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**FEDERICO II**

**UNESCO-IHE**  
Institute for Water Education



## **SULFATE-REDUCING ANAEROBIC IFBR FOR HEAVY METALS REMOVAL FROM WASTEWATER AT LOW PH**



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# Abstract

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## 1. Introduction

Mining activities are releasing extremely acidic leachates with high concentrations of sulfate, metalloids and heavy metals such as copper, nickel, zinc, lead and iron originating from the chemical or biological oxidation of exposed sulfideminerals. As a result, the combination of the generated acid and metal ions constitute the acid mine drainage (AMD). AMD severely affects the population's health due to its characteristics and has been identified as one of the most important environmental problems facing the minerals industry.

These wastewaters can be treated using several technologies prior to discharge into the environment including adsorption, cementation, electrowinning, ion exchange, membrane separation, precipitation or solvent extraction. Traditionally, most industries treated heavy metal containing wastewaters by precipitation with hydroxide because of process simplicity, low costs of chemicals and ease of process control. The drawbacks of this technique usually result in the production of unstable metal hydroxides which lead to greater disposal expense and which are hardly suitable for metal recovery.

In recent years, the use of biological treatment processes, based on the activity of sulfate reducing bacteria (SRB), have become more prominent. In these treatment processes, sulfate reducing bacteria generate sulfide and bicarbonate ions through the oxidation of a suitable electron donor and carbon source. The bicarbonate ions are used to neutralize acidic effluents while the sulfide ions are used to effect precipitation of the dissolved metal ions as metal sulfides. Although several novel treatment technologies based on the sulfate reduction process have been successfully developed and implemented at industrial scale, a number of challenges exist around the precipitation step, particularly where the recovery of valuable metals is desired which is beneficial for both economics and environmental reasons. Further, advantages of sulfide precipitation over hydroxide precipitation are: effluent concentrations are orders of magnitude lower ( $\mu\text{g/l}$  versus  $\text{mg/l}$ ); selective metal removal is possible; reaction rates are higher and metal sulfide sludge is more compact and exhibits better settling, thickening and dewatering characteristics than hydroxide sludge.

The use of biosulfidogenic processes for the production of sulfide and bicarbonate alkalinity has the potential to position metal sulfide precipitation as a viable option for large scale treatment of acidic effluents.

In order to obtain metal sulfide precipitates with good solid-liquid separation characteristics, effective control of the precipitation process is necessary. For optimal control and design of the precipitation process, the influence of operational and material parameters on the parameters must be known.

In recent years, considerable effort has been expended on the development of precipitation processes that produce precipitates with controlled properties using different configuration of reactors.

## **2. Objectives**

The overall objective of this study is to investigate the heavy metal removal from synthetic wastewater by SRB in an Inverse Anaerobic Fluidized Bed Reactor (IFBR).

The specific objectives of the study are:

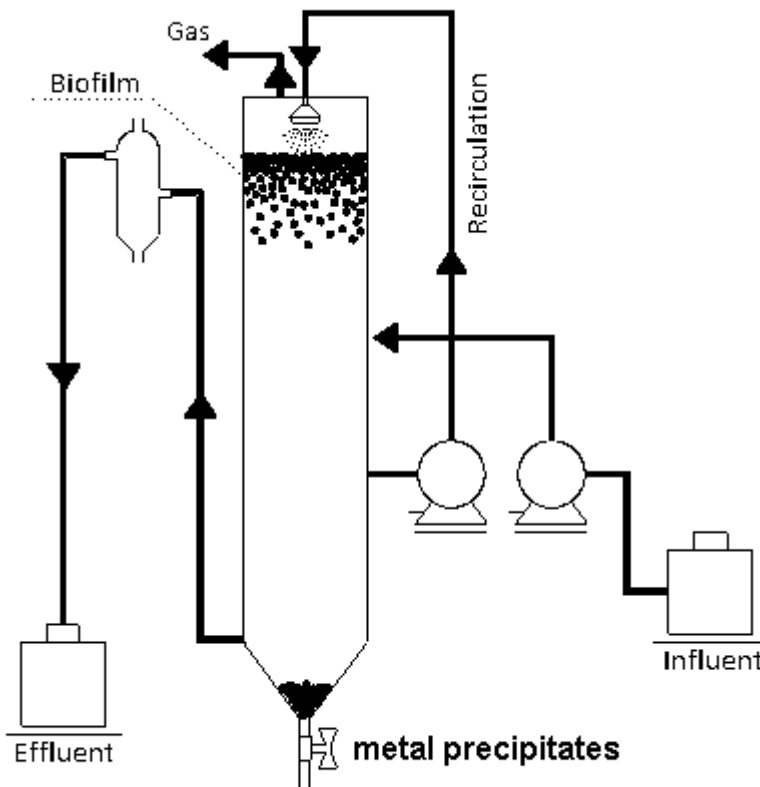
- to study the effect of the decrease of pH values on SRB;
- to investigate the effect of the decrease of pH values on zinc and copper precipitation in an IFBR;
- to achieve the optimum condition of pH values for each metal precipitate that would maximize the metal precipitate and recovery.

