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# Upgrading The Quality of Secondary Treated Industrial Wastewater Discharged into Alexandria Sanitary Network Using Agro Waste Extracts

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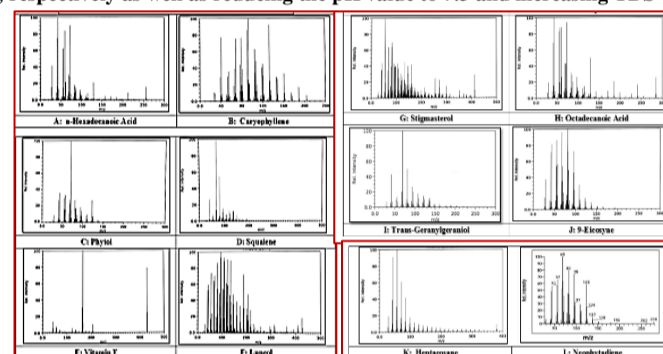
## INTRODUCTION

- Wastewater effluents from food (FIW) and petroleum refining (PRW) industries are of major environmental and public health concern, due to presence of high concentrations of hazardous substances.
- PRW usually contain high concentrations of polycyclic aromatic hydrocarbons (PAHs), oils & greases (O&G), phenols, dissolved minerals, heavy metals, ammonia and nitrogen, hydrogen sulfide, chlorinated compounds, polychlorinated biphenyls (PCBs), dioxins and furans, benzene, toluene and xylene, which are volatile organic compounds (VOCs). These contaminants produce a high COD and, therefore, a deficit of O<sub>2</sub> in the water, as well as having a very harmful effects on human health, environment and aquatic ecosystems.
- Although non-toxic, FIW generates a large amount of waste that is very rich organic content, agrochemicals, antibiotics, hormones and chemicals from food processing, packaging and cleaning. FIW damages aquatic ecosystems, especially if untreated, where it can cause odor, attract pests and contaminate water resources, as well as transmitting diseases by bacteria and viruses that accumulate in the wastewater.
- PRW and FIW discharge into Alexandria main sanitary network contain high concentrations of such hazardous materials where they negatively impact the treatment efficiency and the equipment.
- Conventional physiochemical or secondary wastewater treatment methods fail in terms of high treatments costs, increasing pH that lead to change the color, increase in sludge production and generation of harmful by-products, all of which are undesirable and harmful to the environment and water bodies. Therefore, secondary effluents must be further polished using advanced tertiary treatment that can remove more than 99 percent of the impurities and minimize environmental effects.
- A new trend in wastewater treatment is currently being developed that uses more environmentally friendly materials, such as agro-waste materials, which have a variety of benefits, including reducing costs, preventing variations in the pH of the treated water, reducing production of sludge and providing greater biodegradability.



## RESULTS

- Ethanol was confirmed to be the optimum and most convenient solvent that gave the highest yield (88.6%) of the bioactive compounds of CSLE leaves compared to only 33.76% obtained by the DCE.
- Secondary treated FIW contained 230, 420, 271, 37, 240 mg/L and 1400 CFU of BOD, COD, TSS, O&G, TDS and TVC, respectively. While, the secondary treated PRW contained 413, 830, 540, 69, 430 mg/L and 900 CFU of BOD, COD, TSS, O&G, TDS and TVC, respectively at the starting point of the experiment.
- Contaminants removal efficiencies (REs) showed positive trend with time (increased) and negative trend (decreased) with CSLE. Therefore, the lowest dose (0.1 g/L) and the longest tested exposure time (24 h) considered the optimum conditions to achieve the highest removals.
- Polishing treatment of the secondary treated FW using 0.1 g CSLE for 24 h recorded 88.7, 83.3, 93.4, 86.5, 42.9% as the highest REs% of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), oil and grease (O&G), total viable count of bacteria (TVCB), respectively as well as reducing the pH value to 7.3 and increasing TDS levels of FW by 0.8%.
- Similarly, polishing treatment of the secondary treated PRW recorded 77.7, 71.6, 94.3, 85.5, 55.6% as the highest REs% of BOD, COD, TSS, O&G, TVCB, respectively as well as reducing the pH value to 7.8 and increasing TDS levels of PRW by 11.6%.
- The lowest residual concentrations (RCs) recorded 26, 70, 18, 5, 240 mg/L and 800 CFU/mL in the polished FIW as well as 92, 236, 31, 10, 480 mg/L and 400 CFU/mL in the polished PRW for BOD, COD, TSS, O&G, TDS, TVC, respectively.



