Removal of Cd(II) and Pb(II) from Aqueous Mining Systems by Flotation Techniques

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Metallic ions contained in mining waters are dangerous pollutants representing at the sometime potential sources of useful compounds. Significant levels of cadmium and lead have been reported in acid mine drainage (440–1.000 mg·L^{-1} for Cd(II) and 100–500 mg·L^{-1} for Pb(II)).

The paper presents two methods for M(II) separation (M(II)=Cd and Pb) are proposed:

- precipitate flotation of the Cd(II) and Pb(II) hydroxospecies in interaction with a cationic collector,
- M(II) sorbtion on *Penicillinium c.* support followed by flotation.

For the each method the influence factors were studied (pH, molar ratio (Collector: CM(II)), M(II) concentration, flow gas, respectively biomass concentration. The obtained results were interpreted for the selection of the most efficient method. The studied methods permit both mining waters cleanup and useful compounds recovery.

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1 Introduction

Flotation is a selective and performant separation method, which can be applied for diluted aqueous systems (10^{-6}–10^{-2}M). These systems contain toxically ionic species which can become potential sources of useful compounds. Flotation achieves the separation of ionic species with good separation efficiency (% R ≥ 95) and simultaneously decreasing of ions concentration in aqueous phase to values less then 1 mg·L^{-1}, which represent an important aspect from environmental protection point. The quantitative recovery of extracted compounds as well as the study of possibility to obtain useful compounds, maintain the applicability of this method in comparison with other clean up methods (GIHAZY 1995; LIN & LIU 1996; MATIS et al. 1995; MATIS & ZOUBOULIS 2001; SCORZELLI 1999).

The research design aims to the systematic study of monocompound aqueous solution, $[M(OH_2)_x]^{n+}$ type (where M=Cd(II) and Pb(II)), by flotation (BRECH & VOLGER 1993). The first condition for separation is preliminary hydrophobicity of ionic species by insolubilisation of these as hydroxospecies associates with intervention of a tensioactive agent, STA-alckylamine (A) and sorption on inactive biomass followed by flotation of loaded support (B) (GUNNERIUSSON et al. 1994; JOULIVET et al. 1994).

The last ten years researches demonstrated that heavy metals removal from aqueous systems could be successfully accomplished by using active or inactive biomass, the process being already known as "biosorption". If the biosorption process is operated in stirred tanks using a suspended biomass (JACKSON et al. 1992), a subsequently solid/liquid separation stage is required. The specific characteristics of the sorbat/biomass system make difficult the separation by filtration (the process needs more time and may face filter blocking problems especially in the case of fine or ultrafine particles), centrifuging (apparent more expensive) or sedimentation (relatively slow process inadequate to biological materials which are usually of low density). Some flotation techniques were applied for microorganism separation (GADD 1988) with favourable results and this was the start point for combining biosorption with flotation for loaded biomass separation (MATIS et al. 1995; ZOUBOULIS & MATIS 1993).

The residual biomass, loaded with metallic ions retained by sorption in a preliminary step may be considered a very stable solid suspension. Meanwhile, being of organic nature, the biomass particles present a natural flotation tendency, a supplementary hydrophobic being not necessary.

Thus, flotation became of great interest among the bioseparation processes, too.

The main scope of research design is:

- reduction of metallic ions concentration from diluted solutions (10^{-6}–10^{-2}M) under limits in force of low established;
- separation of complex species, simple oxide precursors, or salts obtained by recovery processing of the foam from flotation result.

The research design covers two major interest areas:

- environmental protection, clean up of aqueous systems and recovery of metallic ions as useful compounds,
- obtaining of oxide material precursors by wet way in mild thermal conditions to apply flotation technique.

2 Experimental

2.1 Reagents

Aqueous "model" systems of $[M(OH_2)_y]^{2+}$type have been studied (M=Cd, Pb) by hydroxo-species flotation, in interaction with a suitable collector N donor (laurylamine and quaternary ammonium salt). The influencing factors, the separation efficiency and the ways of turning into account the extracted components have been also investigated.