The experimental work about all these questions has been conducted for the Environmental Resources Department of the UNESCO-IHE Institute for Water Education located in Delft, the Netherlands.

## **3. Materials and Method**

An inverse anaerobic fluidized bed reactor (IFBR) is an innovative configuration of reactors recently used for sulfate removal and metal precipitation.

A scheme of a bench-scale IFBR is the following one:



4. Figura 3.1 – Simple scheme of a bench-scale inverse fluidized bed reactor

A synthetic wastewater rich of sulfate, organic matter and heavy metals is pumped in the middle of the reactor by means of a peristaltic pump. The support formed by little bullets, floats on the surface of the water because it is realized in a material lighter than water. In the operated reactors a polyethylene support is used. Once the influent is pumped into the reactor, it begins to move towards the bottom realizing in this the “down-flow”. The down-flow is also given by the presence of a recirculation flow pumped to the top of the reactor and spread on the support that needs for the fluidization of the bed; in this way there is the formation of turbulence and the contact between substrates (sulfate and organic matter) and microorganism attached to the bed is promoted. The value of recirculation flow is established to let the bed expand of about 25% of the initial height.

Below the fluidized bed there is no more turbulence and so the reaction between the dissolved sulfide, generated from the reduction of sulfate by SRB present in the biofilm, and heavy metals (zinc and copper) is possible. The formation of un-dissolved metal sulfide crystals occurs and

they tend to precipitate on the bottom of the reactor. In the top of the column an outlet for the gas is also present.

The experiments were carried out on two laboratory scale inverse fluidized bed reactors (IFBR) implemented in the laboratory of UNESCO-IHE Institute for Water Education in Delft, The Netherlands (Figure 3.2) under different pH values for reactor 1 (R1) and reactor 2 (R2).



**Figure 3.2 – IFBR's used in the lab, electrode used to measure and control the pH and example of turbulence of the bed.**

Each reactor consisted of a conical bottom column with the following features:

- total volume of 2.5 l;
- diameter of 0.05 m
- height of 1 m.

Both reactors were operated at a room temperature of  $25\pm 2^{\circ}\text{C}$ . A Data Acquisition Card (DAQ) was used to acquire data on a hardware. It was stored, displayed and analyzed through the computer program LabVIEW version 2009. Different interfaces at the program were developed to read and control the pH inside the columns by means of electrodes and acid/base pumps.

For the R1 the experimental period was divided in 2 periods, before and after the pH was increased from 5 to 7 because of his crash:

- Period I from day 1 to 48 – pH 5;
- Period II from day 49 to 150 – pH 7;

For the R2 the working time was divided in 4 periods:

- Period I from day 1 to 48 - pH 7;
- Period II from day 49 to 77 - metals addition;
- Period III from day 78 to 115 - decreasing of the pH from 7 to 5 and COD from 2 to 1 g/l;
- Period IV from day 116 to 150 - decreasing pH from 5 to 4.

The synthetic wastewater described in Table 3.1 was used in the operations of IFBRs.

