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Chania, Greece, 21 - 24 JUNE 2023

Microbial transformations by sulfur bacteria can recover value from Phosphogypsum : Sulfate bio-reduction from phosphogypsum leachates and sulfur biorecovery.

<u>Ayoub BOUNAGA</u> , Anwar Alsanea, Mohammed Danouche, Bruce E. Rittmann, Chen Zhou, Rachid Boulif, Youssef Zeroual, Rachid Benhida, Karim Lyamlouli.

21-24 June 2023

Agenda

Introduction & Problematic

Methodology & Results

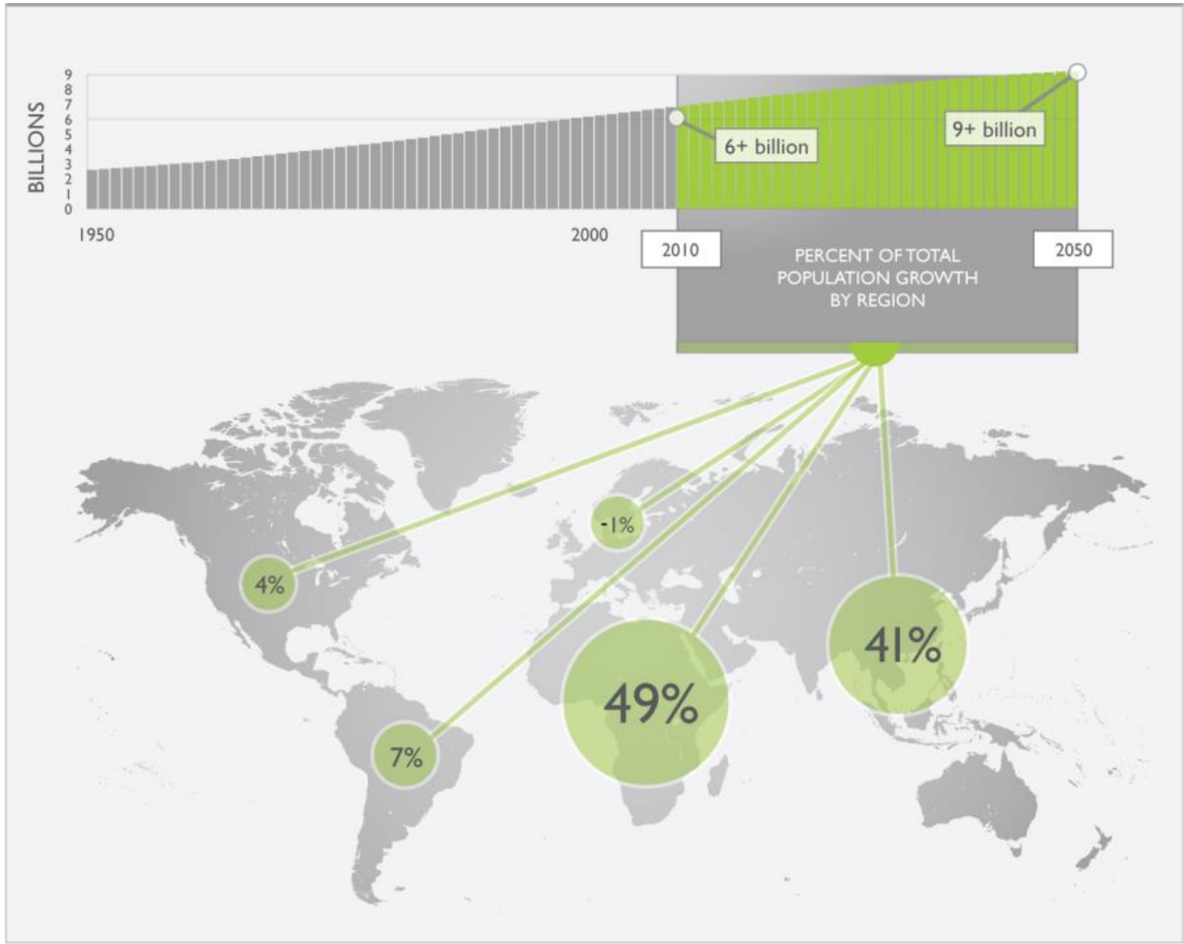
THL & Perspectives

Questions

Introduction & Problematic

Global Demand for Food Is Rising. Can We Meet It ?

- Today, according to the most recent estimate by the UN, there are **8 billion** people, and we may reach **9.7 billion by 2050**.
- Food demand is expected to increase anywhere between **59% to 98% by 2050**.
- Doubling food production by 2050 will undeniably be a major challenge ➔ **Demand on fertilizer especially P based ones will follow the same trend.**
- Demand on P fertilizers is also rising the demand **phosphoric acid production**.

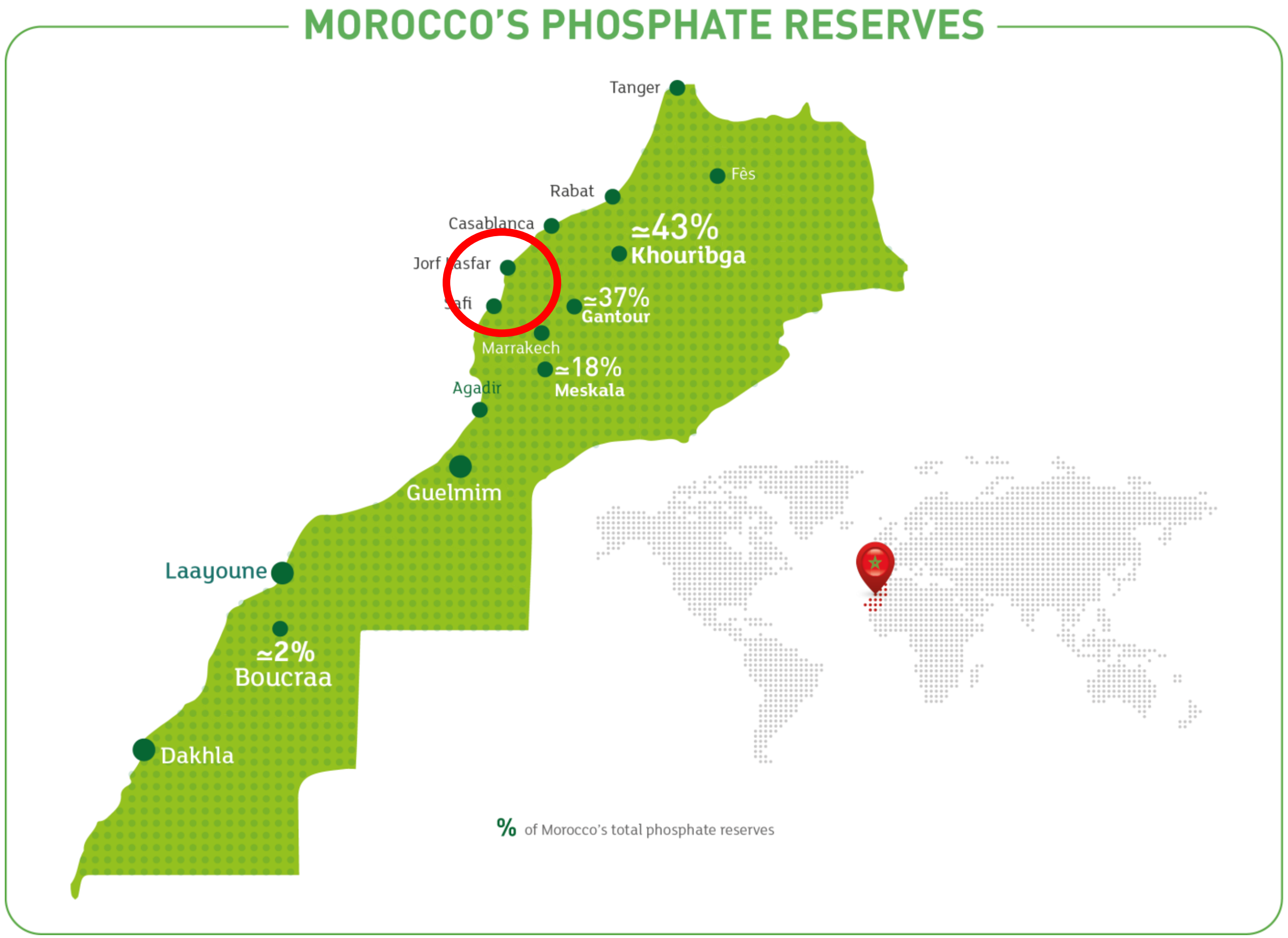


Introduction & Problematic

Morocco Holds the Key to Global Food supply and security

Morocco has **70%** of the world's phosphate reserves, and **OCP** is responsible for mining, processing, manufacturing, exporting and maximizing its value.

