproducibility with 0.25 mol L^{-1} of HNO_3. For this reason, this concentration was used in subsequent experiments.

Additionally, it was possible desorption of 0.37 mmol kg^{-1}; %RSD = 6.76 and 0.64 mmol kg^{-1}; %RSD = 1.11 for Cd(II) and Zn(II), respectively, after two cycles (adsorption–desorption) without any change. The reduction in the third cycle could be due to the destabilization of material.

3.7. Recovery of Cd(II) and Zn(II) in synthetic wastewater

The study of recovery of Cd(II) and Zn(II) using MS was realized with polluted water from an urban reservoir (dam) doped with some heavy metals that are present in hydrometallurgy wastewater (synthetic water) [68]. The composition of the synthetic water was 18 mg L^{-1} of copper, 40 mg L^{-1} of arsenic, 7 mg L^{-1} of chrome, 50 mg L^{-1} of lead, 40 mg L^{-1} of nickel, 141 mg L^{-1} of zinc, and 5 mg L^{-1} of cadmium.

Cadmium and zinc desorption of MS with HNO_3 0.25 mol L^{-1} were 0.19 mmol kg^{-1} ± 1.63% and 10.44 mmol kg^{-1} ± 1.00%, respectively. A *t*-test (95% confidence level) was performed between the system in deionized water (Cd$_{desorbed}$ = 0.12 mmol kg^{-1}, %RSD = 6.78, *n* = 3;
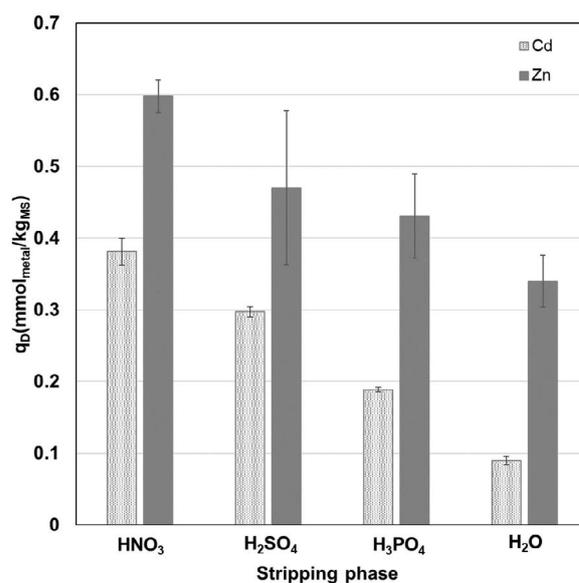

Fig. 4. Effect of the nature of the stripping phase in the recovery of Cd(II) and Zn(II). Experimental conditions: 10 mg L^{-1} of each metal ion in aqueous solution in 1.5 M of HCl, 1.5 g MS prepared with 0.1 $g_{Cy\ 923}/g_{SP}$ in casting solution. Recovery solution 0.5 mol L^{-1}, shake time 2 h.

Zn$_{desorbed}$ = 10.04 mmol kg^{-1}, %RSD = 0.82, *n* = 3) and the value obtained in the sample without an adsorption of the other heavy metals. This showed that the matrix does not have a negative impact on the adsorption of both metals, because there is no adsorption of the possible interferents in the sample due to the selectivity of extractant base on the working conditions [69,70]. An important point is that the recovery solution can be used as an initial solution for the electrodeposition of thin films used in window/buffer layer for solar cell [71].

Table 5
Comparison of bioadsorbents using sorption capacities (mg g^{-1}) according the Langmuir isotherm

Bioadsorbents	$q_{Cd(II)}$ (mg g^{-1})	$q_{Zn(II)}$ (mg g^{-1})
Orange peel [55]	127.02	79.11
Marine algae biomass [56]	85.43	52.92
MS^a	8.90	45.43
Zeolite 4A [57]	30.24	43.48
Zeolite 13X [57]	29.56	38.31
Palm kernel shell based activated carbon [58]	53.13	36.83
Bentonite [57]	28.43	35.17
Chlorella vulgaris [59]	44.96	31.38
Natural foxtail millet shell [60]	12.48	10.59
Wood ash [61]	8.40	7.50
Bagasse fly ash [62]	6.19	7.03
Chitin [63]	16.18	5.79

^{a}This work.

