# Agricultural wastes for wastewater treatment

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# 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 ≈ 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 mg.L$^{-1}$ Cu (II)

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

# Goals

***What to do with solid waste and wastewaters ?***

**Wastewater**

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

***Quite expensive***

Adsorption

**Solid wastes - dried fruits shells**

- manufacture of animal feed
- fertilizer
- land cover

***Other option***

Adsorbents

## 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

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## Absorbents

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

**Collected from source separated domestic wastes**

### Characterization

**Granulometric analysis** | **Physical analysis**

## Absorbents - Treatments

**Absorbents experimental conditions tests**

| Treatment | Parameter |
|---|---|
| **Natural** | - |
| **Washing with distilled water and drying** | Temperature: 60 and 100 ºC |
| **Sieving** | Different particles size: 0,5 and 1,4 mm |
| **Carbonization** | Temperature: 550ºC |

**Carbonization**


**Walnut shells**


**Peanut shells**

# Materials and Methods

## 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


**Vacuum Filtration**

**Titration - Iodometric**

# Results and discussion

## Shells amount estimation

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

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

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

## Granulometric analysis

**Equivalent diameter > 2 mm**

94.1 % by weight of walnut shells

80.7 % by weight of peanut shells

# Results and discussion

## Physical analysis

Peanut and walnut shells characteristics

| Shells | % weight | | |
|---|---|---|---|
| | Moisture | Volatile matter | Ash |
| **Peanut** | 5.56 | 94.28 | 5.38 |
| **walnut** | 10.52 | 99.01 | 0.89 |

# Results and discussion

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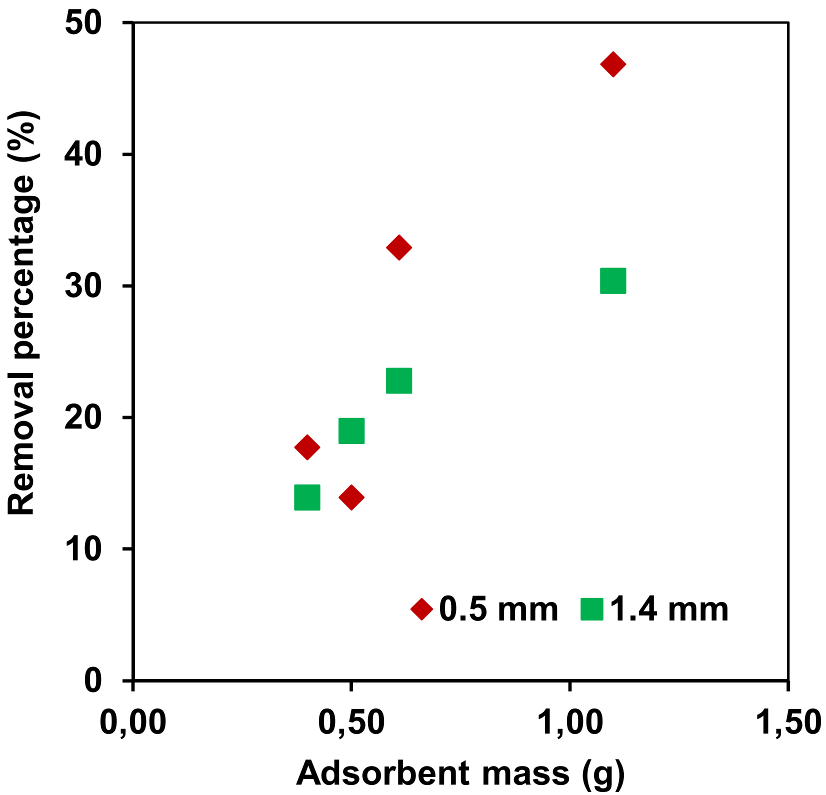
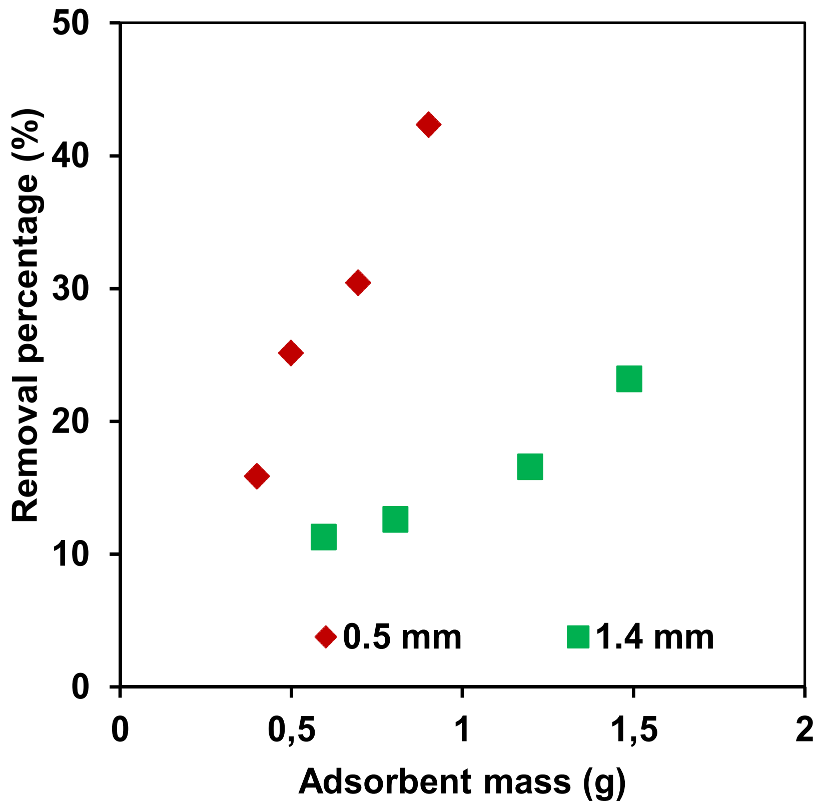
## Adsorption tests