Element	PERIOD I Days 1-48		PERIOD II Days 49-77		PERIOD III Days 78-115		PERIOD IV days 116-150	
	R1	R2	R1	R2	R1	R2	R1	R2
Yeast extract	20	20	20	20	20	20	20	20
NH <sub>4</sub> Cl	300	300	300	300	300	300	300	300
CaCl <sub>2</sub> *2H <sub>2</sub> O	15	15	15	15	15	15	15	15
KH <sub>2</sub> PO <sub>4</sub>	200	200	200	200	200	200	200	200
MgCl <sub>2</sub> *6H <sub>2</sub> O	120	120	120	120	120	120	120	120
KCl	250	250	250	250	250	250	250	250
Lactic Acid	1875	1875	1875	1875	1875	937.5	1875	937.5
Sulfate	3000	3000	3000	3000	3000	<b>1500</b>	3000	1500
Zinc			-	<b>1:2 [H<sub>2</sub>S]</b>	-	1:2 [H <sub>2</sub> S]	-	1:2 [H <sub>2</sub> S]
Copper			-	<b>1:2 [H<sub>2</sub>S]</b>	-	1:2 [H <sub>2</sub> S]	-	1:2 [H <sub>2</sub> S]
pH	3.5	7	7	7	7	<b>5</b>	7	<b>4</b>

Table 3.1 – Synthetic wastewater composition. Changes occurred during the experimental periods are reported in bold font.

IFBR efficiency was obtained by routine analysis based on the pH, COD,  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  concentration using standard methods and instruments described in Table 3.2.

The influent and effluent samples were different for each measured parameter:

- pH: 7 days/week
- COD: 3 days/week
- Sulfate: 3 days/week
- Sulfide : 5 days/week
- Acetate: 3 days/week
- Metals: 3 days/ week
- Particle Size Distribution (PSD): 3 days/week
- SEM Pictures for the precipitated formed in the reactor and in the batch bottle.

Batch experiments with biogenic sulfide was carried out to make a comparison of metals precipitates inside the reactor to batch mode and to investigate the location of precipitation of heavy metals according to the different pH. The biogenic sulfide was collected from the bottom of the reactor and the pH adjusted when it was necessary.

They were carried out three times:

- Experiment 1: triplicates at pH 7;
- Experiment 2: triplicates at pH 3;
- Experiment 3:
  - triplicates at pH 7
  - triplicates at pH 5
  - triplicates at pH 3.

## 4. Results

Conducted experiments on IFBR's demonstrated that:

- the optimal pH in terms of  $\text{SO}_4^{2-}$  and COD removal is 7 (Figure 4.1 a and b);