➔ Making OCP a leader in **phosphoric acid production.**



* Bounaga et al,. 2022, Macías et al., 2017; Saadaoui et al., 2017; Tayibi et al., 2009.

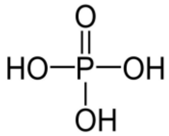
Introduction & Problematic

Phosphate rocks

Sulfuric acid

Wet process

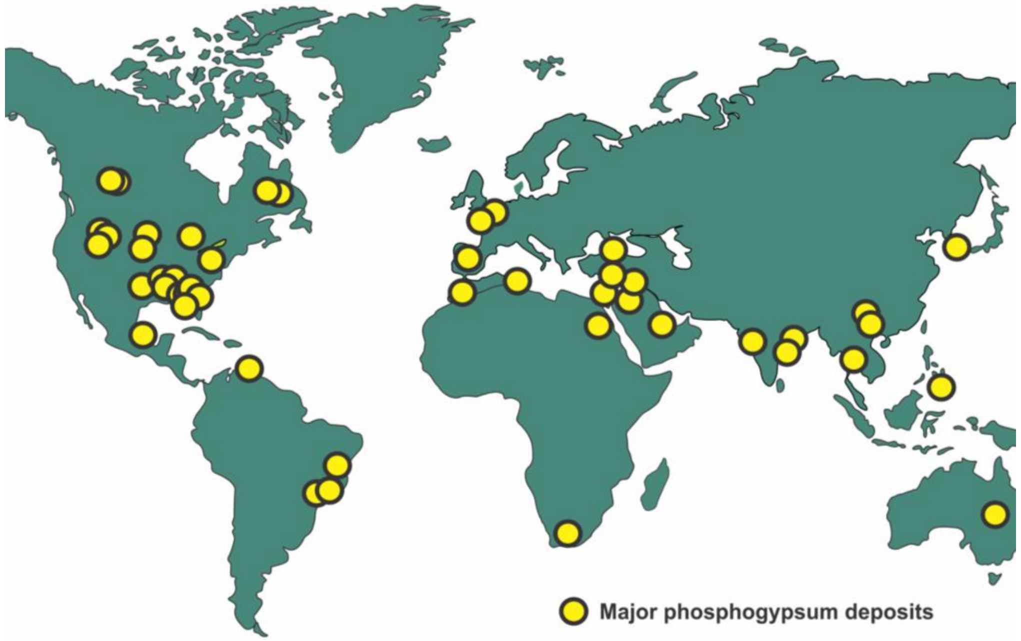
H_3PO_4



Phosphoric acid

Agriculture

Phosphogypsum



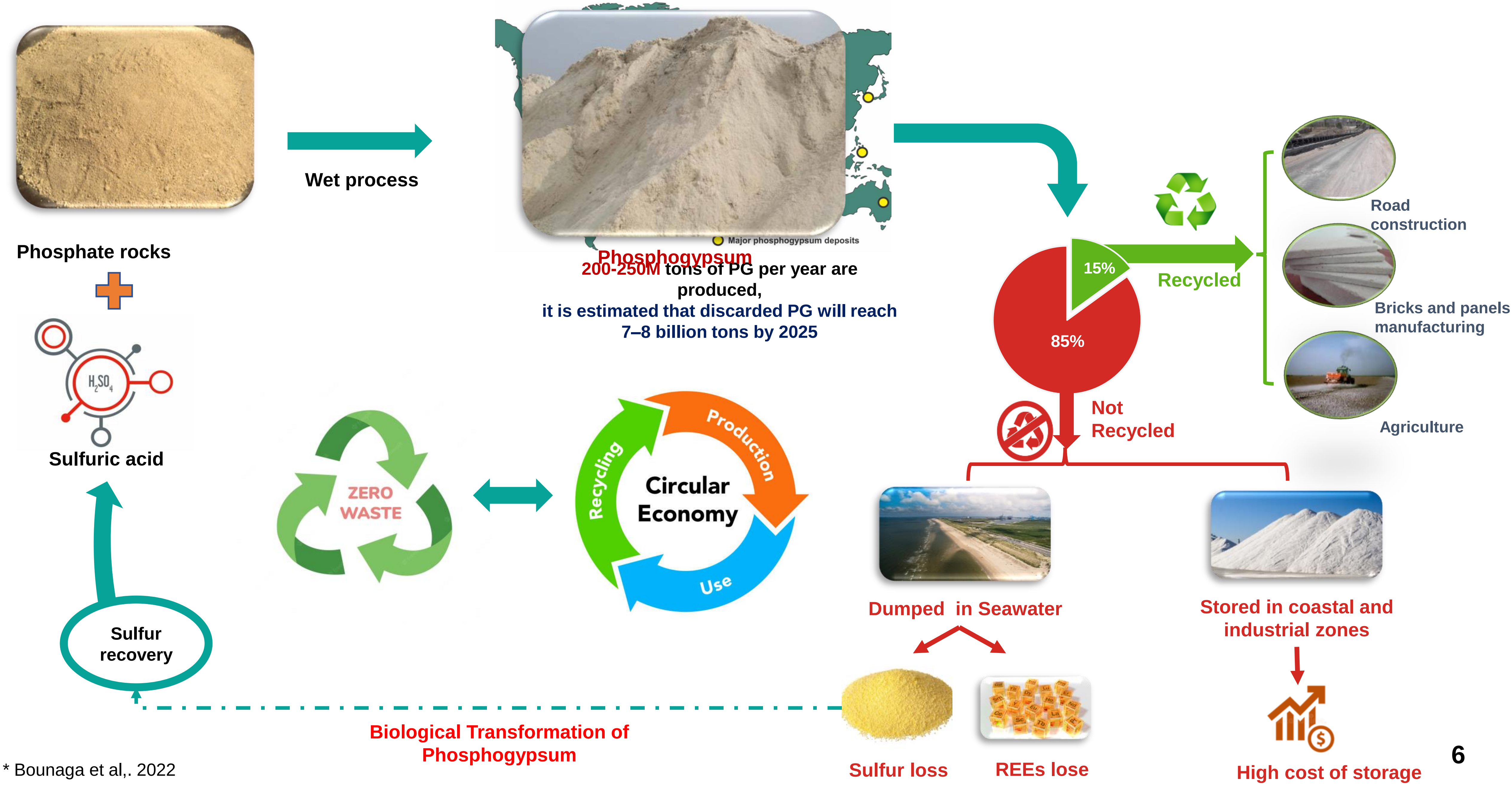
$$Ca_{10}(PO_4)_6F_2 + 10\,H_2SO_4 + 10nH_2O \longleftrightarrow 6H_3PO_4 + 2HF + 10CaSO_4 \cdot nH_2O$$

Approximately 5 tons of PG is generated per ton of phosphoric acid produced.