### Effect of particle size and adsorbent dose




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




Dry walnut shells at 60 ºC with a contact time = 30 min

# Results and discussion

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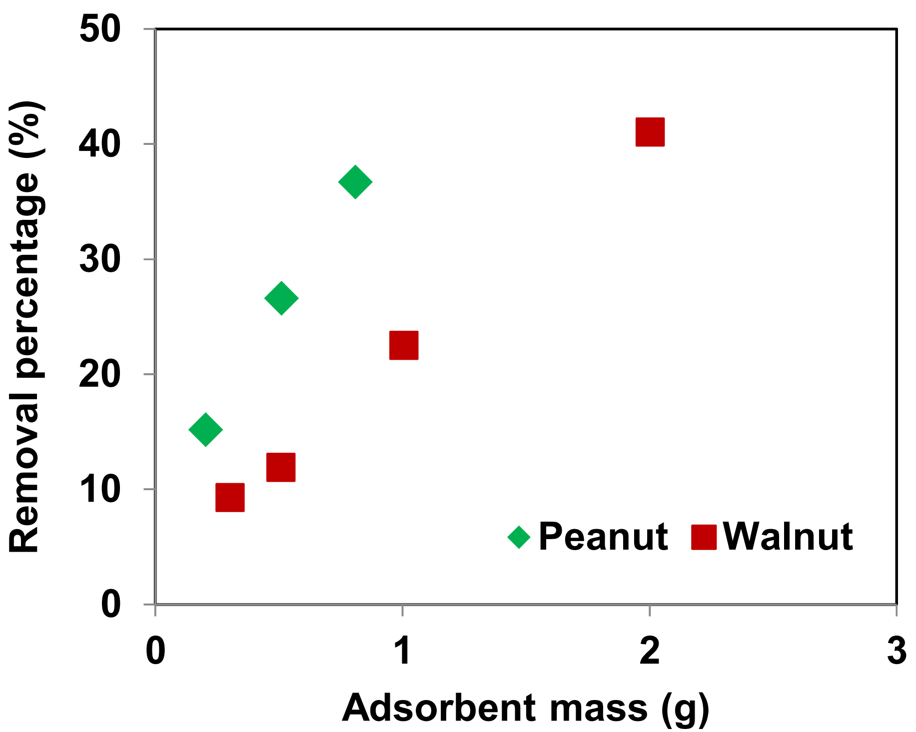
## Adsorption tests