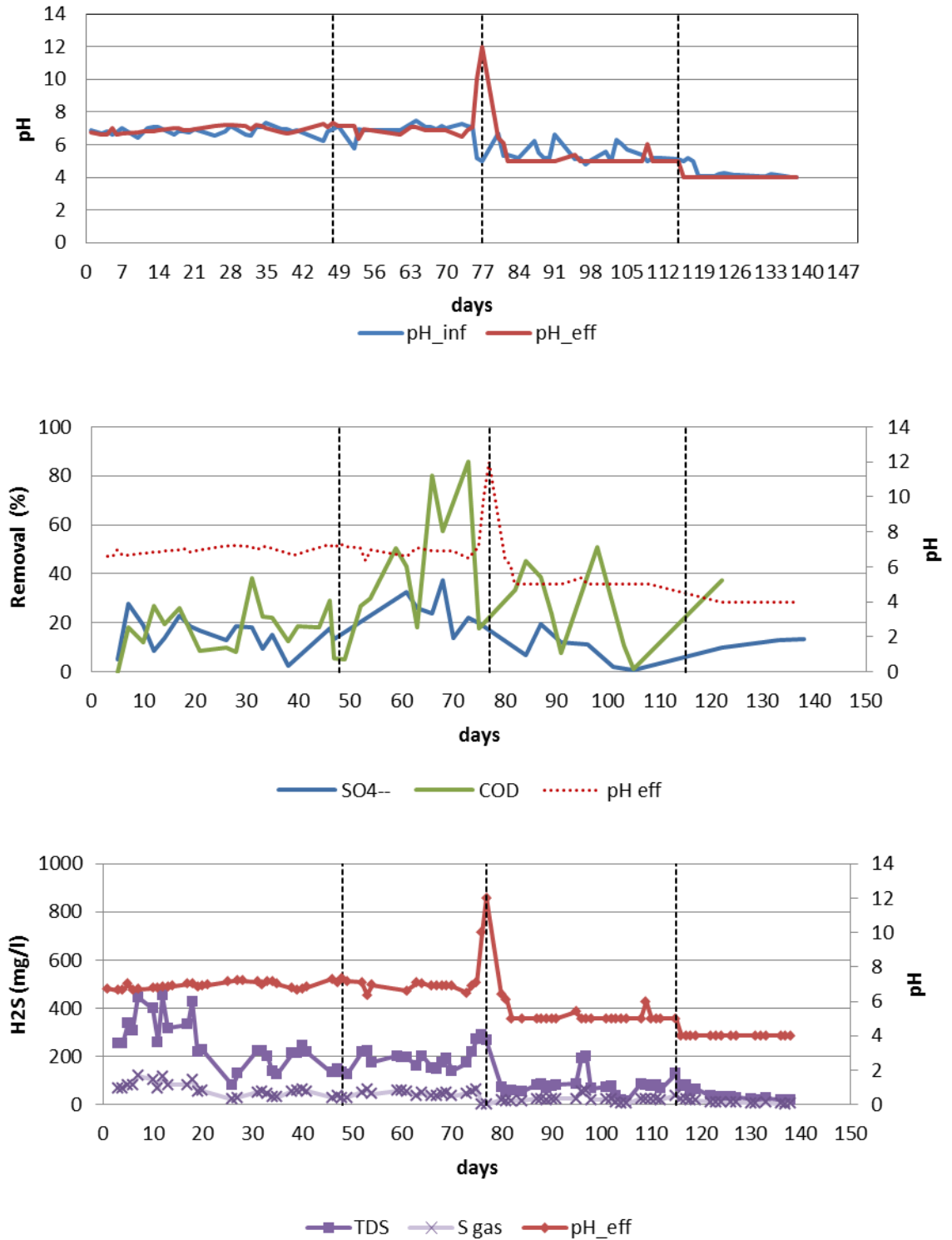


Figure 4.1a, b,c – pH, COD and Sulfate removal and sulfide production trends for the R2.



- The metal removal achieved inside the IFBR at pH 7 and 5 is higher than 90% for both Zn and Cu and selective recovery is not allowed; at pH 4 Zn removal is around 70%, Cu removal is 95% (Figure 4.2a and b); thus, this kind of treatment allowed the metal removal and could be used also as organic-matter-removal-pretreatment;

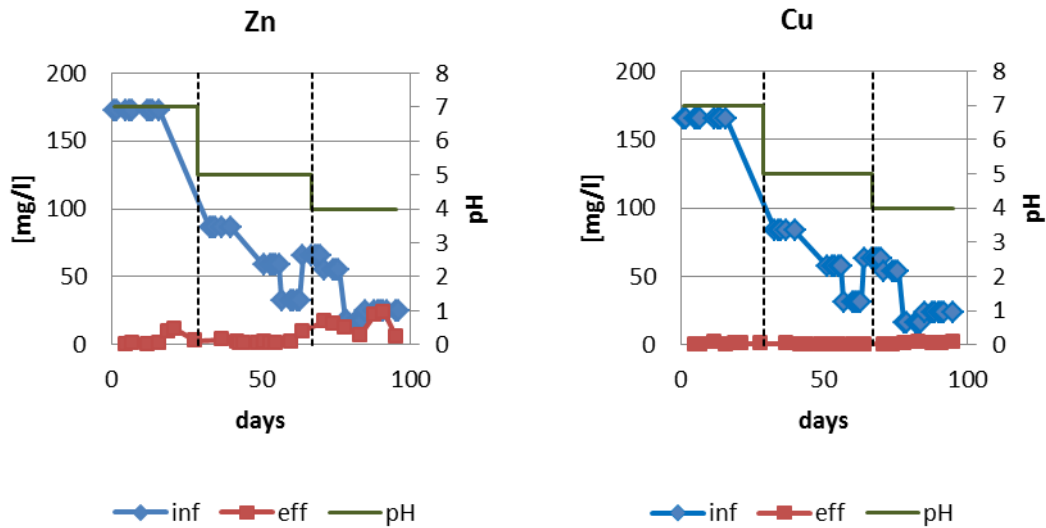


Figure 4.2a, b – Concentration for zinc and copper in the influent and effluent during experimental conditions at different pH