Mass Spectrum of the Most Abundant Compounds Identified in the *Citrus sinensis* Leaves

- RCs levels of BOD, COD, TSS, O&G are much lower than their MPLs (600, 1100, 800 and 100, respectively) for the safe discharging into the general sanitary drainage network. No limits were set for TDS and TVC in the environmental regulation, but generally the proposed treatment efficiently reduced their values in the final effluent.

## AIM OF THE WORK

The main objectives of the present study were:

- To improve the quality of secondary treated PRW and FIW that discharge directly to the main municipal network of Alexandria City.
- Propose the tertiary polishing treatment with bioactive extracts of *Citrus sinensis* (Orange) leaves wastes.
- Investigate, on a bench scale, the impact of *Citrus sinensis* leaves of extract (CSLE) amendment on the parameters values in the PRW and FIW.
- Compare the efficiency of the proposed treatment with the original treatment technologies at the selected industries.



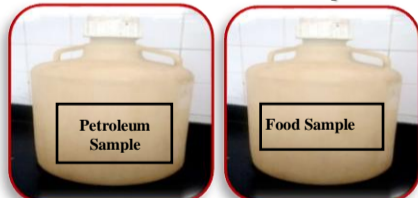
*Citrus sinensis*  
(Leaves and Fruits)

## MATERIALS & METHODS

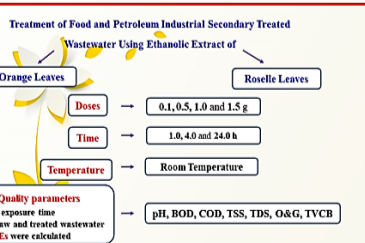
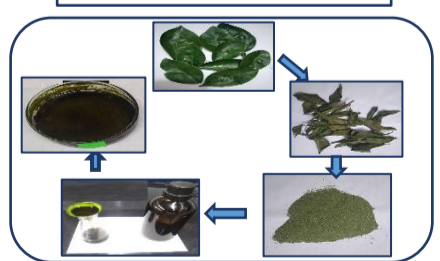
- Petroleum refining and food industrial wastewater samples (FIW & PRW) were collected from the effluent discharge points of the companies at Al-Amriya area and Borg El-Arab City, respectively, Alexandria Governorate. FIW and PRW were characterized before and after the proposed treatments.
- Orange (*Citrus sinensis*) leaves agro wastes were collected, prepared and their bioactive compounds were extracted using ethanol and 1, 2-dichloroethane (DCE).
- Phytochemical composition of *Citrus sinensis* leaves extract (CSLE) was determined using Gas Chromatography-Mass Spectrometry.
- Secondary effluents of FIW and PRW were individually tertiary treated with CSLE at different doses (0.1, 0.5, 1.0 and 1.5 g) and time (1.0, 4.0 and 24.0 h) at room temperature and compared with their control samples under the same conditions.
- Residual concentrations (RCs) or density (CFU/mL) of quality parameters {pH, BOD, COD, TSS, TDS, O&G and total viable count of bacteria (TVCB)} were determined at each exposure time in the raw and treated wastewater and their removal efficiencies (REs%) were calculated. The efficiency and feasibility of the proposed treatments towards the tested industrial wastewaters were discussed and compared.