### Effect of adsorbent type

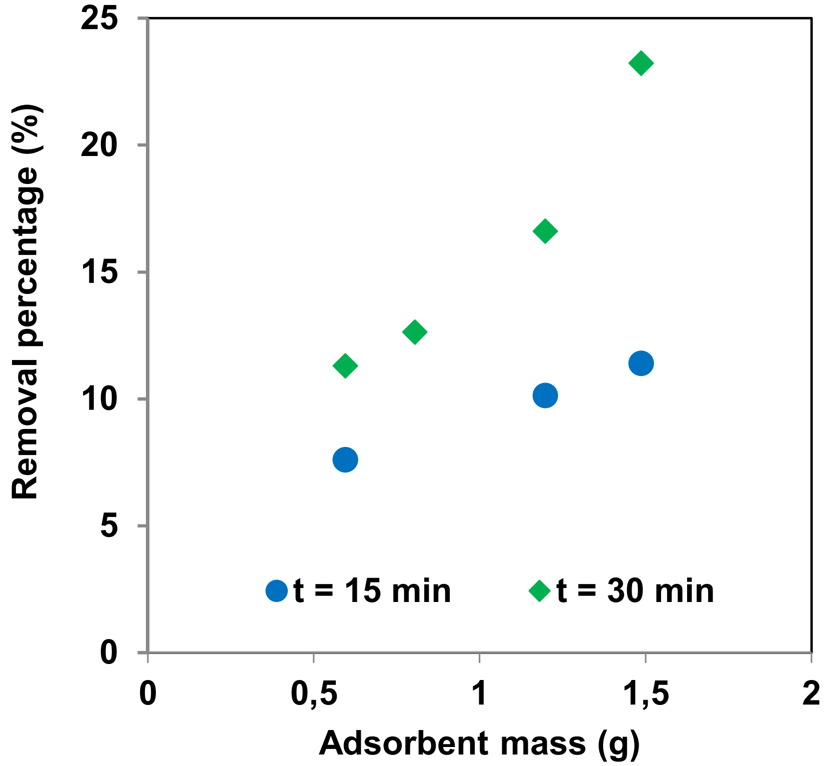



Adsorption efficiency of Cu (II) onto dry shells at 60 ºC

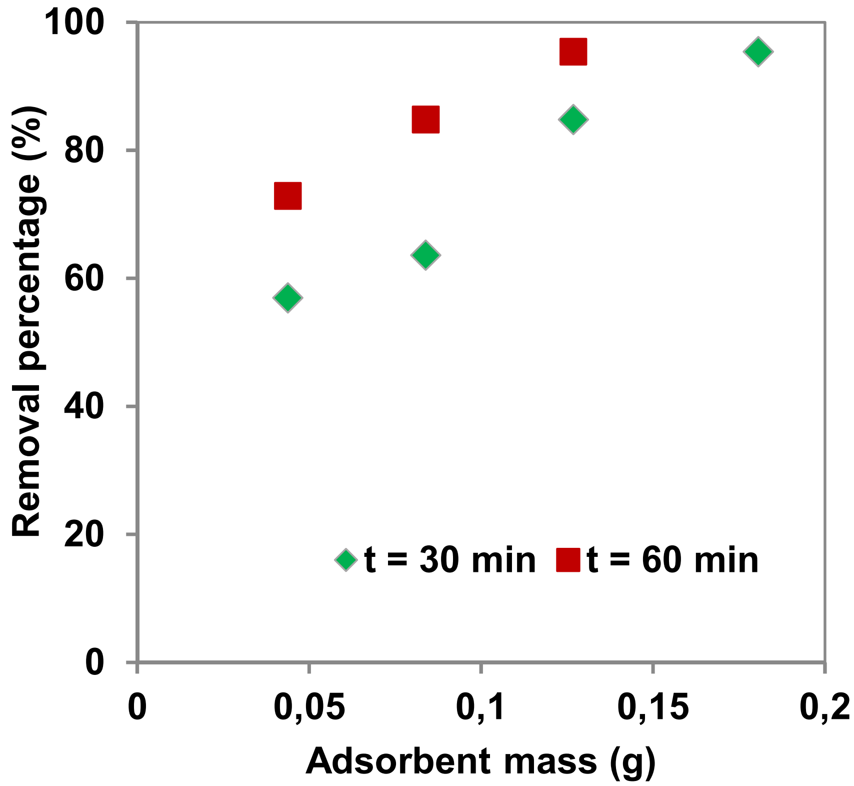
# Results and discussion

## Adsorption tests

## Effect of time




Dry walnut shells

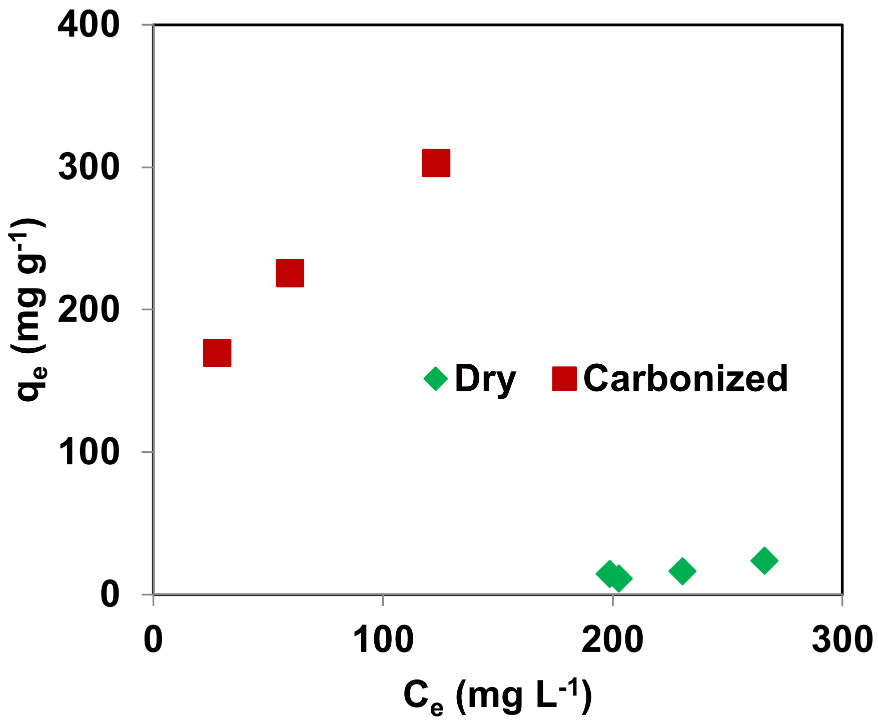



Peanut carbonized

# 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***

$$\frac{1}{q_e} = \frac{1}{q_{max}K_L}\frac{1}{C_e} + \frac{1}{q_{max}}$$

$q_{max}$ - the maximum adsorption capacity (mg $g^{-1}$),

$K_L$ - the affinity of binding sites and is related to the energy of sorption, (L $mg^{-1}$)

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

$K_F$ ((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** peanut shells

| Adsorbent | Time (min) | Freundlich isotherm | | | Langmuir isotherm | | |
|---|---|---|---|---|---|---|---|
| | | $K_F$ ((mg g$^{-1}$)(L mg$^{-1}$)$^{1/n}$) | n | $R^2$ | $K_L$ (L mg$^{-1}$) | $q_{max}$ (mg g$^{-1}$) | $R^2$ |
| **Natural (Ø = 1,4 mm)** | 30 | 0.061 | 0.585 | 0.935 | - | - | - |