- Selective recovery is allowed at pH 3 during batch experiments conducted using biogenic sulfide from the IFBR (Figure 4.6 and 4.7);

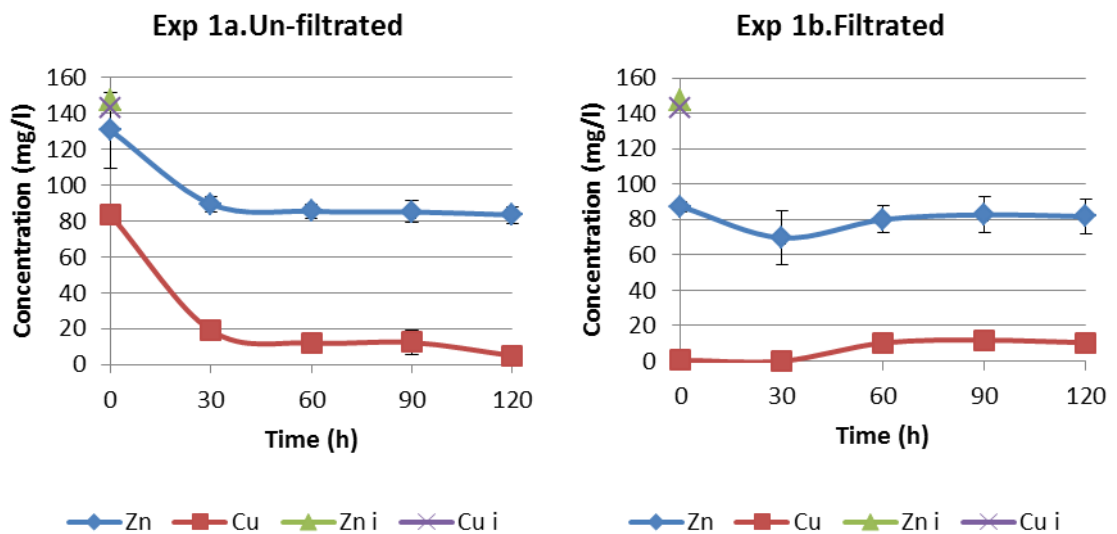


Figure 4.3 a, b – Evolution of metals concentration in the batch Experiment 1 at pH 7. Green triangle and purple cross shown the initial concentration of zinc and copper respectively.

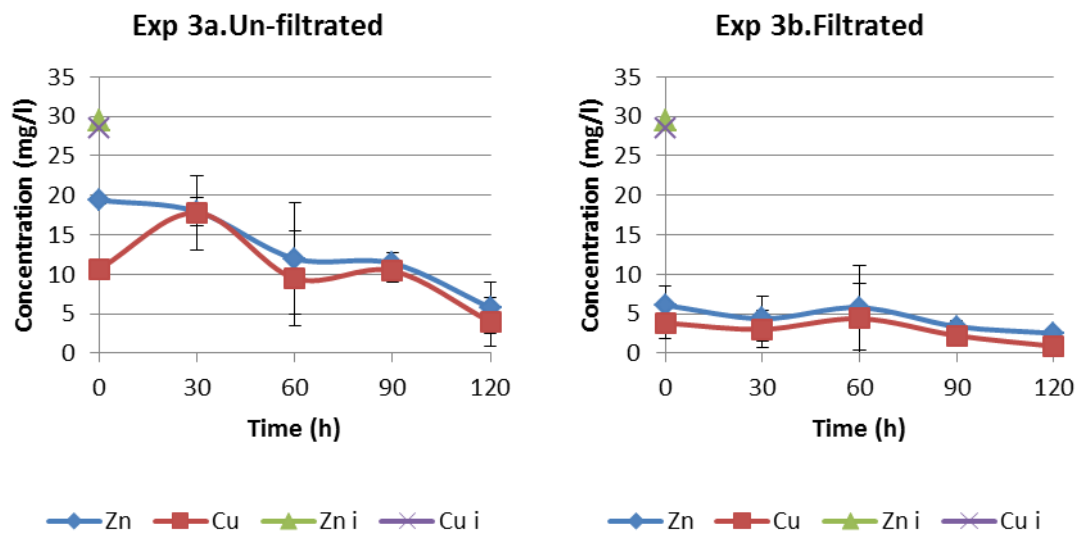


Figure 4.4 a, b – Evolution of metals concentration in the batch Experiment at pH 7. Green triangle and purple cross shown the initial concentration of zinc and copper respectively.