200-250M tons of PG per year are produced, it is estimated that discarded PG will reach 7–8 billion tons by 2025

* Bounaga et al,. 2022, Macías et al., 2017; Saadaoui et al., 2017; Tayibi et al., 2009.

Introduction & Problematic



* Bounaga et al,. 2022

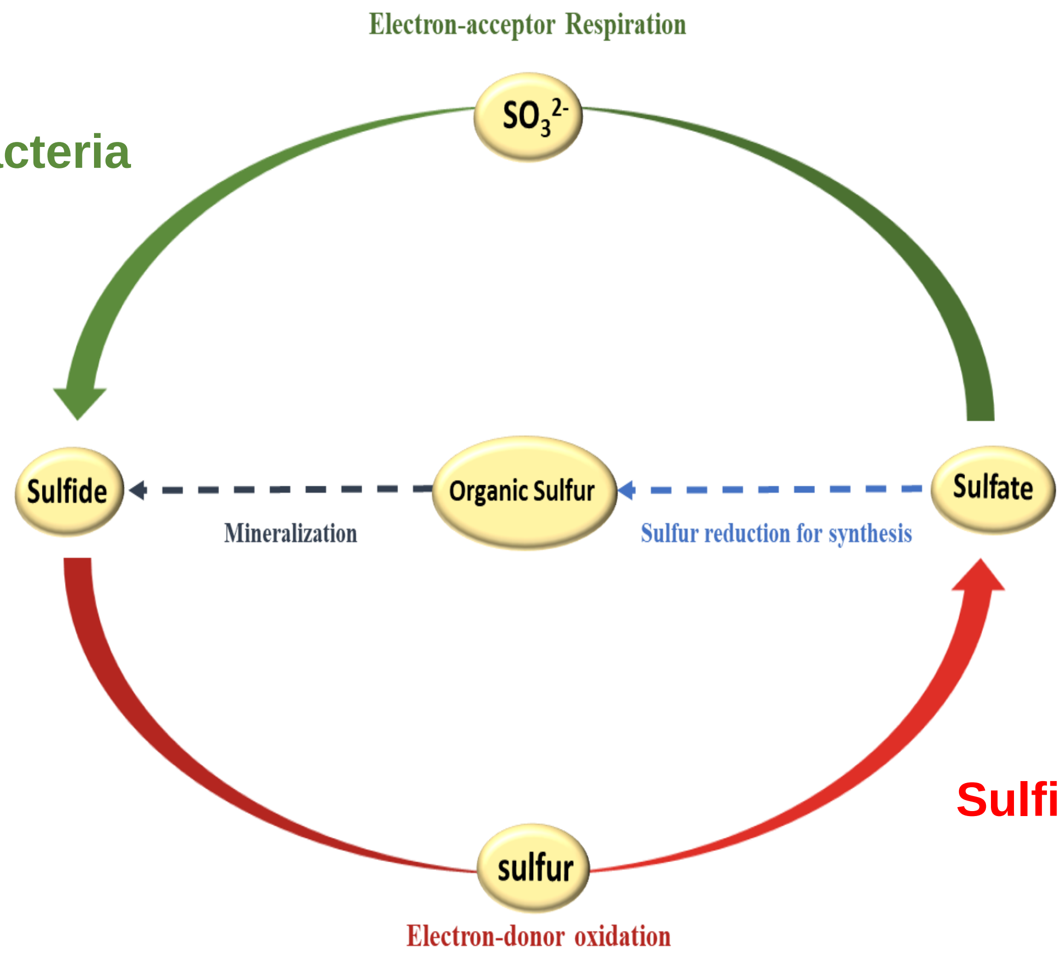
Introduction & Problematic

Biological Transformation of Phosphogypsum

$$SO_4^{2-} + 4.21\ H_2 + 0.105\ CO_2 + 0.021\ NH_4^+ + 0.98H^+ \rightarrow HS^- + 0.021\ C_5H_7O_2N + 4.17\ H_2O$$

Sulfate reducing bacteria

Biological Cycle of Sulfur



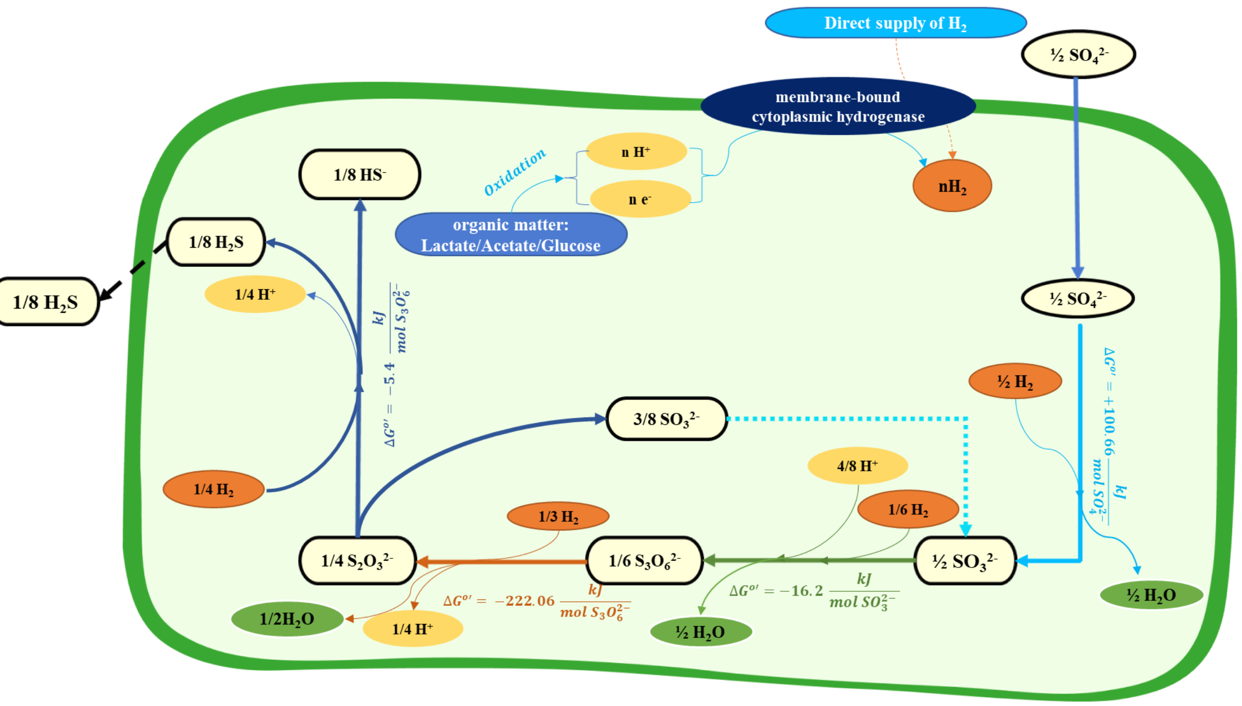
Sulfide oxidizing bacteria

$$0.4\ O_2 + H_2S + 0.08\ CO_2 + 0.02\ HCO_3^- + 0.02\ NH_4^+ \rightarrow S^0 + 0.02\ C_5H_7O_2N + 0.98\ H_2O$$