| **Drying (Ø = 1,4 mm)** | 30 | 0.188 | 0.857 | 0.940 | - | - | - |
| **Carbonized** | 30 | 1.274 | 0.539 | 0.974 | 5.523 | 263.15 | 1 |
| | 60 | 1.491 | 0.546 | 0.886 | 0.152 | 303.03 | 0.918 |

| | | | | | |
|---|---|---|---|---|---|
| **Peanut shells (W+D+M +S<30 µm)** | **3.09** | **2.97** | **0.022** | **25.39** | **Witek-Krowiak et al., 2011** |

# Results and discussion

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## Adsorption tests

**Isotherms** walnut shells

| Adsorbent | Time (min) | Freundlich isotherm | | |
|---|---|---|---|---|
| | | $K_F$ ((mg g$^{-1}$)(L mg$^{-1}$)$^{1/n}$) | n | $R^2$ |
| **Natural (Ø = 1,4 mm)** | 30 | 0.968 | 2.77 | 0.998 |
| **Drying (Ø = 1,4 mm)** | 15 | 1.246 | 1.97 | 0.998 |
| | 30 | 9.985 | 6.79 | 0.895 |

| | | | |
|---|---|---|---|
| **Walnut shell (W+D 80ºC + S < 1 mm)** | 0.256 | 2.27 | 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.**

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# Thank you for your attention

## Questions ?