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Advanced Treatment of Pistachio Processing Industry Wastewater by Fenton Process

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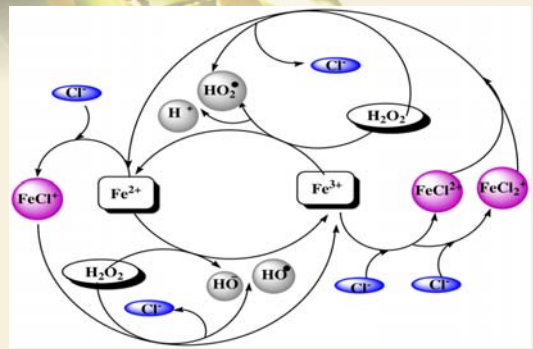
INTRODUCTION

Pistachio industry = rapidly developing in Turkey

Estimated yield in Turkey = 44 thousand tons (2015) →
3rd biggest producer in the world

Pistachio industry water consumption: up to 6 tons of clean water



Pistachio processing industry wastewater (**PPIW**):
- components **not easily biodegradable**
- high chemical oxygen demand (COD)
- high total organic carbon (TOC)
- high total phenol (TP)
- high toxic organic impurities content

Advanced oxidation processes (AOP)→ **Fenton oxidation:**
- ✓ organic substances
- ✓ toxicity reduction
- ✓ preliminary treatment step before biological treatment
- ✓ colour removal

INTRODUCTION

Fenton oxidation

- reaction of peroxodyne (mostly hydrogen peroxide: H_2O_2) with iron ions to form active oxygen types
- hydroxyl radicals ($OH^{\bullet}$) formation under low pH (2-6) & reducing conditions
- $OH^{\bullet}$ attack organic matter & breaks down pollutants
- H_2O_2 presense: continuous recycle between Fe^{+2} & Fe^{+3}

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\bullet} + OH^{-} \quad (1)$$

$$Fe^{+2} + OH^{\bullet} \rightarrow Fe^{+3} + OH^{-} \quad (2)$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + HO_2^{\bullet} + H^{+} \quad (3)$$

$$Fe^{+3} + HO_2^{\bullet} \rightarrow Fe^{+2} + O_2 + H^{+} \quad (4)$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (5)$$

OBJECTIVES

i) examine Fenton oxidation efficiency for lab-scale treatment of wastewater from the processing of red peppered pistachio nuts

ii) define optimal treatment operating conditions

(e.g. pH, Fe^{+2} dosage, H_2O_2 concentration & reaction time)

MATERIALS & METHODS

o Wastewater: industrial facility with average daily processing capacity=24 tonnes of peanuts day^{-1}

Parameter	Units	Value
Conductivity	($\mu s\ cm^{-1}$)	4,750 – 5,750
Turbidity	(NTU)	150-250
pH	-	5-5.5
COD	($mg\ L^{-1}$)	15,000-18,000
TOC	($mg\ L^{-1}$)	5,000-5,500
TP	($mg\ L^{-1}$)	3,800-4,500
Oil-Grease	($mg\ L^{-1}$)	50-59
Cl	($mg\ L^{-1}$)	600-650

Experimental set-up for lab-scale Fenton oxidation treatemnt of PPlW

RESULTS

Effect of Fe^{+2} concentration on the system performance

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\bullet} + OH^{-} \quad (1)$$

$$Fe^{+2} + OH^{\bullet} \rightarrow Fe^{+3} + OH^{-} \quad (2)$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + HO_2^{\bullet} + H^{+} \quad (3)$$

