Treatment of industrial wastewater

Prof. Dr. D. A. Aznar Jiménez
Dpto. C. e I. de Materiales e I. Química
UNIVERSIDAD CARLOS III DE MADRID
• Energy production: vaporization
• Heat transport
• Raw materials transport
• Waste transport
• Mechanical action
• Product manufacturing
• Transport of ions
• Cleaning or washing-up of pieces
• Extinction of incandescent products
• Gas washing
• Bath preparation
• Air conditioning
• Pressure maintenance
• ...
WATER CONSUMPTION IN FACTORIES

- Chemical Ind.: 30%
- Food and drink: 11%
- Paper: 28%
- Petroleum refining: 6%
- Leather: 4%
- Rubber transf.: 3%
- Building Mat.: 4%
- Textile: 4%
- Others: 1%
- Food and drink: 11%
- Paper: 28%
- Petroleum refining: 6%
- Leather: 4%
- Rubber transf.: 3%
- Building Mat.: 4%
- Textile: 4%
- Others: 1%
Water input

PROCESS

Effluent (95%)

Product (5%)
• Chemical reactors
• Heat exchangers
• Drying/ Evaporation
• Crystallization
• Distillation
• Absorption
• Extraction
• Adsorption
• Other operations
Chemical reactors

- Core of the production process
- Main source of waste
  - Partial conversion and lateral reactions
- Performance improvements
  - Mixing
    - Use of baffles
    - Higher speed stirring
    - Modification of blades
  - Distribution improvements (in beds)
  - Improvement of the process control
- Washing processes
● Direct contact (Cooling towers)
● Indirect contact (exchangers)
● Waste generation
  - Crud formation. Reduces efficiency
    ● Addition of chemical products
    ● Cleaning improvements
  - Formation of sediments and sludge
    ● Reduction of vapor temperature or hot fluid
  - Leaks
• Use of energy to remove water from a material.
• Operations with an intensive consumption of energy.
  – Use of mechanical means (filtration) previous to thermal drying
• Evaporated gases must be condensed and reprocessed or be treated as a waste.
• Inappropriate operation will cause the detachment of solids and their transfer as waste in the gaseous flow
- Generation of upstream water oversaturated with crystalline material
- Adhesion of material to reactor walls
• Energy intensive process. Need of energetically efficient systems. Can be improved by:
  – Increase the reflux ratio
  – Increase column height
  – Improve feeding distribution
  – Changes in filler type
  – Isolating or preheating influent
  – Reducing pressure loss in column
• Used for material recovery
• Possible formation of subproducts in the column
• Emissions of volatiles (purge, tanks,...)
• Tails are sometimes useless materials
If transfer is not efficient a high consumption of water and energy is produced.
Adsorption

- Can be used to separate and concentrate a product, and therefore a later step is necessary.
- The absorber must be replaced or regenerated, thus generating another waste.
• Used in the removal of oil and grease from waste (soil, water or sludge)
• Removal of phenol in effluents from petroleum industry (with methyl isobutyl ketone)
• Recovery of acetic acid from industrial wastewater (with ethyl acetate)
• Extraction with supercritical fluids
  – Pharmaceutical industry
  – Waste treatment
### Other Operations

<table>
<thead>
<tr>
<th>MECHANICAL SEPARATION</th>
<th>SOLID-FLUID</th>
<th>SOLID-SOLID</th>
<th>FLUID-FLUID</th>
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<tbody>
<tr>
<td></td>
<td>Sedimentation</td>
<td>Manual screening</td>
<td>Decantation</td>
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<td>Flotation</td>
<td>Magnetic separation</td>
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<td>Filtration</td>
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<td>Powder collection</td>
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<td><strong>Drying</strong></td>
<td>Extraction with</td>
<td><strong>Evaporation</strong></td>
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<td>solvents (lixiviation)</td>
<td><strong>Distillation</strong></td>
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<td><strong>Adsorption</strong></td>
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<td>MOLECULAR SEPARATION</td>
<td><strong>Drying</strong></td>
<td>Extraction with</td>
<td><strong>Extraction</strong></td>
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<td></td>
<td>Adsorption</td>
<td>solvents</td>
<td><strong>desorption</strong></td>
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<td></td>
<td>Ion exchange</td>
<td>(lixiviation)</td>
<td><strong>Extraction</strong></td>
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<td>Crystalization</td>
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<td><strong>with solvents</strong></td>
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<td><strong>Membranes</strong></td>
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Each one is a potential source of waste
Other equipment must also be considered:
- Fluid transport (pipes, joints, chimney)
- Pumps, aerators, compressors
- Storing equipment

Main problems:
- Leaks
- Spills

Fugitive emissions
Palliative solutions:

CONTAMINATE-DECONTAMINATE

- Destroy: incineration, biodegradation, ...
- Concentrate: sludge, precipitates, solutions, ...
- Dilute: emissaries, ponds, ...

