Process intensification in acidic wastewater treatment and waste valorization

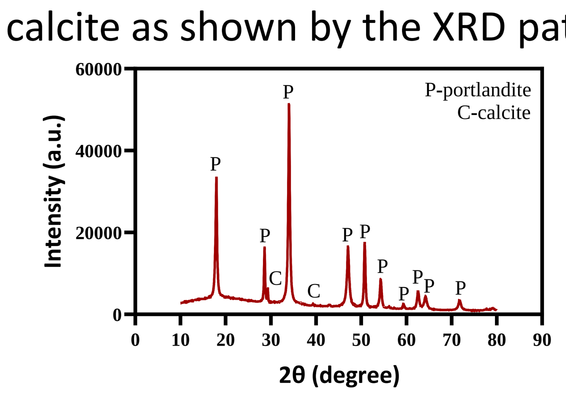
Amirhossein Dini[a], Stefano Trasatti[b] and Gian Luca Chiarello[a]
[a]Department of Chimistry, University of Milan, Via Golgi 19, 201333, Milan
[b]Department of Environmental Science, University of Milan, Via Celoria 2, 20133, Milan

Introduction

Edible oils, essential for nutrition and biodiesel production, are derived from palm, soybean, olive, cottonseed, and sunflower. The refining and processing of these oils generate significant amount of waste, particularly wastewater during stages like degumming, deacidification, soap splitting, deodorization, and neutralization. This vegetable oil refinery wastewater (VORW) is characterized by high levels of organic and inorganic compounds such as sulfates, phosphates, heavy metals, oil, and grease. Hence, it contains high levels of COD and BOD. High phosphorus content results from degumming with phosphoric acid, while neutralization produces acidic, oily wastewater from soap stock splitting with sulfuric acid [1]. Effective treatment necessitates advanced physicochemical and biological methods. One promising physicochemical method involves neutralization/precipitation using lime (CaO), a versatile and cost-effective solution, for treating acidic wastewaters [2].