$$Fe^{+3} + HO_2^{\bullet} \rightarrow Fe^{+2} + O_2 + H^{+} \quad (4)$$

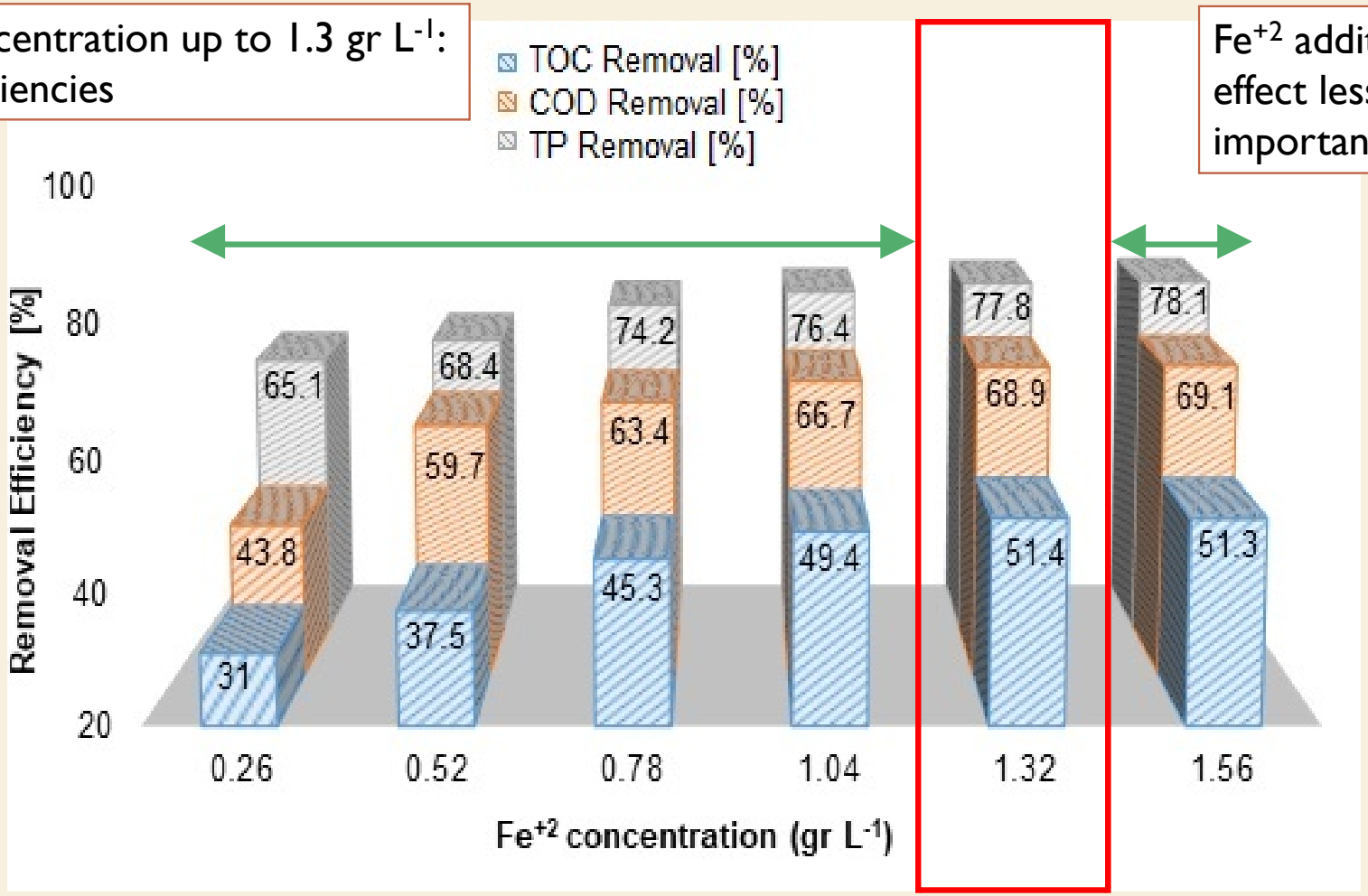
$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (5)$$

- 1st reaction rate important for determining the efficiency & process cost of Fenton process
- Effect of Fe^{+2} concentration: 6 different Fe^{+2} concentrations tested from 0.26-1.56 gr L^{-1}
  - Theoretically calculated 19.2 gr L^{-1} H_2O_2 concentration constant
  - No adjustment of the PPIW pH

RESULTS

Effect of Fe^{+2} concentration on the system performance

↑ the Fe^{+2} concentration up to 1.3 gr L^{-1}:
↑ removal efficiencies



Fe^{+2} addition effect less important

RESULTS

Effect of Fe^{+2} concentration on the system performance

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\bullet} + OH^{-} \quad (1)$$

$$Fe^{+2} + OH^{\bullet} \rightarrow Fe^{+3} + OH^{-} \quad (2)$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + HO_2^{\bullet} + H^{+} \quad (3)$$

$$Fe^{+3} + HO_2^{\bullet} \rightarrow Fe^{+2} + O_2 + H^{+} \quad (4)$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (5)$$