Table 6
Effect of the re-extractant concentration in the desorption capacity of Cd(II) and Zn(II)^a

Concentration HNO$_3$ (mol L^{-1})	$q_{R_{Cd(II)}}{}^b$ (mmol kg^{-1})	$q_{R_{Zn(II)}}{}^b$ (mmol Kg^{-1})
0.10	0.36 (7.33)	0.63 (6.53)
0.25	0.35 (0.16)	0.63 (0.82)
0.50	0.38 (5.14)	0.62 (6.68)
0.75	0.36 (7.06)	0.63 (2.24)
1.00	0.35 (2.10)	0.61 (1.71)

^{a}Experimental conditions: 10 mg L^{-1} of each metal ion in aqueous solution in 1.5 M of HCl; 1.5 g MS prepared with 0.1 g$_{Cy\,923}$/g$_{SP}$ in casting solution. Stripping phase HNO$_3$ with shake time of 2 h
^{b}Percentage of relative standard deviation in parenthesis.

4. Conclusions

The present study suggests that it is possible an adsorption and desorption of Cd(II) and Zn(II) using a MS of cellulose acetate with Cyanex 923 for the recovery of Cd(II) and Zn(II).

This study showed that the presence of HCl in the sorption solution has a significant impact on the absorption capacity of Cd(II) and Zn(II) due to the chloro-complex formation. Also, more Cyanex 923 in casting solution increased the sorption capacity. The studies revealed that H$_2$O is a good re-extractant agent of both metals; however, the best desorption capacity was obtained with HNO$_3$ due to the destabilization of the chloro-complex. Considering this, the best performance conditions was: metal solution with 1.5 mol L^{-1} of HCl; 1.5 g SM prepared with 0.1 g$_{Cy\,923}$/g$_{SP}$ in casting solution and stripping phase of 0.25 mol L^{-1} of HNO$_3$ with shake time of 2 h in both cases (adsorption and desorption). According to all the results, the developed MS are an good option for the recovery of Cd(II) and Zn(II) from synthetic hydrometallurgy without the matrix effect.

References

[1] P.B. Tchounwou, C.G. Yedjou, A.K. Patlolla, D.J. Sutton, Heavy metals toxicity and the environment, Natl. Inst. Health, 101 (2012) 133–164.

[2] J.O. Duruibe, M.O.C. Ogwuegbu, J.N. Egwurugwu, Heavy metal pollution and human biotoxic effects, Int. J. Phys. Sci., 2 (2007) 112–118.

[3] T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yang, M. Zhou, Z. Tan Z, X. Wang, Biosorption of cadmium(II), zinc(II) and lead(II) by *Penicillium simplicissimum*: isotherms, kinetics and thermodynamics, J. Hazard. Mater., 160 (2008) 655–661.

[4] M. Jaishankar, T. Tseten, N. Anbalagan, B.B. Mathew, K.N. Beeregowda, Toxicity, mechanism and health effects of some heavy metals, Interdiscip. Toxicol., 7 (2014) 60–72.

[5] EPA, Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category, 2020. Available at: https://www.epa.gov/sites/production/files/2015–11/documents/mp-m_dd_2003.pdf

[6] H.M. Zwain, M. Vakili, I. Dahlan, Waste material adsorbents for zinc removal from wastewater: a comprehensive review, Int. J. Chem. Eng., 2014 (2014) 1–13.

[7] M. Chamsaz, A. Atarodi, M. Eftekhari, S. Asadpour, M. Adibi, Vortex-assisted ionic liquid microextraction coupled to flame atomic absorption spectrometry for determination of trace levels of cadmium in real samples, J. Adv. Res., 4 (2013) 35–41.