* Bounaga et al,. 2022

Introduction & Problematic

Biological Transformation of Phosphogypsum



Biological reduction of sulfates Pathway

PG = 50% of SO_4^{2-}

Biological reduction

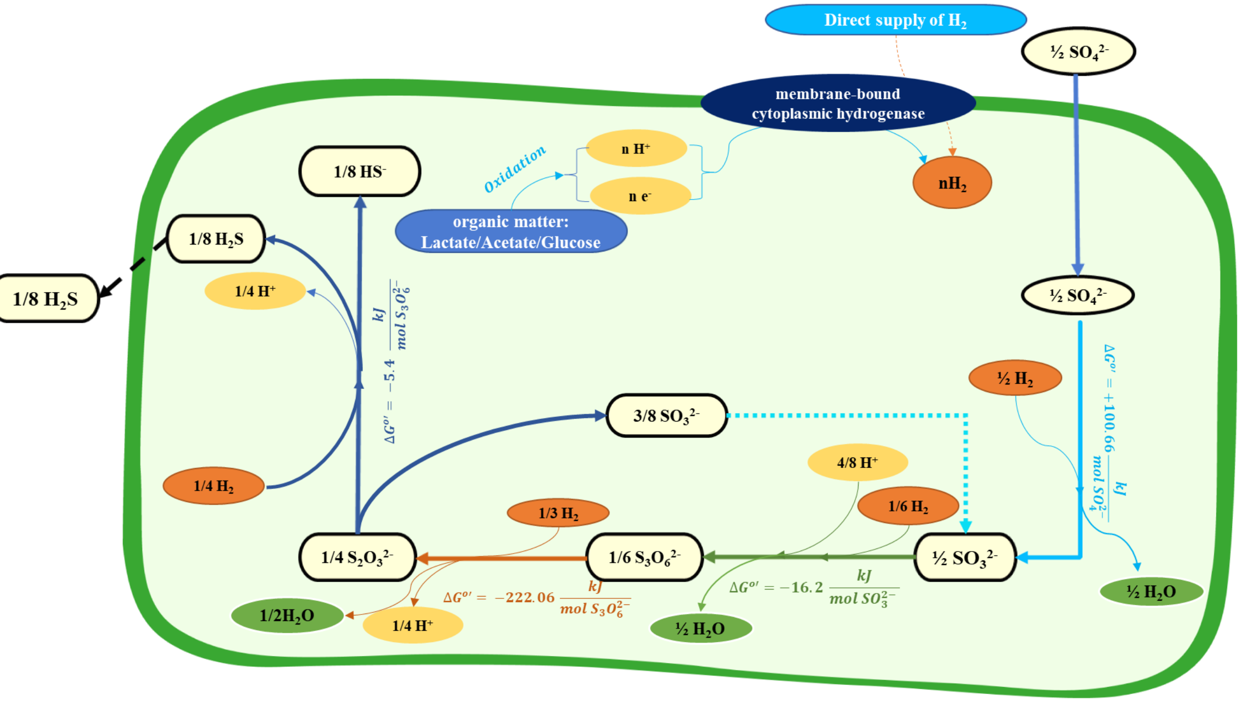
Anaerobic reduction by Sulfate reducing bacteria

H_2S

* Bounaga et al,. 2022

Introduction & Problematic

Biological Transformation of Phosphogypsum



Biological reduction of sulfates pathways

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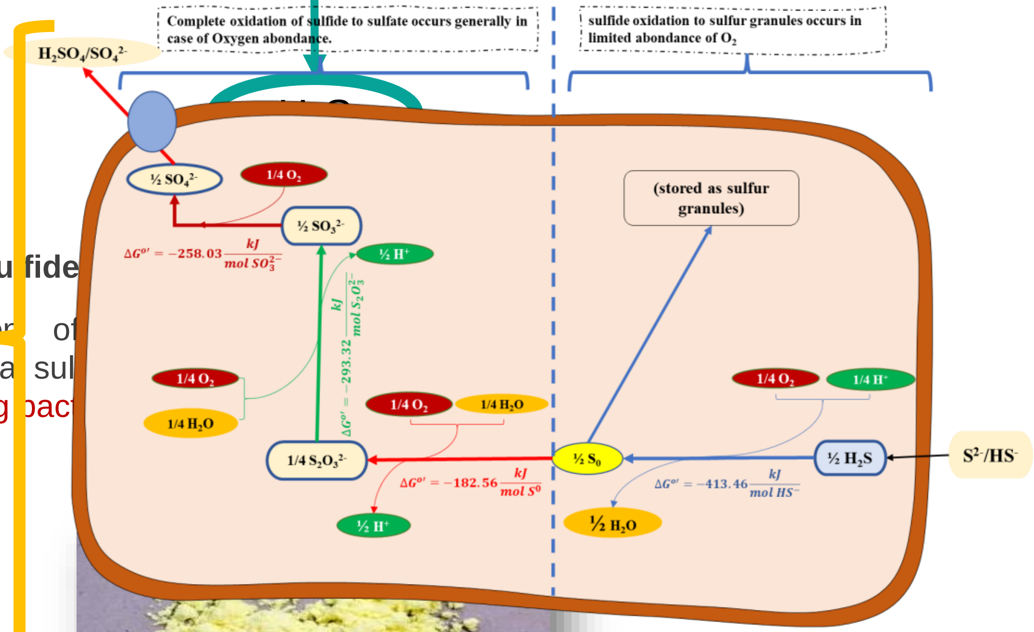
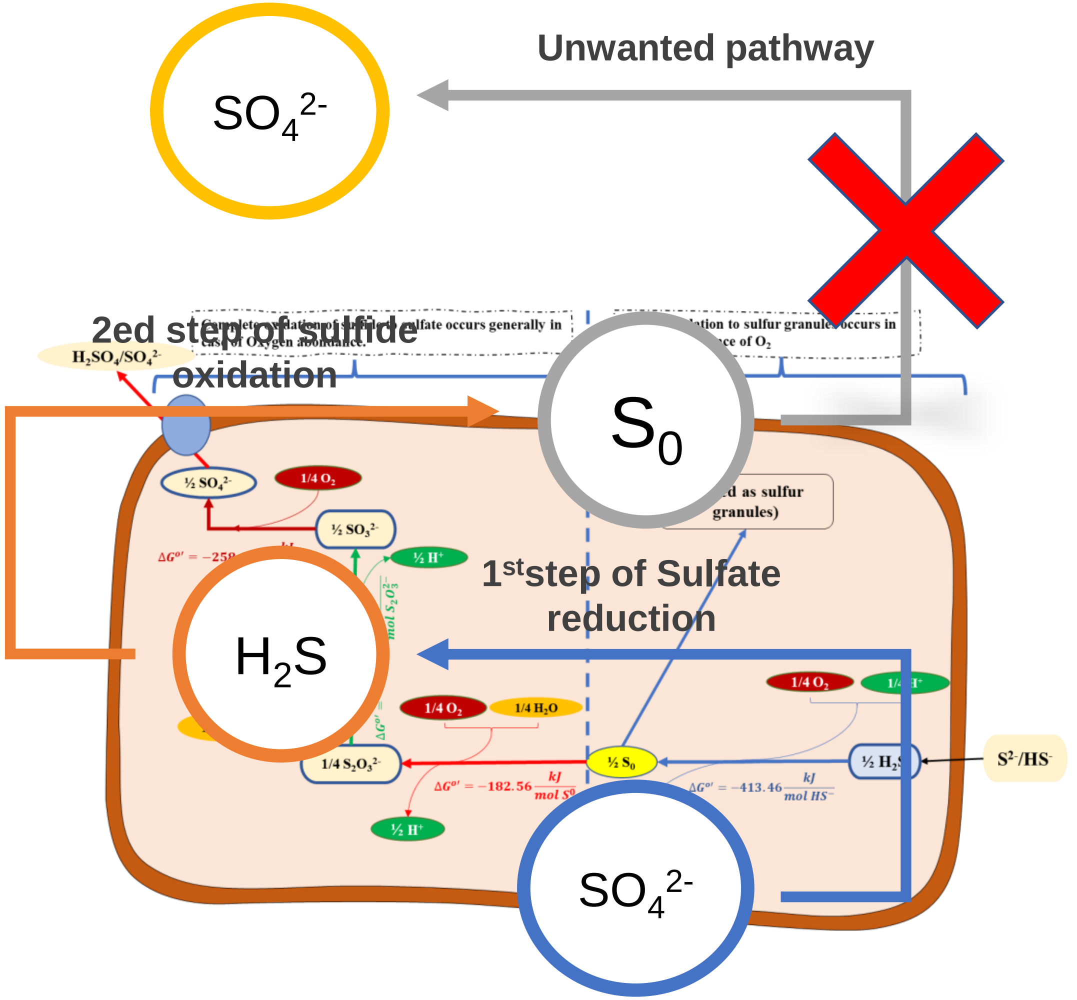