- ↑ Fe^{+2} concentration → $OH^{\bullet}$ consumption (reaction 2)

  → removal efficiency↓

- excessive Fe^{+2}: H_2O_2 conversion to H_2O

$$Fe^{+2} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{+3} + H_2O$$

RESULTS

Effect of the H_2O_2 concentration on the system performance

- H_2O_2 : production source of $OH^{\bullet}$ → most significant factor limiting process efficiency
- Unused H_2O_2: positive intervention in COD analyses

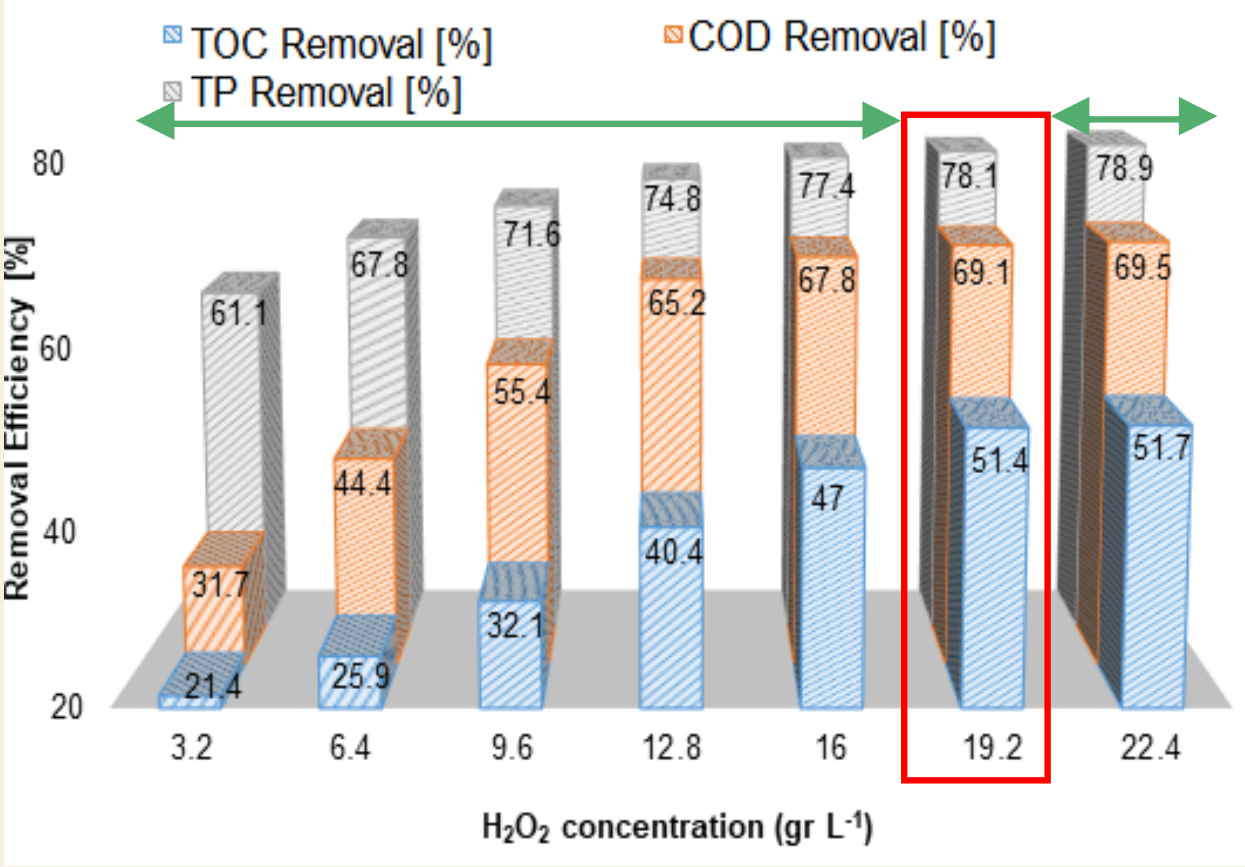
→ H_2O_2 optimal value essential for treatment efficiency + minimized cost