$CdSO_4$ 8/3H_2O, $Cd(NO_3)_2$ and $Pb(NO_3)_2$, high purity degree, (stock solution 10^{-3}M) has been used to prepare working solutions, according to metallic ions concentration in real systems; NaOH, high purity degree, as precipitation reagent, solution 2M; laurylamine (LA) solution 0.2 % in ethanol/water 2/1 v.v, as collector.

Cd(II) and Pb(II) aqua solutions were treated under stirring with the precipitation reagent and collector then submitted to flotation.

As biomass, a *Penicillium chrysogenum* residue resulting from industrial fermentation in a Romanian factory for antibiotics was used. The mycelial residue was pretreated by a succession of operations and the obtained biomass was also characterized by the authors [articol trimis spre publicare]. The biomass particles, in a spherical shape, were of d< $0,25\cdot10^{-3}$ m .

The physico-chemical characterization revealed some important properties for performing good biosorption or biosorption-flotation in depolluting purposes: the specific surface value and the allure of adsorption isotherm indicates that the biomass belong to the class of the macroporous and mezoporous solids, the sorption of metallic ion species may be partly achieved by the acidic functional groups emphasized by potentiometric titration and also by IR spectrometry, the filamentous structure revealed by electronic microscopy and also the organic structure proved by chemical and thermic analysis explains the very good floatability of the biomass.

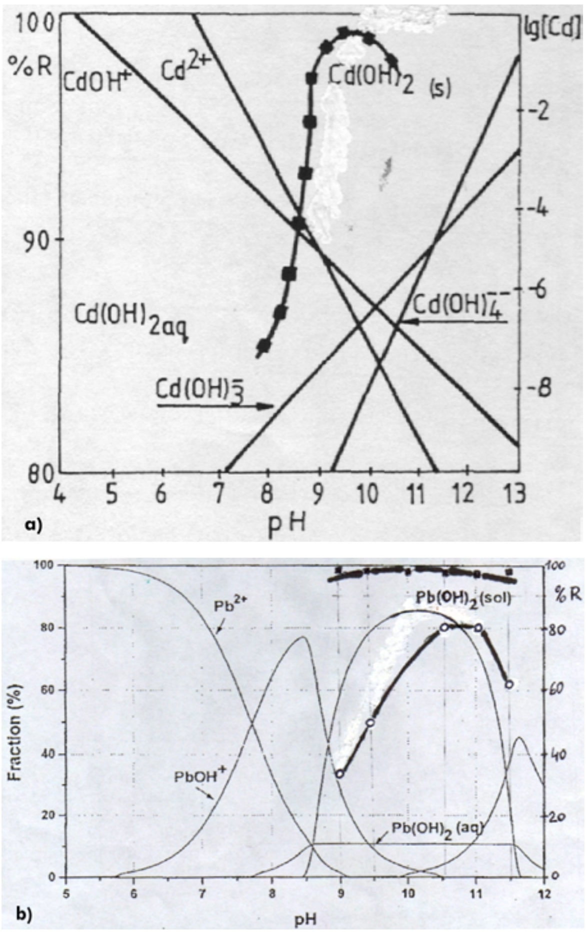

Figure 1: Flotation of M(II) hydroxides.

a) **$C_{iCd(II)}$=500 mg L^{-1}**

■ $Cd(OH)_2$ nH_2O-LA(C_C:$C_{Cd(II)}$= $5\cdot10^{-2}$)
— lg[Cd] ionic equilibria (GIHAZY 1995; STUMM & MORGAN 1981)

b) **$C_{iPb(II)}$=100 mg L^{-1}**
° $Pb(OH)_2$ nH_2O-LA(C_C:$C_{Pb(II)}$=10^{-1})
▪ $Pb(OH)_2$ nH_2O-LA(C_C:$C_{Pb(II)}$=10^{-1}) for effluent supernatant
— Pb(II) ionic equilibria (GIHAZY 1995; STUMM & MORGAN 1981)

The removal efficiencies were calculated with:

- % R = (1 - C_f/C_i) 100
- where: C_i=initial M(II) concentration or of loaded biomass, mg·L^{-1};

- C_f=final M(II) concentration or of loaded biomass at the end of the separation process, $mg \cdot L^{-1}$.