S_0

* Bounaga et al,. 2022

Introduction & Problematic

Biological Transformation of Phosphogypsum



$$H_2S + 0.5O_2 \rightarrow S^0 + H_2O,$$

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+.$$

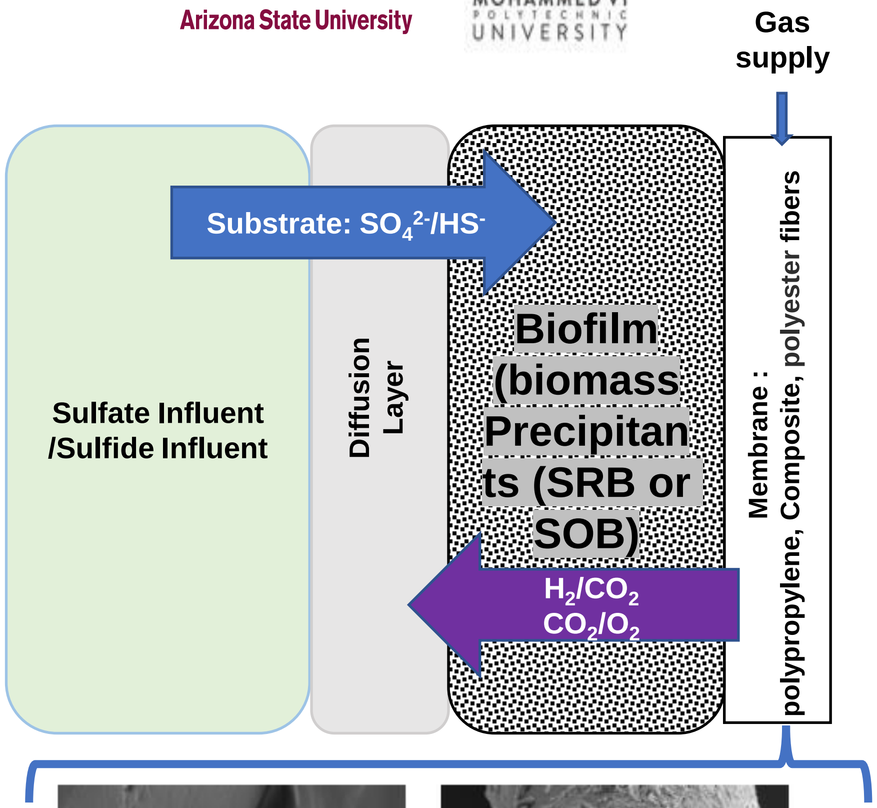
Micro-aerobic condition are needed ➔ MBfR technology

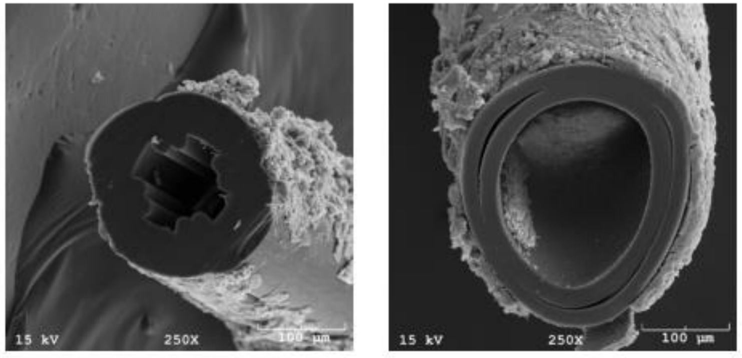
Cai, Zheng, Qaisar, & Zhang, 2017

Introduction & Problematic

Micro-aerobic condition are needed ➔ MBfR technology

- **The membrane biofilm reactor (MBfR):**
    - **Natural partnership of a membrane and biofilm,**
    - **Gas-transfer membrane delivers a gaseous substrate (O_2 or H_2) Biofilm grows on the membrane's outer wall.**
- **MBfR applications :**
    - **reducing oxidized contaminants in many water-treatment : Drinking water, Ground water, Wastewater, and Agricultural drainage.**





Introduction & Problematic

ELSEVIER

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Research review paper

Microbial transformations by sulfur bacteria can recover value from phosphogypsum: A global problem and a possible solution

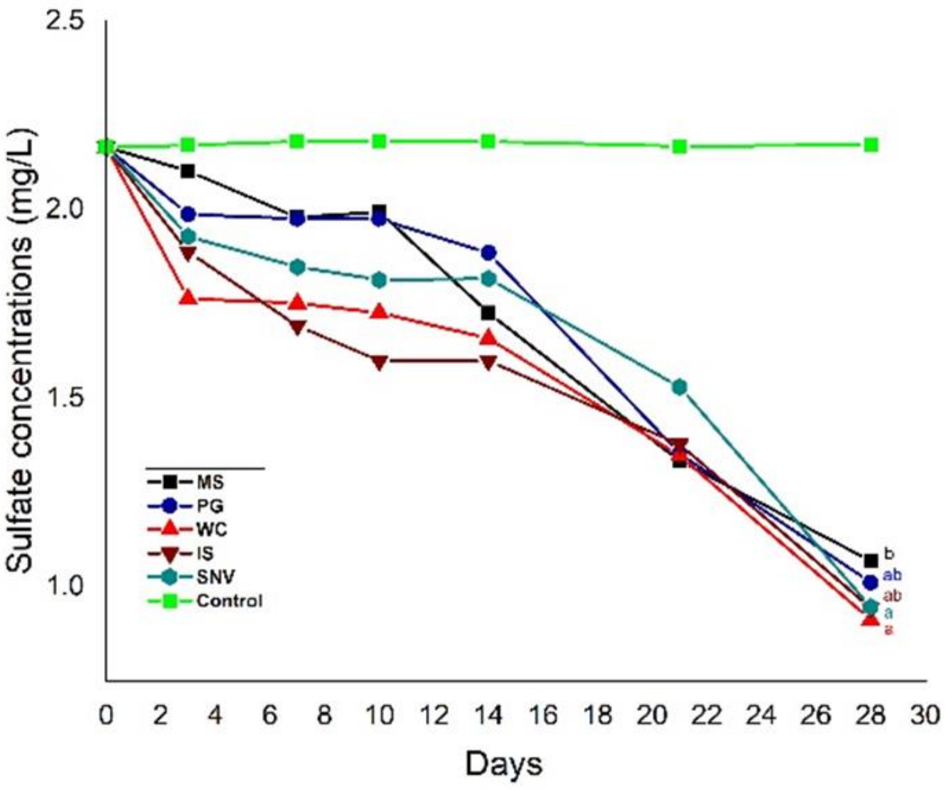
Ayoub Bounaga [a], Anwar Alsanea [b], Karim Lyamlouli [c], Chen Zhou [b], Youssef Zeroual [d], Rachid Boulif [a], Bruce E. Rittmann [b]

Methodology & Results

1. **Laboratory tests to reduce sulfates from PG biologically using Sulfate reducing bacteria.**

- **SRB consortia enrichment and bio-reduction of sulfates from Na_2SO_4.**

- **5 SRB consortia were isolated from different environments and are tested with referential medium using Na_2SO_4 as source of sulfates :**
    - **Industrial sludge**
    - **Marine sediments**
    - **Phosphogypsum**
    - **Winogradsky column**
    - **Sludges from petroleum industry**



Sulfate reduction activity

Methodology & Results

1. **Laboratory tests to reduce sulfates from PG biologically using Sulfate reducing bacteria.**

- **Bio-reduction of sulfates from PG-water leachate**

- PG-water leachate as source of sulfates with different Carbone sources : Lactate, Acetate and glucose.