- Effect of 6 different H_2O_2 concentrations from 3.2-22.4 gr L^{-1} tested
  - Optimal Fe^{+2} concentration (1.3 gr L^{-1})
  - No adjustment of the PPIW pH

RESULTS

Effect of the H_2O_2 concentration on the system performance

↑ the H_2O_2 concentration up to 19.2 gr L^{-1}: ↑ removal efficiencies

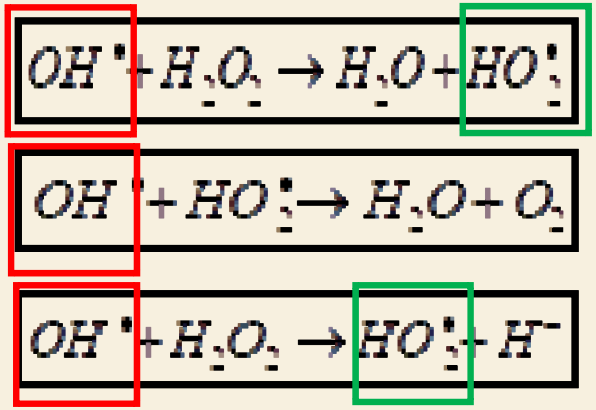


H_2O_2 addition effect less important

RESULTS

Effect of the H_2O_2 concentration on the system performance

H_2O_2 ≡ production source of $OH^{\bullet}$: H_2O_2 concentration ↑ → $OH^{\bullet}$ ↑



- H_2O_2 =radical scavenger at higher concentrations
- $HO_2^{\bullet}$ formation (lower oxidation capacity)
- $OH^{\bullet}$ radicals consumption → ↓removal efficiency

RESULTS

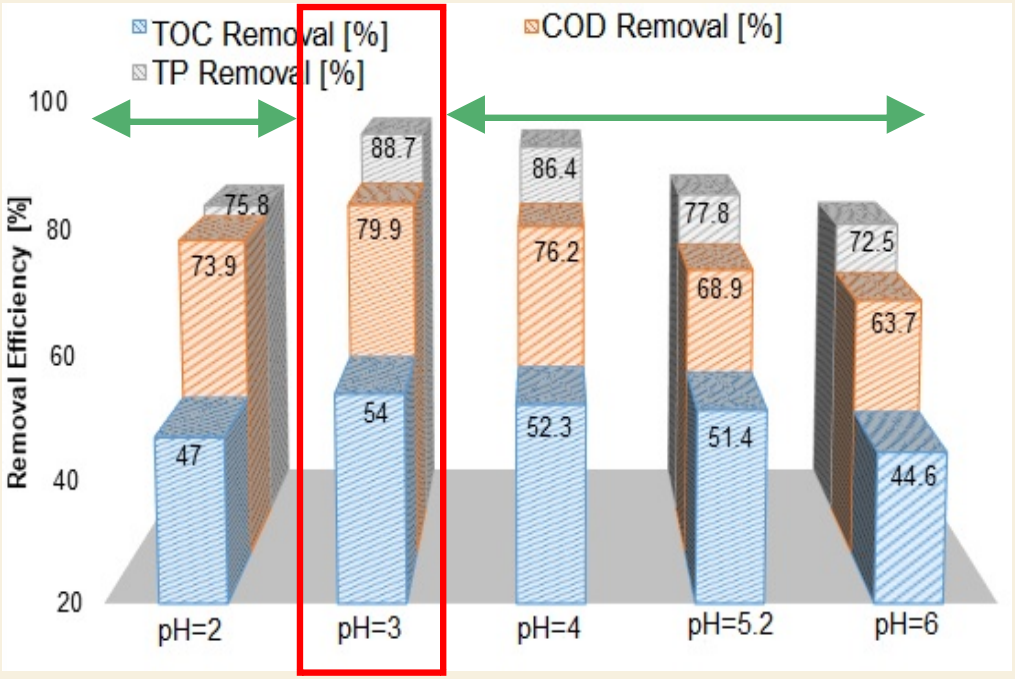
Effect of initial PPIW pH on system variables