2.2 Methods and Apparatus

- A DAF cell were used for flotation experiments;
- The pH control was made with ORION 290 A
- M(II) concentrations were determined with Pye Unicam Atomic Absorption Spectrophotometer (SP9);
- For the foam collection (metalloaded biomass) and for remaining solution sampling special arrangements were provided. Stirring of model samples (0.200 L), containing cadmium or lead ions and the biomass was carried on by an electrical stirrer;
- The concentration of biomass was measured gravimetrically, by standard solid suspension determination;
- Otherwise stated, the $V_{sample}:V_{deionised\ water}$ was 3:1, flotation time 4 minutes, biomass concentration 2 $g \cdot L^{-1}$, initial cadmium or lead concentration 10 $mg \cdot L^{-1}$.

3 Results and Discussions

3.1 Precipitate Flotation Separation

3.1.1 Reagents Selection

The divalent cations M(II), as stable aqueous complexes $[M(OH_2)_4]^{2+}$ (M=Cd, Pb) are present in aqueous solutions at low pH values. In the presence of amine type collector, the M(II)-collector interactions are important and the process becomes more complex. The polymeric-hydroxospecies resulted by olation and/or oxolation process, $[M_p(OH)_y(OH_2)_x]^{np-y}$ are involved in the flocculation process.

Flotation permits the separation of these complex species in which the collector has a double role, both as surfactant and ligand. In the latter case the sublates are the complex coordinative compounds of M(II) cations with amine (the collector molecules). It is important to establish the best separation conditions regarding the precipitation reagent and the collector type, in the first stage of the separation process. The structure of Cd(II), Pb(II) specific hydroxospecies at pH=8–10.5 and the low values of the solubilities ($P_{SCd(OH)2}=1.2 \cdot 10^{-14}$ $P_{SPb(OH)2}=3 \cdot 10^{-16}$) permit the choice of NaOH as precipitation reagent and of the amine as collector. Collector reagent selection was based on Cd(II) and Pb(II) position in Ahrland series (cations B type) with affinity for $NH_3>HO^->H_2O$.

The descending aspect of the surface tension isotherm suggest the high surface activity of LA in connection with surface forces and the coordinating power of LA (through N-atom as donor) proving that LA could be among the suitable collector, for Cd(II) and Pb(II) separation.

In order to establish the best experimental conditions, the influence factors have been studied individually, in Cd(II)and Pb(II) removal.

3.1.2 pH Flotation

The concentrating tendency of hydrophobic species in foam depends on the pH flotation. In order to find the optimum pH flotation, the separation efficiency has been studied by %R=f(pH) function. Figure 1a shows the influence of pH on efficiency separation in the Cd(II)-collector system and Pb(II)-collector system (figure 1b), in comparison with pH influence on the existent Cd(II) and Pb(II) hydroxospecies. These pH values correspond to the structure of metallic species and to the ligand role of the collector. Optimal pH flotation is 9.5 for Cd(II)-LA system and 10.0 for Pb(II)-LA system.

3.1.3 Collector Concentration

In precipitate flotation, the collector concentration is, generally, under stoichiometrical values and has to be established in correlation with maximum %R; finally the collector concentration in aqueous solutions must be under allowed limits. Table 1 shows the experimental results regarding the relationship $\%R=f(C_C:C_{M(II)})$. The Cd(II) and Pb(II) removal by using LA as collector occurs with good efficiency even at $5 \cdot 10^{-3}$–1 molar ratio.

3.1.4 Colligend Concentration

In the range of 5–1000 $mg \cdot L^{-1}$ colligend concentration, flotation can be performed (under corresponding optimal pH and molar ratio) and the dependence $\%R=f(C_{M(II)})$ has been established. As can be observed in table 2, for the remaining concentration of metallic ions, $C_f < 1\ mg \cdot L^{-1}$, the good yields obtained prove the efficiency of the chosen method, in Cd(II) -LA and Pb(II)-LA systems.Gas flow

The necessary gas flow in the DAF separation has been obtained by pressurizing the diluting water (p=3.5–5·10^{-5} N·m^{-2}) followed by releasing the pressure in the flotation cell. Gas bubbles must have dimensional homogeneity and an optimum flow rate, in order to concentrate the sublate and avoid the collapse of the foam. The experimental results regarding the influence of the quality of air required, on the flotation efficiency were correlated with Cd(II)-LA and Pb(II)-LA sublates foam height.