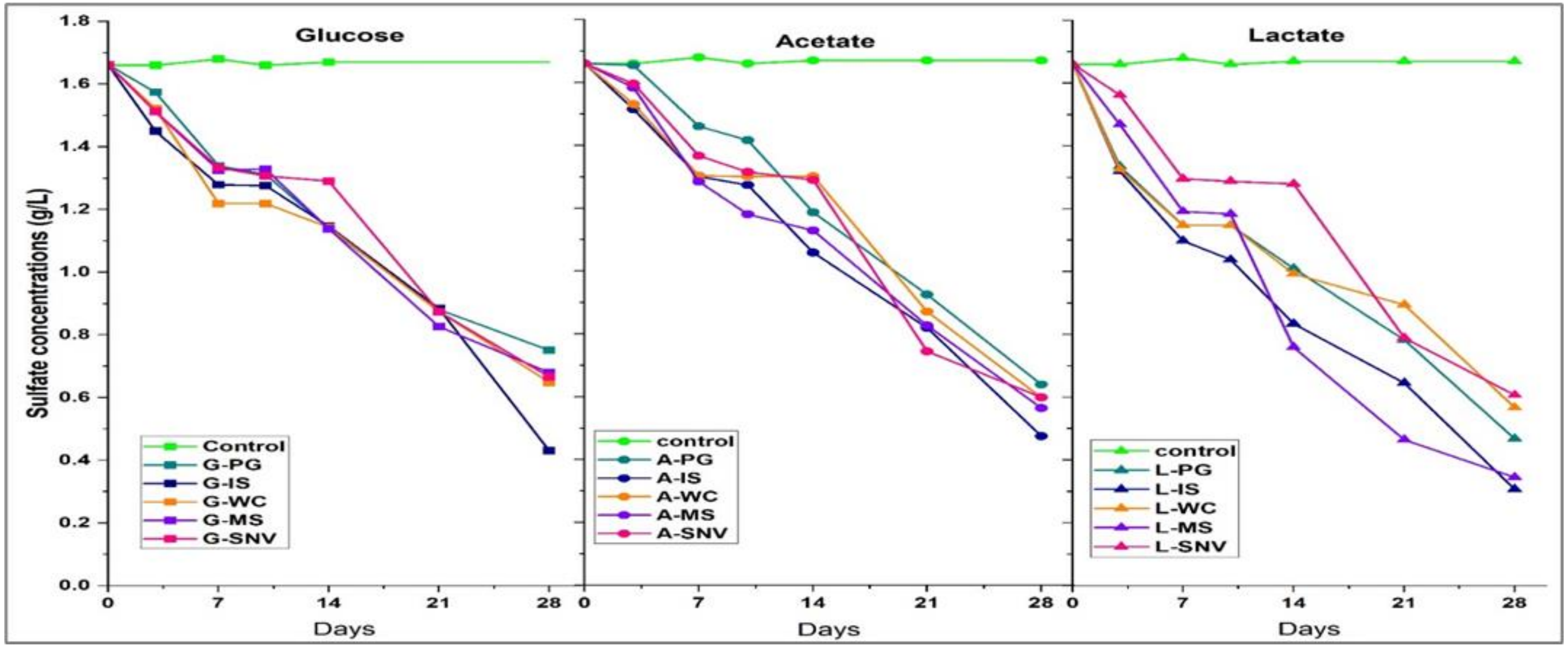


Figure : Sulfate reduction activity for using lactate, acetate or Glucose as electron and Carbone source

- **Lactate showed the highest sulfate reduction rates compared to acetate and glucose,**
- **The final pH while using lactate and acetate was alkaline ➔ Dissolved H_2S**

Methodology & Results

2. Optimization of Sulfates leaching from PG and biological reduction of the leachate.

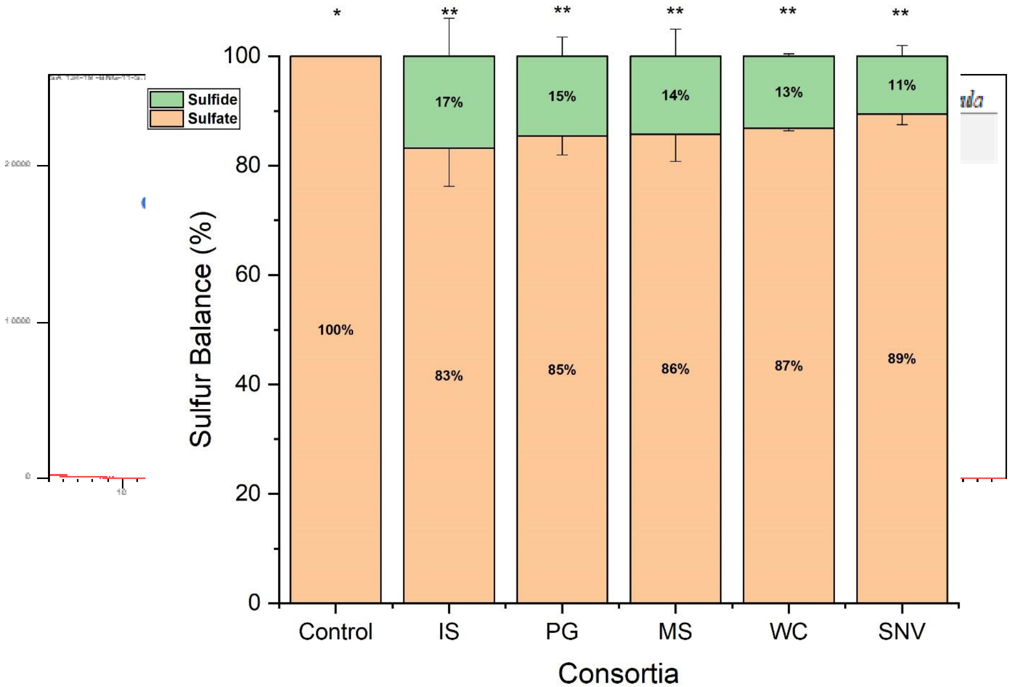
- Bio-reduction of high sulfate concentrations from alkaline PG leachate.

