Agricultural wastes for wastewater treatment

M. T. Santos¹, J. F. Puná¹, ², A. M. Barreiros¹ and M. Matos¹

¹ ADEQ, Instituto Superior de Engenharia de Lisboa - ISEL/IPL,

² CERENA, Instituto Superior Técnico, Universidade de Lisboa – IST/UL
Topics

- Introduction
- Goals
- Methodology
- Results and discussion
- Conclusion
- Future work
Introduction

Agriculture and alimentary industry

Solid wastes
Dried fruits and cereals

Portugal production

Walnuts > 4,000 ton/year and imported 1,000 ton.

Peanuts ≈ 10,000 ton/year of importation and 2,500 ton/year of exportation.
**Introduction**

Shells

*Dried fruits and cereals*

According to INE data - 1 kg of walnuts or peanuts $\approx 0.27$ kg of shells.

In 2013 the shells estimation is **1,150 ton for walnuts** and **2,025 ton for peanuts**.
Introduction

Industry activities

Metal cleaning, paint, electroplating, plating baths paper and wood production, air conditions and fertilizer industries

*Industrial wastewater* - heavy metal such as copper, cadmium, chromium, cobalt, iron, lead, nickel, and zinc.

Minimum quality of a superficial water - $0.1 \text{ mg.L}^{-1} \text{ Cu (II)}$

Irrigation water - $5 \text{ mg.L}^{-1} \text{ Cu (II)}$
**Goals**

*What to do with solid waste and wastewaters?*

**Wastewater**
- chemical precipitation,
- coagulation/flocculation,
- ion exchange,
- membrane process.

**Solid wastes - dried fruits shells**
- manufacture of animal feed
- fertilizer
- land cover

**Goal**

To investigate and describe the equilibrium of sorption of metals (e.g. Cu (II) and Ni (II)) on walnut and peanut shells in order to obtain the right adsorbent amount and the suitable operating conditions.
Materials and Methods

Absorbents

Walnut (*Juglans regia* L.) shells  
Peanut (*Arachis hypogaea* L.) shells

natural adsorbents

Collected from source separated domestic wastes

Characterization

Granulometric analysis  
Physical analysis
## Materials and Methods

### Absorbents - Treatments

**Absorbents experimental conditions tests**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td>-</td>
</tr>
<tr>
<td>Washing with distilled water and drying</td>
<td>Temperature: 60 and 100 ºC</td>
</tr>
<tr>
<td>Sieving</td>
<td>Different particles size: 0,5 and 1,4 mm</td>
</tr>
<tr>
<td>Carbonization</td>
<td>Temperature: 550ºC</td>
</tr>
</tbody>
</table>

**Carbonization**

**Walnut shells**

**Peanut shells**
Adsorption tests

**Batch mode** varying the absorbents dose or the metal concentrations.

Working volume of 100 to 150 mL in an orbital agitator with a mixing rate around 150 rpm
Results and discussion

Shells amount estimation

**Walnuts** - 0.56 kg of shells per kg

**Peanut** - 0.26 kg of shells per kg.

Granulometric analysis

**Equivalent diameter > 2 mm**

- 94.1 % by weight of walnut shells
- 80.7 % by weight of peanut shells

INE data - 1 kg of walnuts or peanuts ≈ 0.27 kg of shells.
Results and discussion

Physical analysis

Peanut and walnut shells characteristics

<table>
<thead>
<tr>
<th>Shells</th>
<th>% weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moisture</td>
</tr>
<tr>
<td>Peanut</td>
<td>5.56</td>
</tr>
<tr>
<td>walnut</td>
<td>10.52</td>
</tr>
</tbody>
</table>
Results and discussion

Adsorption tests

Effect of particle size and adsorbent dose

Dry peanut shells at 60 °C with a contact time = 15 min

Dry walnut shells at 60 °C with a contact time = 30 min
Results and discussion

Adsorption tests

Effect of adsorbent type

Adsorption efficiency of Cu (II) onto dry shells at 60 ºC
Results and discussion

Adsorption tests

- **Dry walnut shells**
- **Peanut carbonized**

**Effect of time**

- t = 15 min
- t = 30 min
- t = 60 min
Results and discussion

Adsorption tests

Effect of adsorbent treatment

Carbonized and dry peanut shells
Results and discussion

Adsorption tests

Isotherms

Langmuir

✓ monolayer adsorption of solutes;
✓ surface comprised of a finite number of identical sites with homogeneous adsorption energy.

Freundlich

✓ empirical expression;
✓ heterogeneity of the surface
✓ multilayer adsorption to the binding sites located on the sorbent surface.

Linear form

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}} K_L C_e} + \frac{1}{q_{\text{max}}}
\]

\[\log q_e = \frac{1}{n} \log C_e + \log K_F\]

\(q_{\text{max}}\) - the maximum adsorption capacity (mg g\(^{-1}\)),
\(K_L\) - the affinity of binding sites and is related to the energy of sorption, (L mg\(^{-1}\))

\(K_F\) ((mg g\(^{-1}\))(L mg\(^{-1}\))\(^{1/n}\)) - capacity of adsorption
\(n\) - intensity of adsorption,
\[n\]
2–10 good,
1–2 moderately difficult,
< 1 poor adsorption
## Results and discussion

### Adsorption tests

#### Isotherms

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Time (min)</th>
<th>Freundlich isotherm</th>
<th>Langmuir isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$K_F$ (mg g$^{-1}$)(L mg$^{-1}$)$^{1/n}$</td>
<td>$n$</td>
</tr>
<tr>
<td>Natural (Ø = 1,4 mm)</td>
<td>30</td>
<td>0.061</td>
<td>0.585</td>
</tr>
<tr>
<td>Drying (Ø = 1,4 mm)</td>
<td>30</td>
<td>0.188</td>
<td>0.857</td>
</tr>
<tr>
<td>Carbonized</td>
<td>30</td>
<td>1.274</td>
<td>0.539</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.491</td>
<td>0.546</td>
</tr>
<tr>
<td>Peanut shells (W+D+M +S&lt;30 µm)</td>
<td>3.09</td>
<td>2.97</td>
<td>0.022</td>
</tr>
</tbody>
</table>
## Results and discussion

### Adsorption tests

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Time (min)</th>
<th>$K_F$</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural (Ø = 1,4 mm)</td>
<td>30</td>
<td>0.968</td>
<td>2.77</td>
<td>0.998</td>
</tr>
<tr>
<td>Drying (Ø = 1,4 mm)</td>
<td>15</td>
<td>1.246</td>
<td>1.97</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>9.985</td>
<td>6.79</td>
<td>0.895</td>
</tr>
</tbody>
</table>

Walnut shell (W+D 80°C + S < 1 mm)  

$K_F = (\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$

Feizi, et al., 2015
Conclusions

• The selected adsorbents remove Cu (II) from water.

• The highest Cu (II) removal was obtain with carbonized peanut shells.

• The amount of Cu (II) adsorbed increased with sorbent particle size decrease.

• The adsorption equilibrium was best described by the Freundlich isotherms.
Future Work

• The pre-treatment adsorbents increases the cost - conditions optimization;

• The work is still in progress with other metals (Ni, Cr, Al or Pb) and shells (shrimps or eggs);

• Application of the absorbents to remove other pollutants like dyes from wastewater.
Acknowledgements:

We thank to the industries in providing the wastes.

email: tsantos@deq.isel.ipl.pt
Thank you for your attention

Questions ?