Sorption of metals on biological waste material

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Goals

- Low-cost biological material – orange peel;
- Possible replacement for the current expensive adsorbent for a remove of heavy metals;
- Adsorption studies;
- Pb(II), Ni(II) ions from test metallic solutions;
- Investigate the efficiency of adsorption for the removal of heavy metal ions from different concentration of solutions;
- Assess experimental data by several types of adsorption isotherms.
Preparation of biosorbent

- Waste from locally available orange company;
- Grinding in a coffee mill – fraction smaller than ca 0.5 mm;
- Magnetic iron oxide nanoparticles – FERROFLUID;

Orange peel in methanol + Ferrofluid mix (one hour) rinse by methanol
Reagents

- Water-soluble metal salts (\( \text{Pb(NO}_3\text{)}_2 \), \( \text{NiSO}_4 \cdot 7\text{H}_2\text{O} \) compounds);

- Pb and Ni solutions were prepared at concentrations ranging from 1 to 1000 mg.L\(^{-1}\);

- Working solutions – by diluting the stock solutions.
Analytical techniques

- Surface – SEM with EDX (SEM LYRA3 TESCAN);
- Specific surface area – Quadrasorb EVO/S;
- Metal concentration – AAS-FA (UNICAM SOLAAR M6).
Sorption experiments

magnetically modified orange peel
+ stock solution
(with defined initial ion concentration)

stirring and filtration
Isotherm study

- **Langmuir adsorption isotherm model** – homogenous adsorption surface;

- **Freundlich adsorption isotherm model** – heterogeneous system;

- **Temkin adsorption isotherm model** – the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent – adsorbate interactions; uniform distribution of binding energies, up to a maximum binding energy;

- **Dubinin-Radushkevich adsorption isotherm model** – adsorption mechanism based on the potential theory assuming a heterogeneous surface.
RESULT AND DISCUSSIONS
Material characterization

- Iron in the magnetically modified orange peel took forms:
  - magnetite (FeO·Fe$_2$O$_3$)
  - wustite (FeO)
  - non-stoichiometric iron oxide

- Specific surface area before modification – 0.45 m$^2$.g$^{-1}$
- Specific surface area after modification – 1.60 m$^2$.g$^{-1}$
Morphological appearance
Morphological appearance

Fe Lα1_2

Pb Mα1

500μm
Effect of pH

- metal concentration – 10 mg.l\(^{-1}\)
- pH range 3 – 7
Effect of contact time

- metal concentration – 10 mg.l\(^{-1}\)
- time range 5 – 168 hours
Effect of initial concentration

- metal concentration range – 10 – 1000 mg.l\(^{-1}\)
- pH range – (Ni) 6-7 and (Pb) 4-5
The experimental adsorption data were described by the linear form of adsorption isotherms and the linear coefficient of determination ($R^2$);

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Isotherm constant</th>
<th>Pb</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{max}$ (mg/g)</td>
<td>181.818</td>
<td>142.857</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$K_L$</td>
<td>0.010</td>
<td>0.001</td>
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<tr>
<td></td>
<td>$R_L$</td>
<td>0.088-0.906</td>
<td>0.478-0.989</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.9530</td>
<td>0.1998</td>
</tr>
<tr>
<td></td>
<td>$K_F$ (l/g)</td>
<td>2.103</td>
<td>0.166</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>1.938</td>
<td>0.767</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>0.516</td>
<td>1.303</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.9964</td>
<td>0.9134</td>
</tr>
<tr>
<td></td>
<td>$b_T$</td>
<td>78</td>
<td>77</td>
</tr>
<tr>
<td>Temkin</td>
<td>$a_T$</td>
<td>0.139</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.8757</td>
<td>0.8744</td>
</tr>
<tr>
<td></td>
<td>$a_D$</td>
<td>88.792</td>
<td>48.429</td>
</tr>
<tr>
<td></td>
<td>$b_D$</td>
<td>7.301E-07</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.8509</td>
<td>0.8003</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td></td>
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</tbody>
</table>
Adsorption isotherms

- The maximum monolayer coverage capacity:
  - 181.8 mg.g\(^{-1}\) (Pb)
  - 142.8 mg.g\(^{-1}\) (Ni);

- The linearized isotherm can be used to interpret the type of adsorption by using the values of R as follows:
  - R > 1.0 – not suitable;
  - R = 1.0 (0 < R < 1.0) – suitable;
  - R = 0 – irreversible;

- Sorption is favourable.
Adsorption isotherms

- \( K_F \) and \( n \) are parameters characteristic of the sorbent-sorbate system;
- Correlate sorption data – \( 1/n \) is a heterogeneity parameter (the greater the expected heterogeneity);
- Value of parameter \( n \) indicates – favorable sorption process;

![Graphs of Ni and Pb adsorption isotherms](image-url)
Stability of an adsorbent

- Leaching of iron was observed during sorption experiments;

- The concentration of iron in solution after sorption and desorption was very low;

- The iron oxides are very strongly fixed onto the surface and that the material could be used as Pb and Ni sorbent.
Conclusions

- Magnetically modified orange peel was used to prepare a biological sorbent;

- Suitable material for sorption of metals Pb and Ni from water solution;

- Results indicate that the adsorbate formed a heterogeneous adsorbent surface;

- A better adsorption efficiency was for low concentration of Ni (60%) and Pb (90%);

- The results of this study indicated that magnetically modified orange peels can be used as low cost, eco-friendly adsorbent for Ni and Pb removal with high efficiency.
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Thank you for your attention

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