[8] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, J. Environ. Manage., 92 (2011) 407–418.

[9] K. Takeshita, K. Watanabe, Y. Nakano, M. Watanabe, Extraction separation of Cd(II) and Zn(II) with Cyanex301 and aqueous nitrogen-donor ligand TPEN, Solvent Extr. Ion. Exch., 22 (2004) 203–218.

[10] H. Mahandra, R. Singh, B. Gupta, Liquid–liquid extraction studies on Zn(II) and Cd(II) using phosphonium ionic liquid (Cyphos IL 104) and recovery of zinc from zinc plating mud, Sep. Purif. Technol., 177 (2017) 281–292.

[11] M. Daryabor, A. Ahmadi, H. Zilouei, Solvent extraction of cadmium and zinc from sulphate solutions: comparison of mechanical agitation and ultrasonic irradiation, Ultrason. Sonochem., 34 (2017) 931–937.

[12] M. Regel, A.M. Sastre, J. Szymanowski, Recovery of Zinc(II) from HCl spent pickling solutions by solvent extraction, Environ. Sci. Technol., 35 (2001) 630–635.

[13] M. Regel-Rosocka, Ł. Nowak, M. Wiśniewski, Removal of zinc(II) and iron ions from chloride solutions with phosphonium ionic liquids, Sep. Purif. Technol., 97 (2012) 158–163.

[14] A.P. de los Ríos, F.J. Hernández-Fernández, F.J. Alguacil, L.J. Lozano, A. Ginestá, I. García-Díaz, S. Sánchez-Segado, F.A. López, C. Godínez, On the use of imidazolium and ammonium-based ionic liquids as green solvents for the selective recovery of Zn(II), Cd(II), Cu(II) and Fe(III) from hydrochloride aqueous solutions, Sep. Purif. Technol., 97 (2012) 150–157.

[15] A. Demirbas, E. Pehlivan, F. Gode, T. Altuna, G. Arslan, Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin, J. Colloid Interface Sci., 282 (2005) 20–25.

[16] L. Doulakas, K. Novy, S. Stucki, C. Comninellis, Recovery of Cu, Pb, Cd and Zn from synthetic mixture by selective electrodeposition in chloride solution, Electrochim. Acta, 46 (2000) 349–356.

[17] Y. Suneetha, B.N. Kumar, Y. Harinath, H.K. Reddy, K. Seshaiah, Functionalization of cross linked chitosan with 2-aminopyridine-3-carboxylic acid for solid phase extraction of cadmium and zinc ions and their determination by atomic absorption spectrometry, Microchim. Acta, 176 (2012) 169–176.

[18] A. Andelescu, M.A. Nistor, S.G. Muntean, M.E. Rădulescu-Grad, Adsorption studies on copper, cadmium, and zinc

ion removal from aqueous solution using magnetite/carbon nanocomposites, Sep. Sci. Technol., 53 (2018) 2352–2364.

[19] W. Amass, A. Amass, B.A. Tighe, Review of biodegradable polymers: uses, current developments in the synthesis and characterization of biodegradable polyesters, blends of biodegradable polymers and recent advances in biodegradation studies, Polym. Int., 47 (1998) 89–144.

[20] H.N. Cheng, An Overview of Degradable Polymers, K. Khemani, C. Scholz, Eds., Degradable Polymers and Materials: Principles and Practice, American Chemical Society, Washington, DC, 2012, pp. 13–14.

[21] L. Avérous, E. Pollet, Biodegradable Polymers, L. Avérous, E. Pollet, Eds., Environmental Silicate Nano-Biocomposites, Green Energy and Technology, Springer-Verlag, London, 2012, pp. 13–39.