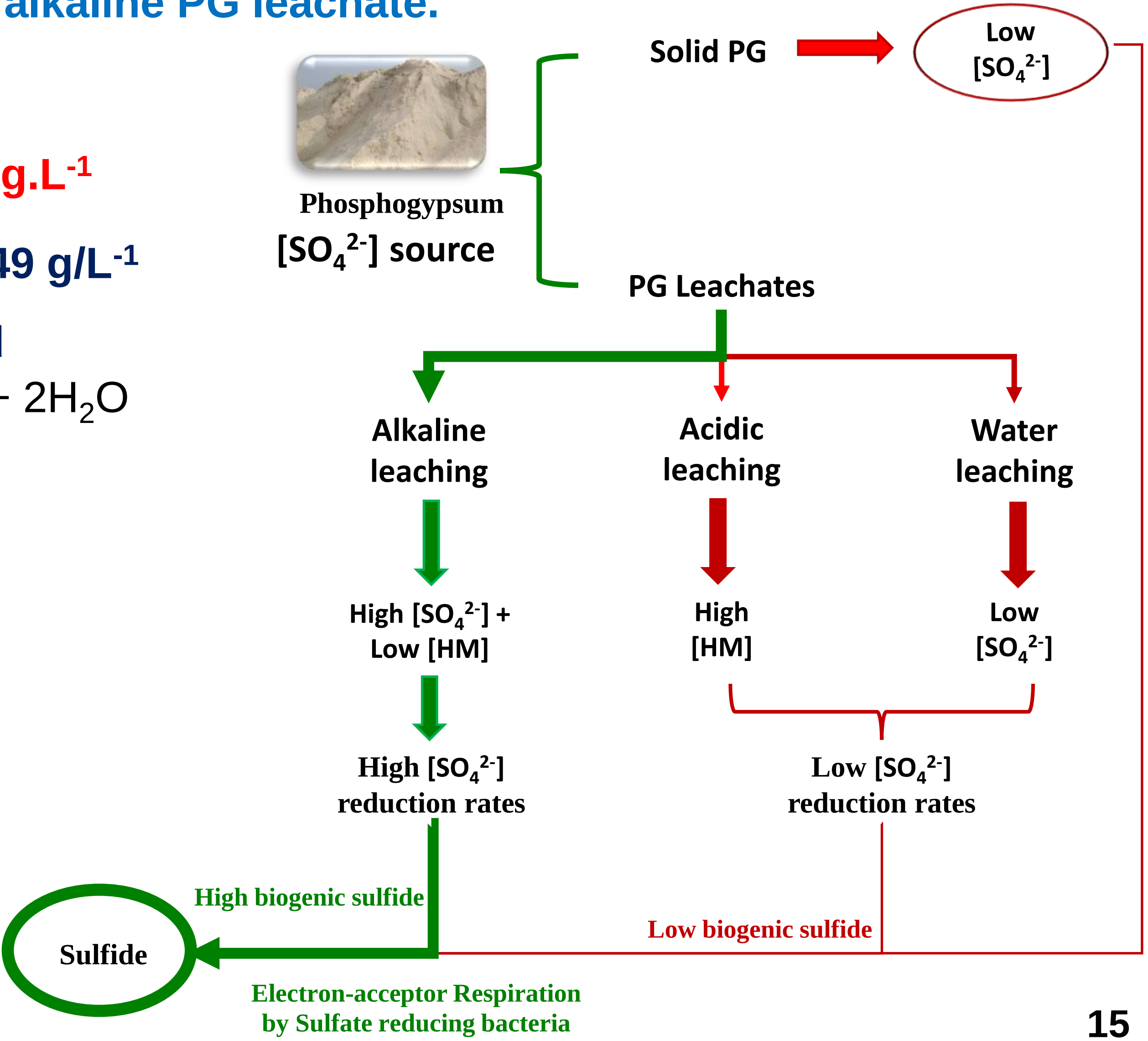
- Sulfate leaching : 97%
- Low HM concentration
- High Sulfate concentration in the leachate : 49 g/L^{-1}
- Higher sulfate reduction rates were achieved comapred to water leachate.

Water leachate ➔ Low PG solubility : 2.7 g.L^{-1}

$CaSO_4 + 2NaOH \rightarrow Ca(OH)_2\downarrow + 2Na^{2+} + SO_4^{2-}$

$CaSO_4{\cdot}2H_2O + 2NaOH + CO_2 + CaCO_3\downarrow + Na_2SO_4 + 2H_2O$

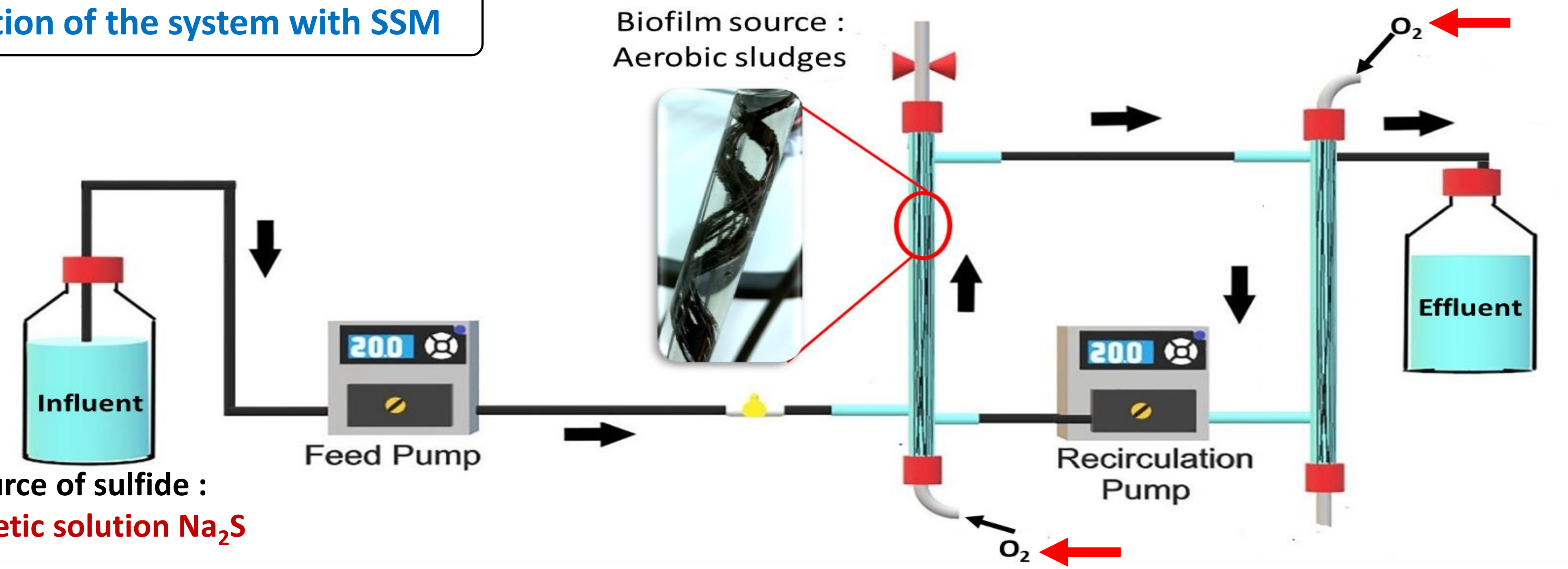




Methodology & Results

3. Biological oxidation of sulfides through application of Sulfur oxidizing bacteria with O_2-MBfR.

1st STEP : Set un and operation of the system with SSM



- **HRT** = **V/Q** :**Hydraulic Retention Time**
- **Sulfide Surface Loading Rate (g S^{2-}/m^2-day)**. = **The concentration of Sulfide in the system.**
- **Oxygen surface loading rate (g O_2/m^2-day)**. =**The needed oxygen concentration based on the influent sulfide concentration.**

$$0.4\ O_2 + H_2S + 0.08\ CO_2 + 0.02\ HCO_3^- + 0.02\ NH_4^+ \rightarrow S_0 + 0.02\ C_5H_7O_2N + 0.98\ H_2O$$

- **Flux= Q (S_o-S)A** : **The Flux represent the real performance of the Reactor based on the difference on sulfide concentrations ($t - t_0$).**