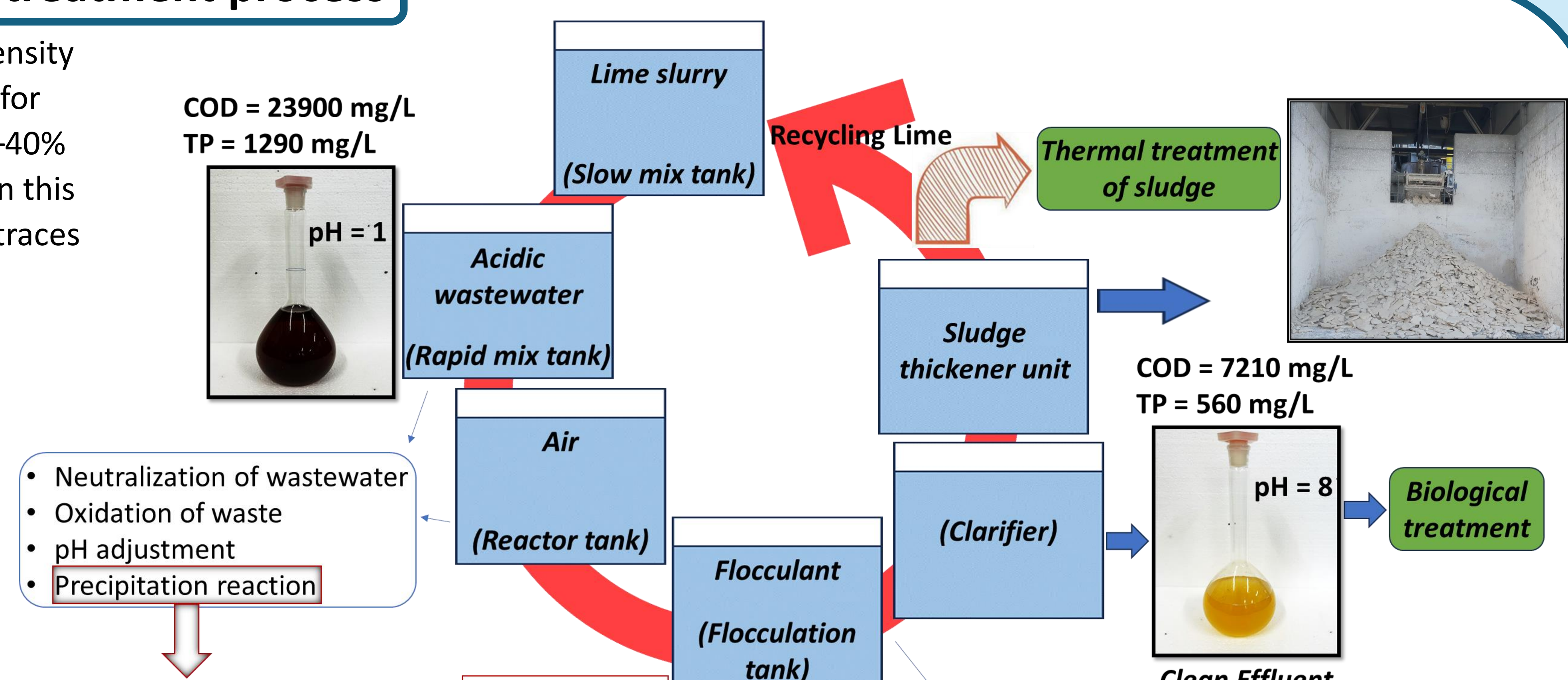
Lime treatment process

Two lime treatment processes for acidic wastewater exist: Low-Density (LDS) and High-Density Sludge (HDS): LDS (1–5% solids) is a conventional method that requires larger volumes for clarifiers or settling ponds, recovers less water, and needs more disposal space. HDS (30–40% solid) yields more stable sludge with less leaching, and experiences fewer scaling issues. In this work a HDS process has been considered. The starting raw lime was mainly $Ca(OH)_2$ with traces of calcite as shown by the XRD pattern.



There are two possible sludge valorization processes:

- **Way 1**: Conversion of calcium sulfate back to calcium oxide (Through reduction decomposition of $CaSO_4$ at temperatures above 1050 °C in the reaction atmosphere of O_2-CO-CO_2-N_2) [3].
- **Way 2**: Thermal treatment to obtain pure gypsum at 600 °C.

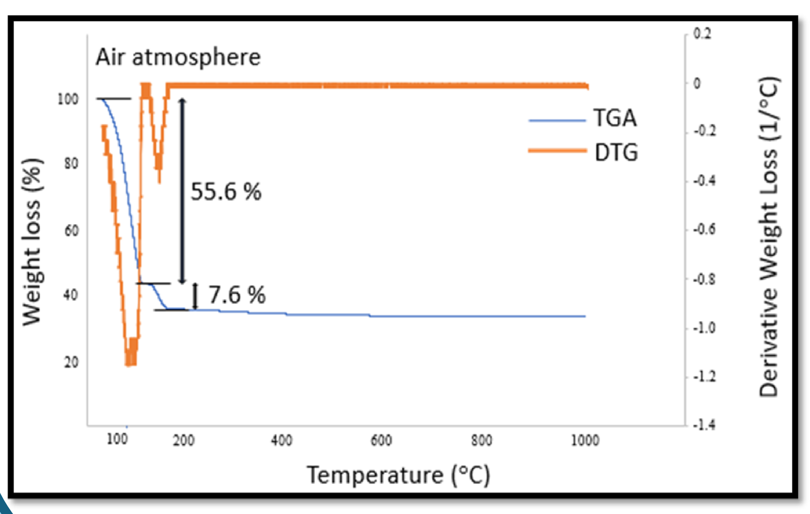


$$HM^{2+} + SO_4^{2-} + Ca(OH)_2 + 2H_2O \rightarrow HM(OH)_2 \downarrow + CaSO_4 \cdot 2H_2O \downarrow$$