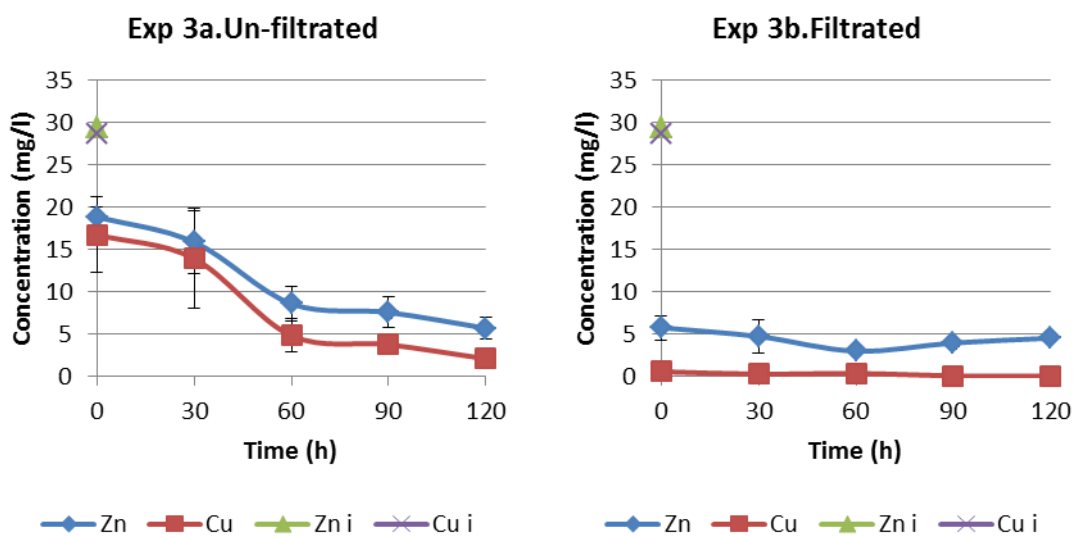


Figure 4.5 a, b – Evolution of metals concentration in the batch Experiment 3 at pH 5. Green triangle and purple cross shown the initial concentration of zinc and copper respectively.

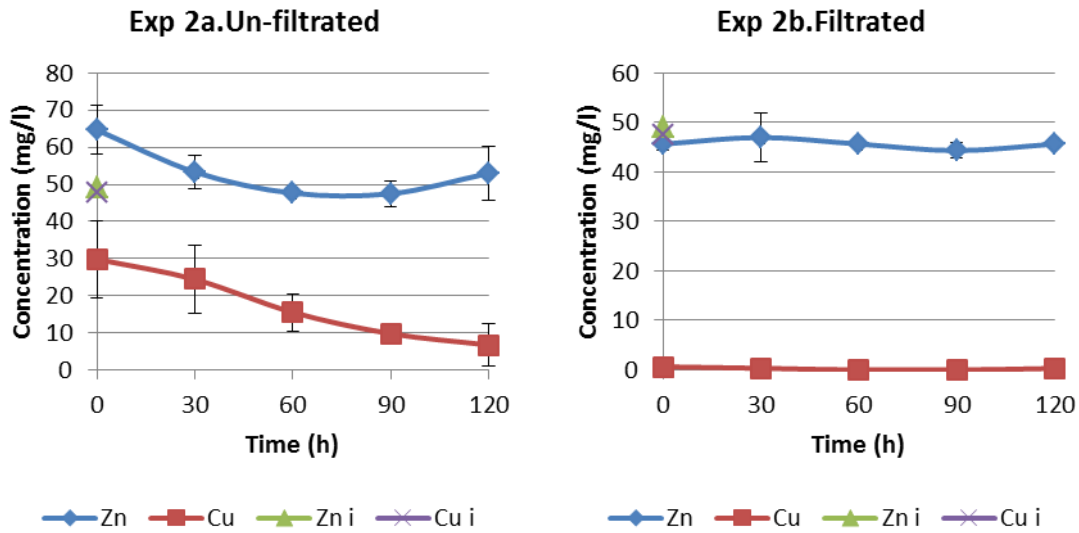


Figure 4.6 a, b – Evolution of metals concentration in the batch Experiment 2 at pH 3. Green triangle and purple cross shown the initial concentration of zinc and copper respectively.