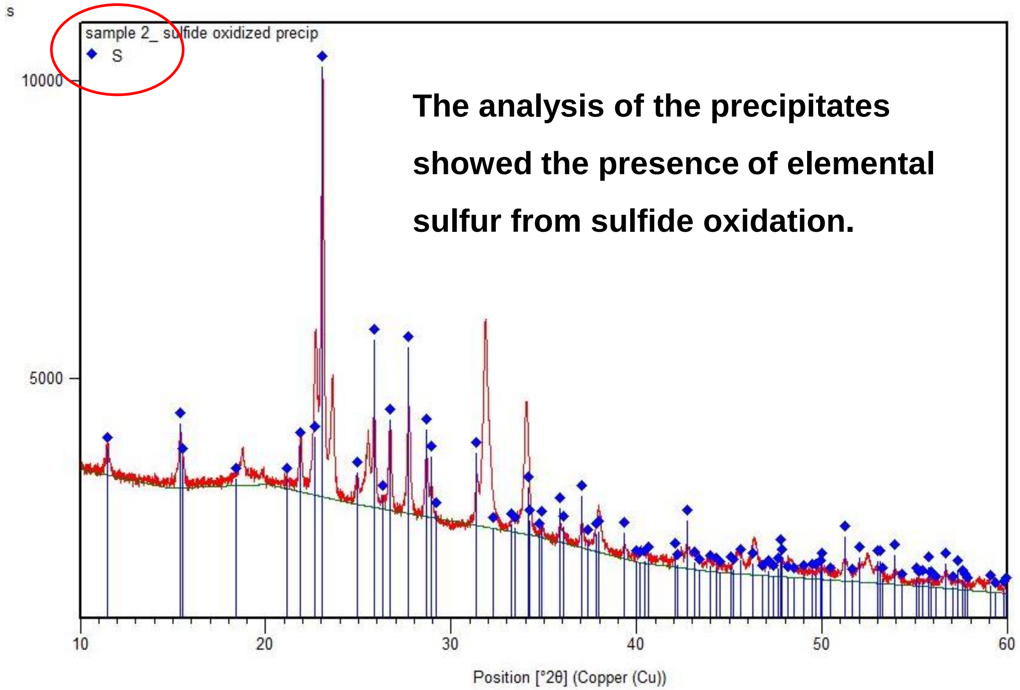
V = volume of the system Q = flow rate A = fiber outer surface area Sº = influent concentration S = effluent concentration in mg/L S^{2-}

Methodology & Results

3. Biological oxidation of sulfides through application of Sulfur oxidizing bacteria with O_2-MBfR.

1st STEP : Set un and operation of the system with SSM

	Days	Sulfide surface loading (g S/m^2-day)	Oxygen Delivery capacity (g O_2/m^2-day)	Sulfide flux (g S/m^2-day)	sulfide oxidation (%)	Conversion to elemental sulfur (%)	Elemental sulfur production (g S^0/m^2-day)
Phase 1	1-69	1.44	1.04	1.38	95.42	77.40	1.03
Phase 2	69-149	2.71	1.04	2.53	93.26	80.70	1.89
Phase 3	149-165	3.05	1.38	3.00	98.37	93.00	2.66



The analysis of the precipitates showed the presence of elemental sulfur from sulfide oxidation.

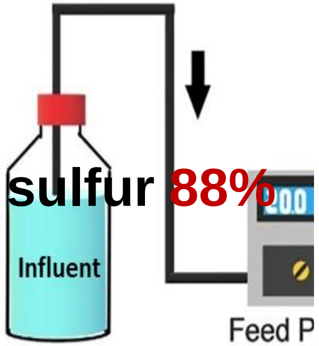
Methodology & Results

3. Biological oxidation of sulfides through application of Sulfur oxidizing bacteria with O_2-MBfR.

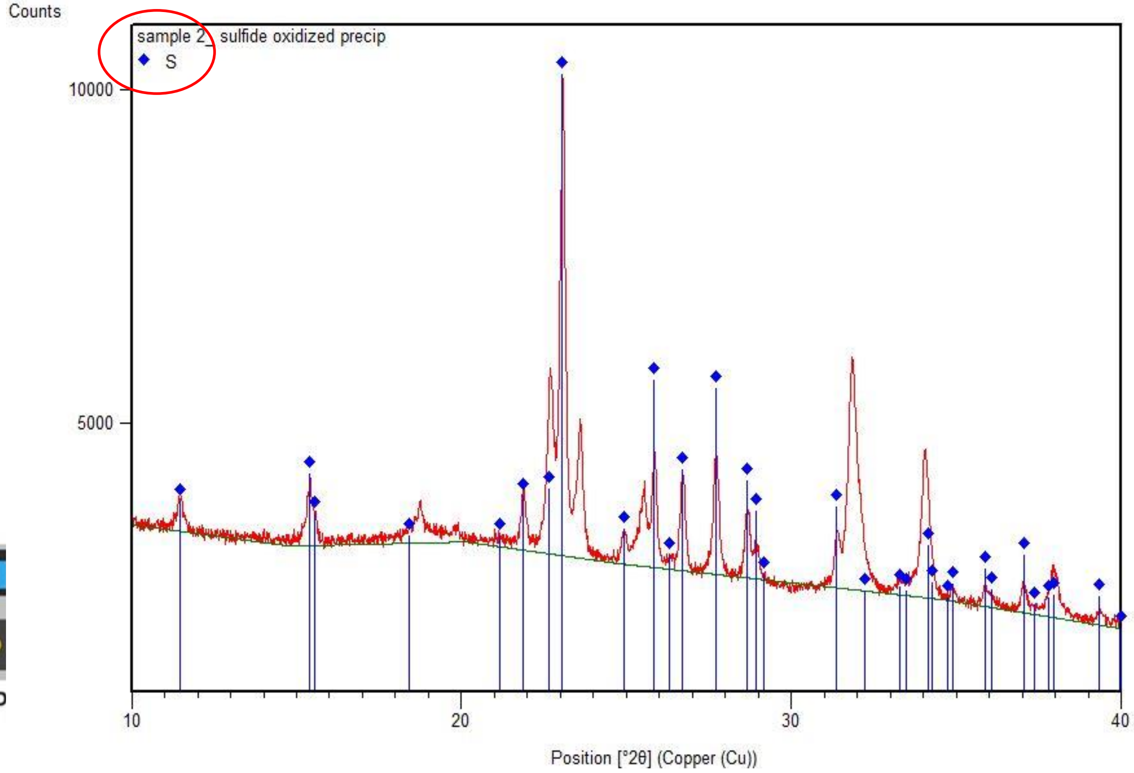
2nd STEP : Biogenic sulfide from PG reduction.

Preparing Biogenic sulfide from PG leachate reduction activity

- **Sulfide flux : 1.7**
- **Sulfide oxidation up to 93%**
- **Sulfide conversion rate to Elemental sulfur 88%**



Biogenic sulfide from PG reduction.



The DRX analysis of the precipitates.

Take Home Lessons

- ✓ Alkaline leachate is a good pretreatment of Phosphogypsum before SRB activity.
- ✓ O_2-MBfR technology allows to control the gas delivery through the fibers and allows to control the micro-aeration desired to oxidize sulfide to elemental sulfur.
- ✓ Sulfur recovery from Phosphogyspum using MBfR is promising eco-freindly strategy.

Perspectives

- ➢ Optimizing the reduction activity using the same technology with more economically efficient electron donor and carbon source such as the combination of H_2/CO_2
- ➢ Combining the two steps in One system.

Acknowledgements

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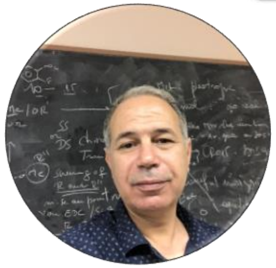

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Thank you for your attention

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