- Fenton process: strongly pH-dependent (interaction between Fe^{+2} & H_2O_2)
- PPIW treatment via Fenton oxidation: usually in pH 2-6
- pH>6 ~~recommended~~ due to Fe^{+2} precipitation

(Fe^{+2}:1.3 gr L^{-1}, H_2O_2: 19.2 gr L^{-1})

$OH^{\bullet}$ production ↓ & $H^+ = OH^{\bullet}$ radical scavenger =

$$OH^{\bullet} + H^+ + e^- \rightarrow H_2O$$

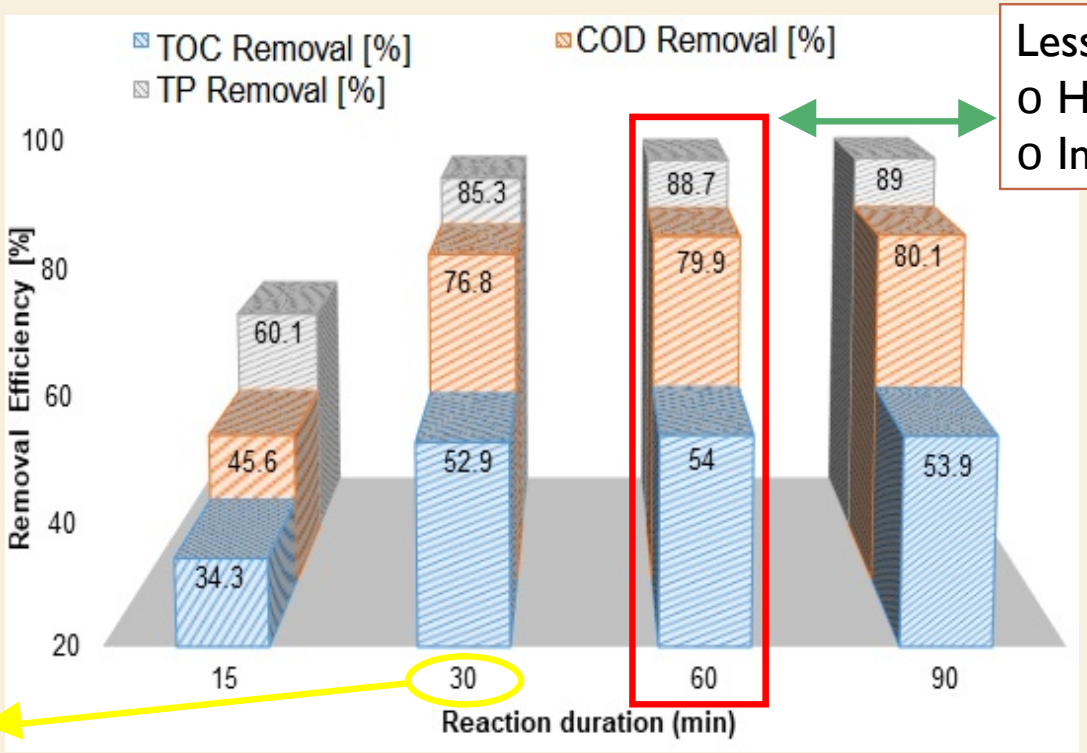


H_2O_2 forms O_2 & H_2O: oxidation activity ↓

RESULTS

Reaction time effect

Under optimum conditions (Fe^{+2}:1.3 gr L^{-1}, H_2O_2: 19.2 gr L^{-1}, initial PPIW pH=3):

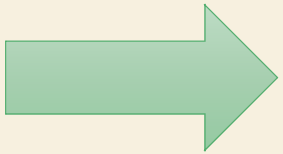


Less important effect
- o H_2O_2 absence
- o Inhibition by produced $OH^{\bullet}$

Analyses: 99% of added H_2O_2 already consumed after 30 min!

CONCLUSIONS

Optimum conditions determined as:
- pH=3
- 1.3 gr L^{-1} Fe^{+2}
- 19.2 gr L^{-1} H_2O_2
- 60 min of reaction time



- COD removal=79.9%
- TOC removal=54%
- TP removal=88.7%

✓ Fenton oxidation=effective treatment for PPIW
✓ Potential pre-treatment for wastewaters with high organic content


THANK YOU
FOR
YOUR ATTENTION