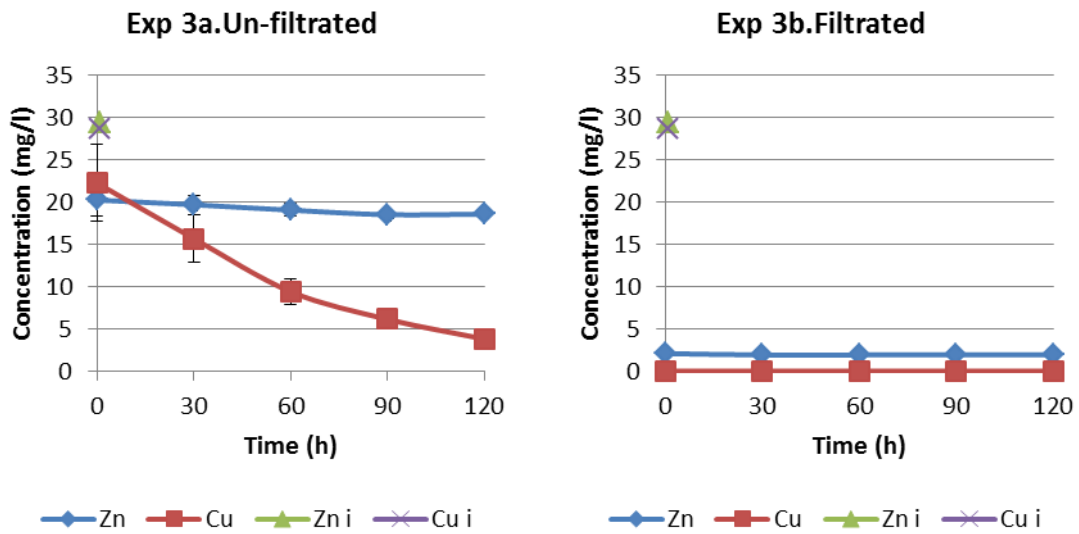
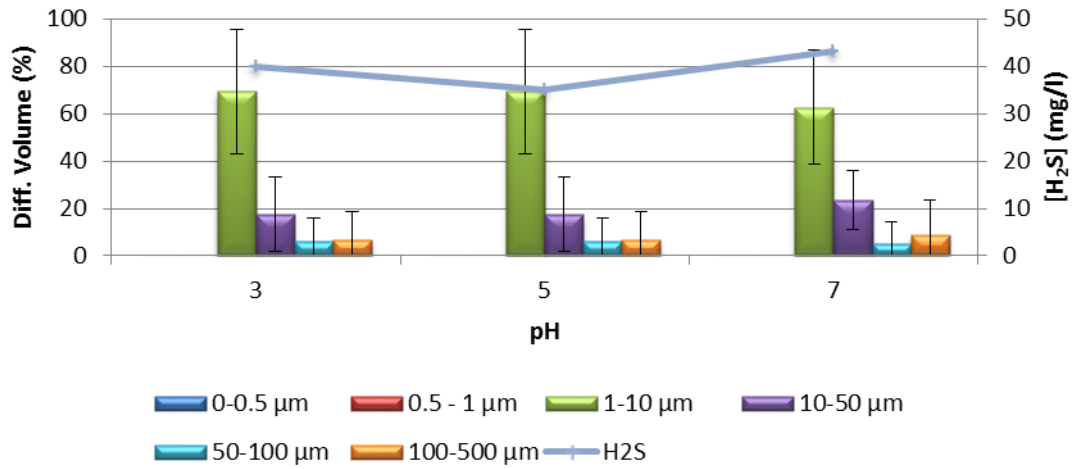


Figure 4.7 a, b – Evolution of metals concentration in the batch Experiment 3 at pH 3. Green triangle and purple cross shown the initial concentration of zinc and copper respectively.