[22] M.K. Trivedi, G. Nayak, S. Patil, R.M. Tallapragada, R. Mishra, Impact of biofield treatment on chemical and thermal properties of cellulose and cellulose acetate, J. Bioeng. Biomed. Sci., 5 (2015) 1–7.

[23] D.W. O'Connell, C. Birkinshaw, T.F. O'Dwyer, Heavy metal adsorbents prepared from the modification of cellulose: a review, Bioresour. Technol., 99 (2008) 6709–6724.

[24] Z. Zhang, G. Sèbe, D. Rentsch, T. Zimmermann, P. Tingaut, Ultralightweight and flexible silylated nanocellulose sponges for the selective removal of oil from water, Chem. Mater., 26 (2014) 2659–2668.

[25] Y. Li, L. Xu, B. Xu, Z. Mao, H. Xu, Y. Zhong, L. Zhang, B. Wang, X. Sui, Cellulose sponge supported palladium nanoparticles as recyclable cross-coupling catalysts, ACS Appl. Mater. Interfaces, 9 (2017) 17155–17162.

[26] D. Lembo, S. Swaminathan, M. Donalisio, A. Civra, L. Pastero, D. Aquilano, P. Vavia, F. Trotta, R. Cavalli, Encapsulation of Acyclovir in new carboxylated cyclodextrin-based nanosponges improves the agent's antiviral efficacy, Int. J. Pharm., 443 (2013) 262–272.

[27] J.A. Muñoz, A. Gonzalo, M. Valiente, Arsenic adsorption by Fe(III)-loaded open-celled cellulose sponge: thermodynamic and selectivity aspects, Environ. Sci. Technol., 36 (2002) 3405–3411.

[28] D. Li, M. Ma, Nanosponges for water purification, Clean Prod. Process., 2 (2000) 112–116.

[29] S.D. Mhlanga, B.B. Mamba, R.W. Krause, T.J. Malefetse, Removal of organic contaminats from water using nanosponge cyclodextrin polyurethanes, J. Chem. Technol. Biotechnol., 82 (2007) 382–388.

[30] R. Shiralipour, A. Larki, Pre-concentration and determination of tartrazine dye from aqueous solutions using modified cellulose nanosponges, Ecotoxicol. Environ. Saf., 135 (2017) 123–129.

[31] S.A. Ogundare, V. Moodley, W.E. van Zyl, Nanocrystalline cellulose isolated from discarded cigarette filters, Carbohydr. Polym., 175 (2017) 273–281.

[32] T.E. Novotny, K. Lum, E. Smith, V. Wang, R. Barnes, Cigarettes butts and the case for an environmental policy on hazardous cigarette waste, Int. J. Environ. Res. Public Health, 6 (2009) 1691–1705.

[33] J. Torkashvand, M. Farzadkia, A systematic review on cigarette butt management as a hazardous waste and prevalent litter: control and recycling, Environ. Sci. Pollut. Res., 26 (2019) 1–13.

[34] T.G. Wang, L.Q. You, Q. Pan, Removal of Cr(VI) from water by used cigarette filters, Environ. Sustainable Ecosyst., (2016) 691–696, doi: 10.2991/iccte-16.2016.117.

[35] P.Z. Al-Salehin, F. Moeinpour, F.S. Mohseni-Shahri, Adsorption isotherm and thermodynamic studies of As(III) removal from aqueous solutions using used cigarette filter ash, Appl. Water Sci., 9 (2019) 1–8.

[36] M. Ajoor, F. Moeinpour, Adsorptive removal of erythrosine dye from aqueous solutions using used cigarette filter ash loaded with Al/Fe oxides, J. Phys. Theor. Chem., 14 (2017) 81–91.

[37] A.A. Baba, F.A. Adekola, Extraction of Zinc(II) by triphenylphosphite (TPP) in hydrochloric acid: kinetics and mechanism, Int. J. Phys., 3 (2008) 104–111.