The optimum dilution ratio was 3:1, for samples pressurised at 4·10^{-5} N·m^{-2}. An increase over this pressure was not necessary.

3.2 Biosorption Flotation Separation

Loaded biomass characteristics, important for the flotation experiments were not modified as a consequence of the biosorption stage. The increasing of the specific height of biomass particles by Cd(II) or Pb(II) retention was not significant. The factors influencing the separation process were studied.

3.2.1 Biosorption pH

pH considered in the flotation process was the one resulted after the sorption stage, the results showing very high recoveries of the loaded biomass for the solution pH values (table 3a and 3b). The fact is of significant importance for the entire biosorption process meaning that a pH correction it is not necessary after the biosorption stage for the flotation to proceed well.

The flotation pH was less than the initial biosorption pH, the values being modified during the biosorption stage, the Cd(II) or Pb(II) recovering efficiency resulting in fact from this process while the loaded biomass separation is the same for all the pH values.

3.2.2 Time

Flotation time is very important for the good development of the biosorption –flotation process being a significant technological parameter. The results showed (table 4a and 4b) that the process is really fast, as 1–2 minutes are enough to obtain loaded biomass recoveries over 80%. After 4 minutes practically the entire biomass is separate from the liquid phase.

3.2.3 Metallic Ions Concentration

Initial concentration of metallic ions in aqueous solution affects the global efficiency of biosorption-flotation process but not the recovery of the loaded biomass from the liquid phase. The experimental results are presented in table 5a and 5b showing the same high recovery of the loaded biomass.

4 Conclusions

1) The separation of Cd(II) and Pb(II) from aqueous mining solutions (10–1000 mg·L^{-1}) by flotation, DAF variant, or biosorption-flotation.
2) The decreasing of metallic cations concentration under allowed limits.
3) The obtained foam to flotation optimum parameters could be process for Cd(II) and Pb(II) quantitative recovery.
4) The recovery over 99% for the loaded Penicillium biomass.
5) The biosorbtion-flotation method efficiency could be better then flotation because of: high separation yield, biomass recycle and reaction agents are not necessary.
6) The proposed methods appear to be cost effective and environmentally acceptable.

Table 1: **%R= f(C_C:$C_{M(II)}$) dependence in M(II)-collector systems. ($C_{iCd(II)}$=500 mg·L^{-1}; $C_{iPb(II)}$=100 mg·L^{-1}; V_s=0.3 L; τ_{fl}=5 min.; V_s:V_w=3:1; p=4 10^5 N·m^{-2}).**

M(II)	optimal pH	C_C:$C_{M(II)}$	$C_{M(II)}$	% R*
Cd(II)	9.5	$5\cdot10^{-3}$	40.0	92.0
		$1\cdot10^{-2}$	29.0	94.2
		$2\cdot10^{-2}$	23.0	95.4
		$3\cdot10^{-2}$	10.5	97.9
		$5\cdot10^{-2}$	0.5	99.9
		$1\cdot10^{-1}$	0.5	99.9
Pb(II)	10.0	$1\cdot10^{-2}$	3.3	96.7
		$1\cdot10^{-1}$	1.5	98.5
		$5\cdot10^{-1}$	0.5	99.5
		1	0.4	99.6
		2	0.5	99.5

* $C_{fM(II)}$ from effluent supernatant

Table 2: **%R= f($C_{M(II)}$) dependence in Cd(II)-collector and Pb(II)-collector systems. ($C_{iCd(II)}$=500 mg·L^{-1}; $C_{iPb(II)}$=100 mg·L^{-1}; V_s=0.3 L; optimal pH flotation; τ_{fl}=5 min.; V_s:V_w=3:1; p=4 10^5 N·m^{-2} (recycling*)).**

$C_{M(II)}$ (mg L^{-1})	C_C:$C_{Cd(II)}$=$5\cdot10^{-2}$		C_C:$C_{Pb(II)}$=$5\cdot10^{-2}$	
	$C_{fCd(II)}$ (mg·L^{-1})	%R	$C_{fPb(II)}$ (mg·L^{-1})	%R*
5	0.8	84.0		
10	0.8	92.0	0.7	91.1
20	1.1	94.5		
50	1.9	96.2	0.6	98.5
100	1.2	98.8	0.3	99.6
200	0.9*	99.5		
500	0.8*	99.9	0.9	99.7
1000	0.9*	99.9	0.6	99.8

* $C_{fM(II)}$ from effluent supernatant

Table 3a: R%= f(pH) for Cd(II) recovery by biosorption-flotation. ($C_{iCd(II)}$ = 0.01g·L^{-1}).