Analyzing the discharge problem

Water → Process → ?Properties? → Discharge

?Properties? → Yes → Depuration

No → Depuration
DECONTAMINATE ≡ NOT-CONTAMINATE

✓ Do not produce effluents or minimize their production.
✓ Reuse the effluent, decreasing the consumption of raw materials, energy and facilities.
✓ Substitute raw material, producing less effluents.
✓ Segregate some effluents for separate treatment attending to their special characteristics.
ALTERNATIVE CONCEPTION (R3)

Water → Process₁

- Reduce? Yes → Modify the process
- Recycle? No → Yes
- Properties? Yes → Process₂
- Properties? No → Depuration

Process₁:
- Reduce? No → Yes
- Properties? Yes → Depuration
- Properties? No → Waste

Process₂:
- Use? Yes → No
- Properties? Yes → Depuration
- Properties? No → Discharge
Zero discharge

- Most of the processes generating waste are removed through changes in the processes.
- As much as possible of the waste produced is reused, recycled or valorized.
- The final waste is removed.
- As not all waste production can be prevented, the objective is that the removed volume is small enough so that elimination can be performed in a safe way.
PREVENTION OF POLLUTION HIERARCHY

At source reduction

Recycling

Reusing

Treatment

Removal

Zero discharge
Externalization of potential impacts

River

Water inlet

Water discharge

PLANT

Other users

Internalization of potential impacts

River

Water discharge

PLANT

Water inlet

A great challenge

Other users
1. Scope and preparation of the audit

2. Divide process in unit operations
3. Construction of flow diagram

4. Determine input
5. Registry of water and input
6. Measure recycling level

7. Environmental legislation
8. Measure of flows
9. Characterization

10. Structuring the information on input and discharge
11. Develop mass balance

12. Identify options to reduce effluents
13. Identify problem effluents
14. Long term reduction

15. Evaluate options
16. Priority of options

17. Design and set up of preventing measures and alternative treatments

- Control and follow-up of Directive
- Fulfillment of standards, legislation and procedures

- Pre-treatment to plant
- Discharge to water flow
- Discharge to sewer
- Treatment outside industry

- Capital, operation, maintenance and other costs
- Feasibility analysis
Pollution prevention
Definition

- The use of materials, processes or practices that reduce or eliminate the creation of pollution or wastes at the source.
- Practices that reduce the use of hazardous materials, energy, water and other resources.
- Practices that protect natural resources through conservation or more efficient use.

(Environmental Protection Agency)
DAIRY INDUSTRY

ORIGINAL PROCESS

1st STEP

1200 l/wash
11 wash/day, 50 ºC

P = 460 kWh/day

RINSE WATER 80 ºC

800 l/wash

Fat recovery

350 l/wash

BOD₅ = 2000 mg/l
Q₁ = 12,65 m³/day

MODIFIED PROCESS

1st STEP

50 l/lwash
11 wash/day, 40 ºC

P = 24,4 kWh/wash

RINSE WATER 80 ºC

400 l/wash

Fat recovery

<1,8 mS

Yes

Fat recovery

No

P = 24,4 kWh/day

BOD₅ = 200 mg/l
Q₁ ≈ 0,55 m³/day

REDUCTION AT THE SOURCE
CERAMIC INDUSTRY (I)

Clay mixture 4t/day
Na stearate 150 kg/day
water 10 m³/day

20% SS
THICKENER

Effluent (7.3 m³/day)
Na stearate 12.3 g/L
SS 10 g/L (Ø particle = 0.1-1 µm)

60% SS
Green Processing

Sintering (1,100 ºC)

Water vapor (2.6 m³/day)
Clay mixture
4t/day
water
10 m³/día
Mixer
20% SS
Effluent (7.3 m³/day)
Na stearate 12.3 g/L
SS 10 g/L ($\Phi_{\text{particle}} = 0.1-1 \, \mu m$)

Na stearate 150 kg/day

Clay mixture
4t/day
water
150 kg/day

20% SS

Thickener
60% SS

Green processing

Sintering (1,100 ºC)

Heat exchanger

Water vapor (2.6 m³/day)

Gas washing
ENERGY RECOVERY

CONVENTIONAL HEATING AND COOLING SYSTEMS

ENERGETIC INTEGRATION OF PROCESSES: REDUCTION IN STEAM AND COOLING WATER
SECONDARY WASTE
WATER
WATER RECYCLING
OPERATION 2
CONDITIONING
WATER
WATER TO REUSE
SEGREGATED WASTEWATER
OPERATION 1
WATER
SECONDARY WASTE
Biodegradable effluent 400 m³/h COD 1200 / BOD₅ 700