[38] M.F. San Román, I. Ortiz-Gándara, E. Bringas, R. Ibañez, I. Ortiz, Membrane selective recovery of HCl, zinc and iron from simulated mining effluents, Desalination, 440 (2018) 78–87.

[39] S. Bunluesin, M. Kruatrachue, P. Pokethitiyook, S. Upatham, G.R. Lanza, Batch and continuous packed column studies of cadmium biosorption by *Hydrilla verticillata* biomass, J. Biosci. Bioeng., 103 (2007) 509–513.

[40] P.R. Kumar, P.A. Swathanthra, V.V.B. Rao, S.R.M. Rao, Adsorption of cadmium and zinc ions from aqueous solution using low cost adsorbents, J. Appl. Sci., 14 (2014) 1372–1378.

[41] A.R. Jaafar, M.H. Isa, S.R.M. Kutty, Adsorption of zinc, cadmium and nickel from aqueous solutions using ground water sludge (GWS), WIT Trans. Ecol. Envorin., 111 (2008) 247–253.

[42] K.V. Kumar, S. Sivanesan, Sorption isotherm for safranin onto rice husk: comparison of linear and non-linear methods, Dyes Pigm., 72 (2007) 130–133.

[43] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J., 156 (2010) 2–10.

[44] A.O. Dada, A.P. Olalekan, A.M. Olatunya, O. Dada, O. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk, IOSR J. Appl. Chem., 3 (2012) 38–45.

[45] A. de Sá, A.S. Abreu, I. Moura, A.V. Machado, Chapter 8: Polymeric Materials for Metal Sorption from Hydric Resources, A. Grumezescu, Ed., Water Purification, Elsevier, Cambridge, MA, 2017, pp. 289–322.

[46] C.K. Lim, H.H. Bay, C.H. Neoh, A. Aris, A. Majid, Z. Ibrahim, Application of zeolite-activated carbon macrocomposite for the adsorption of Acid Orange 7: isotherm, kinetic and thermodynamic studies, Environ. Sci. Pollut. Res., 20 (2013) 7243–7255.

[47] N. Ayawei, A.N. Ebelegi, D. Wankasi, Modelling and interpretation of adsorption isotherms, J. Chem., 2017 (2017) 1–11.

[48] Y.S. Ho, W.T. Chiu, C.C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, Bioresour. Technol., 96 (2005) 1285–1291.

[49] S. Vellaichamy, K. Palanivelu, Preconcentration and separation of copper, nickel and zinc in aqueous samples by flame atomic absorption spectrometry after column solid-phase extraction onto MWCNTs impregnated with D_2EHPA-TOPO mixture, J. Hazard. Mater., 185 (2011) 1131–1139.

[50] N.V. Nguyen, J. Lee, H.T. Huynh, J. Jeong, Extraction and separation of cadmium from the chloride solution of E-waste using Cyanex 923 impregnated Amberlite XAD-7HP resin, Mater. Trans., 56 (2015) 1294–1301.

[51] R. Singh, H. Mahandra, B. Gupta, Solvent extraction studies on cadmium and zinc using Cyphos IL 102 and recovery of zinc from zinc-plating mud, Hydrometallurgy, 172 (2017) 11–18.

[52] R. Navarro, I. Saucedo, A. Núñez, M. Ávila, E. Guibal, Cadmium extraction from hydrochloric acid solutions using Amberlite XAD-7 impregnated with Cyanex 921 (tri-octyl phosphine oxide), React. Funct. Polym., 68 (2008) 557–571.

[53] A.M. Rodríguez, D. Gómez-Limón, F.J. Alguacil, Liquid–liquid extraction of cadmium(II) by Cyanex 923 and its application to a solid-supported liquid membrane system, J. Chem. Technol. Biotechnol., 80 (2005) 967–972.

[54] F.J. Alguacil, S. Martínez, Solvent extraction of Zn(II) by Cyanex 923 and its application to a solid-supported liquid membrane system, J. Chem. Technol. Biotechnol., 76 (2001) 298–302.