Biosorption stage		Flotation stage			
time(min)	pH (initial)	pH	C_f(mg·L^{-1})	Cd(II) R(%)	Biomass R (%)
10	6	4.9	1.9	81.0	99.7
	7	6.0	0.5	95.0	99.7
	8	6.5	0.65	93.5	99.7
	9	6.9	0.8	92.0	99.7
20	6	5.3	0.85	91.5	99.7
	7	6.6	0.4	96.0	99.7
	8	7.1	0.6	94.0	99.7
	9	7.6	0.8	92.0	99.7

Table 3b: R%= f(pH) for Pb(II) recovery by biosorption-flotation. ($C_{iPb(II)}$ = 0.01g·L^{-1}).

Biosorption stage		Flotation stage			
time(min)	pH (initial)	pH	C_f(mg·L^{-1})	Pb (II) R (%)	Biomass R (%)
10	3	3.8	8.4	16.0	99.7
	4	4.2	0.92	90.8	99.7
	4.5	4.3	0.85	91.5	99.7
	5	4.7	0.9	91.0	99.7
20	3	3.9	8.1	19.0	99.7
	4	4.2	0.77	92.3	99.7
	4.5	4.3	0.58	94.2	99.7
	5	4.8	0.82	91.8	99.7

Table 4a: R%= f(time) for Cd(II) recovery by biosorption-flotation. (C_i=10mg·L^{-1}; pH=7; $C_{biomass}$=2 g·L^{-1}).

Biosorption stage	Flotation stage			
time (min)	time(min)	C_f(mg·L^{-1})	Cd(II) R(%)	Biomass R(%)
10	1	0.5	95.0	73.8
	2	0.5	95.0	82.1
	3	0.49	95.1	91.3
	4	0.48	95.2	99.7
20	1	0.41	95.9	73.6
	2	0.4	96.0	82.3
	3	0.4	96.0	91.2
	4	0.39	96.1	99.7
30	1	0.35	96.5	73.7
	2	0.35	96.5	82.3
	3	0.35	96.5	91.4
	4	0.34	96.6	99.8

Table 4b: R%= f(time) for Pb(II) recovery by biosorption-flotation. (C_i=10 mg·L^{-1}; pH=4.5; $C_{biomass}$=2 g·L^{-1}).

Biosorption stage	Flotation stage			
time (min)	time (min)	C_f(mg·L^{-1})	Pb(II) R(%)	Biomass R(%)
10	1	0.85	91.5	73.6
	2	0.85	91.5	82.2
	3	0.85	91.5	91.3
	4	0.84	91.6	99.7
20	1	0.58	94.2	73.7
	2	0.58	94.2	82.3
	3	0.57	94.3	91.2
	4	0.57	94.3	99.8
30	1	0.55	94.5	73.8
	2	0.55	94.5	82.4
	3	0.55	94.5	91.3
	4	0.56	94.6	99.7

Table 5a: R% = f($C_{i\ Cd(II)}$) for Cd(II) recovery by biosorption-flotation. (biosorption time =20 min.; pH=7).

Biosorption stage	Flotation stage		
C_i(mg·L^{-1})	C_f(mg·L^{-1})	Cd(II) R(%)	Biomass R(%)
100	17	83	99.7
50	5	90	99.6
10	0.5	95	99.7

Table 5b: R% = f($C_{i\ Pb(II)}$) for Pb(II) recovery by biosorption-flotation. (biosorption time =20 min.; pH=4.5).

Biosorption stage	Flotation stage		
C_i(mg·L^{-1})	C_f(mg·L^{-1})	Pb(II) R(%)	Biomass R(%)
100	6.24	93.7	99.7
50	0.64	98.72	99.7
10	0.58	94.2	99.8

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