40 m³/h COD 1800 / BOD₅ 200

20 m³/h COD 3000 / BOD₅ 1000

Precipitation/ Flocculation

COD 450 / BOD₅ 200

30 m³/h COD 6000 / BOD₅ 3500

Wet oxidation

COD 8000 / BOD₅ 2000

4 m³/h COD 3000 / BOD₅ 1200

Flotation

Evaporation

475 m³/h COD 1450 / BOD₅ 840

475 m³/h COD 3700 / BOD₅ 690

5 m³/h COD > 100000 / BOD₅ 690

> 10% salts

10 m³/h > 5% Solvents

> 5% Solvents

10% salts

SEGREGATE
STEEL PICKLING (I)

**Chemical Reactions**

- $[\text{HNO}_3] = 6-10\%$  
- $[\text{HF}] = 2-3.5\%$

**Mechanical Cleaning**

- Steel 500 ton/day

**Waste Streams**

- $60 - 320 \text{ m}^3/\text{day}$
- $[\text{Me}] \approx 50/60 \text{ g/l}$

**Reagents**

- $\text{CaO}$  
- $\text{H}_2\text{O}$  
- $\text{Ca(NO}_3\text{)}_2 \text{ (aq)}$

**Discharge**

- SEWER

- AUTHORISED DISCHARGE TO LANDFILL

- $\text{CaF}_2$, $\text{Fe(OH)}_3$, $\text{Ni(OH)}_2$, $\text{Cr(OH)}_3$, $\text{As(OH)}_3$
STEEL PICKLING (II)

HF/HNO₃

[HNO₃] = 6-10%  [HF] = 2-3.5%

Mechanical cleaning

Steel 500 ton/day

60 - 320 m³/day

[Me] ≈ 50/60 g/l

pH = 9-11

Filtration

Microfiltration

1,8N KOH/0,5N KF

Casting

Fe(OH)₃, Ni(OH)₃, Cr(OH)₃
PREVENTION OF POLLUTION AT DESIGN

Potential pollution prevention

Min

Max

Process information

Short term pollution prevention

Long term potential pollution prevention

Basic R+D
Synthesis processes
Conceptual design
Preliminary design
Detailed design
Building and set-up
An improvement in the efficiency of productive processes minimizes the generation of waste.

These modifications may include

- More advanced technologies
- Change to less polluting reactants
- Change in cleaning processes
- Use of catalyzers
- Segregation of waste
- Improve operation and maintenance
IPPC: Integrated pollution prevention and control (Ley 16/2002)

- **Integrated approach**
  
  ✓ **CONSIDER** all and every stages of the productive process.
  
  ✓ **DETERMINE** an adequate ratio between the amount of pollutant emissions produced and the characteristics of the receiving environment.
  
  ✓ **TAKE INTO ACCOUNT** the possible transfer of pollution from a pollution receiving medium to a different medium.
✓ Generation of less waste.
✓ Use of less dangerous substances.
✓ Development of recovery and recycling techniques.
✓ Processes, facilities or methods checked at industrial scale.
✓ Implement scientific and technical improvements.
✓ Characteristics, effects and volume of the discharge.
✓ Date at which facility begun operation.
✓ Time period required to install a BAT.
✓ Reduction of raw materials consumption.
✓ Increase of energetic consumption efficiency.
✓ Prevent or reduce the discharge impact.
✓ Reduction of accident risk.
✓ Information published by EU or international organisms.
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- Optimize the quantity of reactants (do not use too much).
- Avoid adsorption if the adsorbent cannot be regenerated.
- Use of vacuum columns for labile products.
- Use of high performance columns to reduce pressure losses.
- Use continuous process if washing generates a large amount of waste.
- Use of wall scrapers in exchangers with viscous products.
• Improve reactor design
  – Ease cleaning
  – Minimize valves and obstructions
  – Recover fugitive product from drains, venting,…

• Improve reactor control
  – Improve efficiency
  – Decrease side reactions

• Improve separation processes
  – Use mechanical separations if more than one phase exists
  – Avoid over-dimensioning. Use designs effective for a wide range of conditions
  – Favor the transference of the minority component
  – Use high separation factors
• Improve cleaning/degreasing
  – Reduce frequencies
  – Countercurrent tank cleaning
  – Automatic systems for pressure cleaning
  – Minimize the loss of solvents
  – Cleaning with ultrasounds

• Recycling
• Recovery of materials
• Change product
• Storage
• Internal management
  – Good practices
  – Formation
  – Existence of procedures