[55] X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, W. Shao, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, Colloid Surf., A, 317 (2008) 512–521.

[56] P.X. Sheng, Y.P. Ting, J.P. Chen, L. Hong, Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, J. Colloid Interface Sci., 275 (2004) 131–141.

[57] G. Purna, C. Rao, S. Satyaveni, A. Ramesh, K. Seshaiah, K.S.N. Murthy, N.V. Choudary, Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite, J. Environ. Manage., 81 (2006) 265–272.

[58] L.C. Abdullah, Y. Robiah, A.R. Suraya, T. Choong, Single and binary adsorptions isotherms of Cd(II) and Zn(II) on palm kernel shell based activated carbon, Desal. Water Treat., 29 (2011) 140–148.

[59] A. Fraile, S. Penche, F. González, M.L. Blázquez, J.A. Muñoz, A. Ballester, Biosorption of copper, zinc, cadmium and nickel by *Chlorella vulgaris*, Chem. Ecol., 21 (2005) 61–75.

[60] S.H. Peng, R. Wang, L.Z. Yang, L. He, X. He, X. Liu, Biosorption of copper, zinc, cadmium and chromium ions from aqueous solution by natural foxtail millet shell, Ecotoxicol. Environ. Saf., 165 (2018) 61–69.

[61] T. Chirenje, L.Q. Ma, L. Lu, Retention of Cd, Cu, Pb and Zn by wood ash, lime and fume dust, Water Air Soil Pollut., 171 (2006) 301–314.

[62] V.C. Srivastava, I.D. Mall, I.M. Mishra, Modelling individual and competitive adsorption of cadmium(II) and zinc(II) metal ions from aqueous solution onto bagasse fly ash, Sep. Sci. Technol., 41 (2006) 2685–2710.

[63] B. Benguella, H. Benaissa, Effects of competing cations on cadmium biosorption by chitin, Colloid Surf., A, 201 (2002) 143–150.

[64] F.J. Alguacil, F.A. López, The extraction of mineral acids by the phosphine oxide Cyanex 923, Hydrometallurgy, 42 (1996) 245–255.

[65] D. Li, C. Wang, Solvent extraction of Scandium(III) by Cyanex 923 and Cyanex 925, Hydrometallurgy, 48 (1998) 301–312.

[66] A. Arias, I. Saucedo, R. Navarro, V. Gallardo, M. Martinez, E. Guibal, Cadmium(II) recovery from hydrochloric acid solutions using Amberlite XAD-7 impregnated with a tetraalkyl phosphonium ionic liquid, React. Funct. Polym., 71 (2011) 1059–1070.

[67] N.E. El-Hefny, M.S. Gasser, S.E. Rizk, E.A. Saad, J.A. Daoud, Separation and recovery of Zinc(II) and Cobalt(II) from a mixed sulfate/thiocyanate solution using some commercial organophosphorus extractants, Solvent Extr. Ion. Exch., 28 (2010) 244–266.

[68] D. Kalderis, E. Tsolaki, C. Antoniou, E. Diamadopoulo, Characterization and treatment of wastewater produced during the hydro-metallurgical extraction of germanium from fly ash, Desalination, 230 (2008) 162–174.

[69] B. Gupta, A. Deep, V. Singh, S.N. Tandon, Recovery of cobalt, nickel and copper from sea nodules by their extraction with alkylphosphines, Hydrometallurgy, 70 (2003) 121–129.

[70] B. Gupta, A. Deep, S.N. Tandon, Extraction and separation of some 3d transition metal ions using Cyanex 923, Solvent Extr. Ion Exch., 20 (2002) 81–96.

[71] S.Z. Werta, O.K. Echendu, F.B. Dejene, Simplified two-electrode electrochemical growth and characterization of $Cd_{1-x}Zn_xS$ thin films: influence of electrolytic bath pH, Physica B, 580 (2020), doi: 10.1016/j.physb.2019.411939.