Heavy metal cations; Gypsum

TGA of Sludge

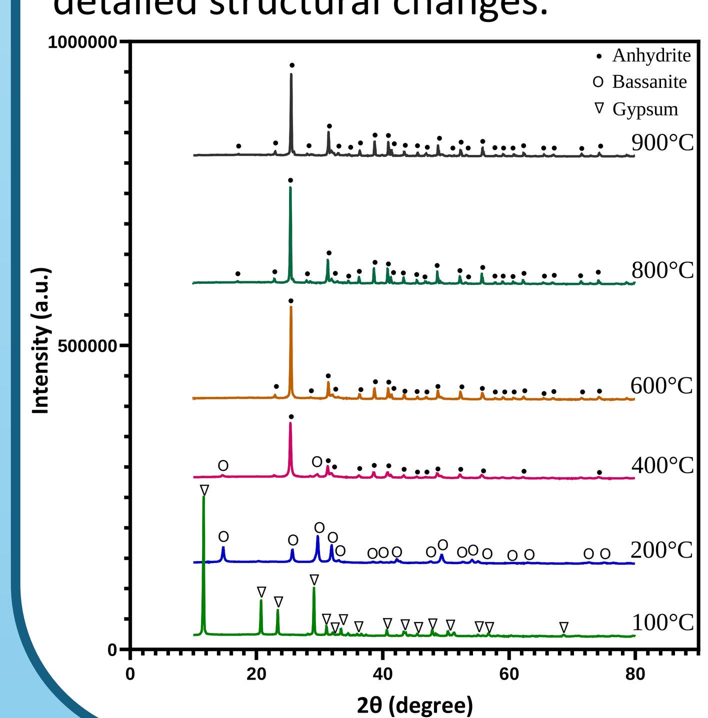
In process intensification for acidic wastewater treatment, valorizing waste products is pivotal. Comprehensive thermal characterization of sewage sludge via thermogravimetric analysis (TGA) provides critical insights into thermal stability, decomposition kinetics, and combustion properties, facilitating waste-to-energy conversion and advancing circular economy principles.



The first endotherm indicates the release of free, or unbound, water from the sludge. However, the second one, illustrates the decomposition of dihydrated gypsum ($CaSO_4 \cdot 2H_2O$) to hemihydrate (bassanite) ($CaSO_4 \cdot ½H_2O$) and anhydrite ($CaSO_4$).

Thermal Treatment of Sludge & XRD

To elucidate phase transformations, sludge underwent thermal treatments at 100-900 °C (10°C/min, 1-hour isothermal hold) in a muffle furnace. Post-calcination characterization via X-ray diffraction (XRD) revealed detailed structural changes.



Temp. (°C)	Weight loss (%)	Possible reactions
100	56.73	Loss of physically bound water present in the raw material
200	5.95	$CaSO_4.2H_2O \rightarrow CaSO_4.{}^1/_2H_2O + {}^3/_2 H_2O\uparrow$
400	2.52	$CaSO_4.{}^1/_2H_2O \rightarrow CaSO_4$ (soluble) + $^1/_2 H_2O\uparrow$
600	-	$CaSO_4$ (soluble) → $CaSO_4$ (insoluble)
800	-	Color changed to white.
900	-	The onset of decomposition and the increase in crystallite size

TGA of sludge revealed fewer distinct peaks than anticipated due to overlapping thermal processes, as it measures overall weight loss and rapid heating rates, consolidating processes into broader peaks. However, thermal treatment with controlled phase transitions at prolonged temperatures enables more distinct process separation.

Valorization

Pros & Cons of Lime Treatment

PROS
- ✓ Operationally convenient ✓ Adjusting the pH to the desired level ✓ Straightforward process
- ✓ Reduction of sulfates through precipitation as gypsum ✓ Cost-effective compared to other alkaline materials

CONS
- ⊗ Substantial amounts of chemicals are needed for neutralization.
- ⊗ Inefficiency of treatment in reducing COD and organic compounds, particularly organic phosphorus.
- ⊗ Creates large volumes of sludge and residue, raising management costs.
- ⊗ Risk of equipment blockages and increased secondary pollution treatment costs.
- ⊗ High water content in the produced sludge and difficulties in dewatering.

Conclusion

We observed the potential of lime in physicochemical pretreatment to increase and regulate the pH of water from highly acidic levels. It also led to gypsum formation, offering opportunities for waste-to-energy conversion and reuse in construction. However, due to the highly complex chemical composition of VORWs, lime was not effective in removing organic substances, as indicated by the COD and total phosphorus levels after treatment. Consequently, the quality of this water did not reach the desired standards required for biological treatment.

Future Objectives

Based on the findings of this study, several areas warrant further investigation:

- Due to gypsum precipitation in the first lime treatment stage and high phosphorus levels in wastewater, a secondary lime treatment can lead to the formation of hydroxyapatite [4].
- Alternatively, replacing lime with sodium hydroxide (NaOH) for pH adjustment, combined with coagulation-flocculation using iron chloride, is highly efficient for treating VORWs. This method effectively removes turbidity, color, dissolved solids, and organic matter. Additionally, it increases the organic matter content in the precipitated sludge, promoting circular economy principles through syngas production [5].

References

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XXVIII Congresso Nazionale della Società Chimica Italiana
MILANO, 26 - 30 Agosto 2024

For info:
amirhossein.dini@unimi.it
gianluca.chiarello@unimi.it
stefano.trasatti@unimi.it

UNIMI Photocatalysis Group (UPG)
http://users.unimi.it/upg