- CuS and ZnS precipitation occurred very fast: measurements made immediately after metals addition showed a metals abatement of 40-50% (Figure 4.3-4.7)
- Experimental conditions play an important role on particles formation and this can influence the sub-sequential removal;

- The main size of the particles produced during batch experiments is in the range of 1-10  $\mu\text{m}$  (Figure 4.8);



• Figure 4.8– Particle size distribution of the particles produced during the batch experiments at pH 3, 5 and 7.

- The bigger amount of solids produced during the precipitation in a settling test is at pH 7 (1% of the total volume) (Figure 4.9);
- The amount of solids produced during the precipitation decreases with the pH (Figure 4.10).

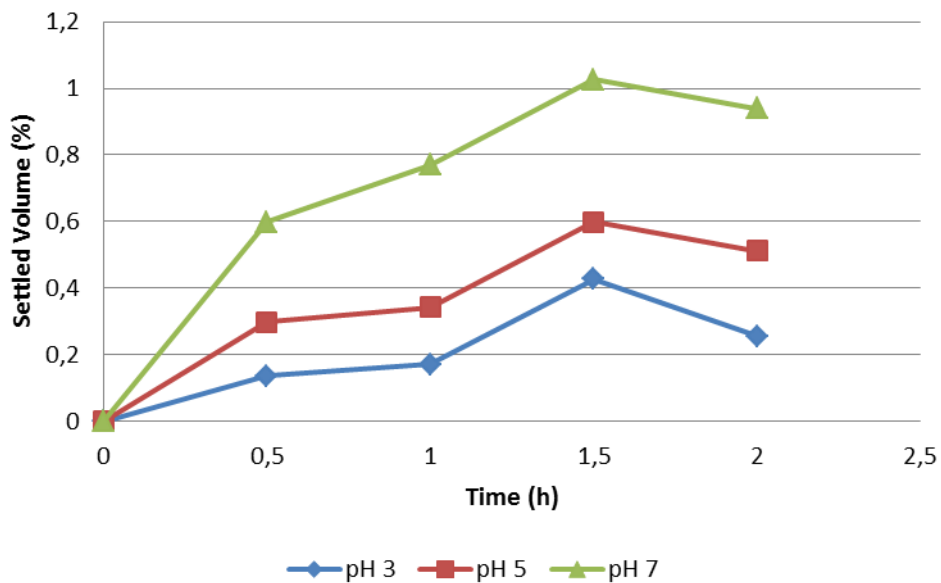
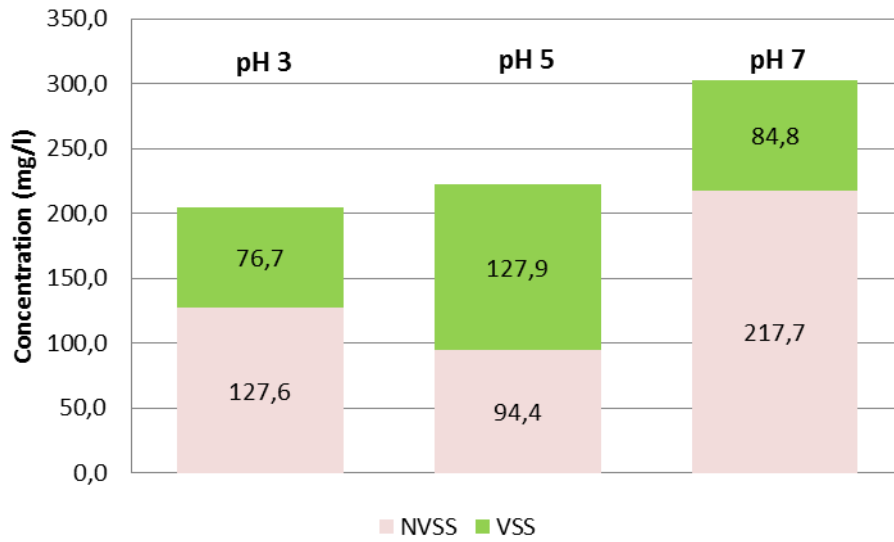


Figure 4.9 – Settled volume during Imhoff cone settling test for the three different solutions at pH 3, 5 and 7.



**Figure 4.10 – Concentration of Non Volatilized Suspended Solid (NVSS) and Volatilized Suspended Solid (VSS) for the three different solutions at pH 3, 5 and 7.**