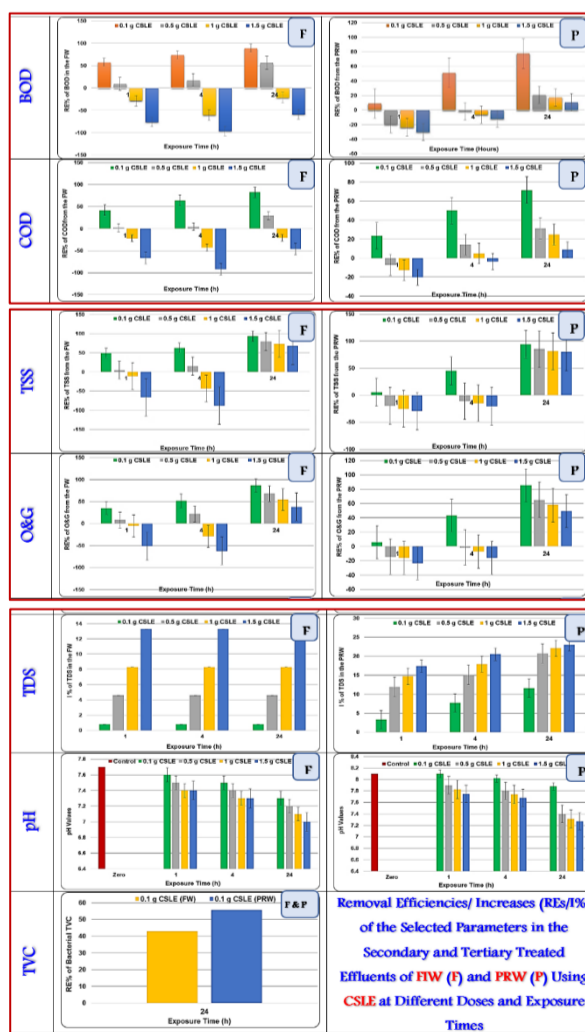
Crude Leaves Extracts of  
*Citrus sinensis*



Preparation of *Citrus sinensis*  
Leaves Extract



Treatability Studies



Removal Efficiencies/Increases (REs/%)  
of the Selected Parameters in the  
Secondary and Tertiary Treated  
Effluents of FIW (F) and PRW (P) Using  
CSLE at Different Doses and Exposure  
Times

### Conclusions of the Polishing (Tertiary) Treatment of FW and PRW Using Ethanol Extract of *Citrus sinensis* Leaves

Highest REs% and % of the Different Parameters in the Secondary and Tertiary Treated Effluents of Food and Petroleum Refining Industries Using 0.1 g CSLE for 24 h

Parameter	A: Food Industry Effluent			*MPL (mg/L)
	Initial RCs in Secondary FW (mg/L)	Tertiary Treated FW RCs (mg/L)	Highest RE% & 1%	
BOD	230	26	88.7	600
COD	420	70	83.3	1100
TSS	271	18	93.4	800
O&G	37	5	86.5	100
pH	7.7	7.3	---	6-9.5
TDS	240	242	0.8	---
TVC	1400 CFU/mL	800	42.9	---

Parameter	B: Petroleum Refining Effluent			*MPL (mg/L)
	Initial RCs in Secondary PRW (mg/L)	Tertiary Treated PRW RCs (mg/L)	Highest RE% & 1%	
BOD	413	92	77.7	600
COD	830	236	71.6	1100
TSS	540	31	94.3	800
O&G	69	10	85.5	100
pH	8.1	7.8	---	6-9.5
TDS	430	480	11.6	---
TVC	900 CFU/mL	400	55.6	---

\*MPL: According to Law No. 93 of 1962 Modified by Decree No. 44 of 2000 Regarding the Discharge Liquid waste into the Public Sanitary Network.

## CONCLUSIONS

- Ethanol was confirmed to be the optimal and most convenient solvent that gave the highest yield percentage of the bioactive compounds of CSLE (88.6%) compared to 33.76% obtained by 1, 2-dichloroethane (DCE), respectively.
- Qualitative analysis of the plant Ethanol extracts revealed that terpenoids (e.g., Caryophyllene, Squalene,  $\alpha$ -Tocopherol and Lupeol), steroids (e.g., Stigmasterol,  $\delta$ -sitosterol) and fatty acids (e.g., n-hexadecanoic acid, octadecatrienoic acid) are the main chemical groups identified in the CSLE.
- CSLE showed high removal of the tested pollutants from the two tested industrial wastewater producing high quality effluents comply with the regulations and safe for discharging into the main sanitary network, which is mainly attributed to its phytochemical constituents.
- Within the tested ranges of time (1-24 h) and dose (0.1-1.5 g/L), the lowest dose (0.1 g/L) and the longest tested exposure time (24 h) considered the optimum conditions to achieve the highest removals by CSLE.
- Finally, results confirmed that the use of *Citrus sinensis* for the treatment of highly polluted and hazardous industrial wastewater is a feasible option to enhance removal of the included contaminants and produce high quality effluents.
- Moreover, the usage of such natural materials can reduce health risk from long term usage of chemical coagulants along with reduction of sludge production, cost and protecting the receiving environments.