The use of biosorbents in the treatment of polluted waters

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Few words about myself

Outline of the presentation

2. Types of biosorbents. Peat as a biosorbent.
3. Biosorption of heavy metals.
4. Overview of studies, where biosorbents have been tested in laboratory scale batch experiments:
   - Experimental setup
   - Pre-treatment and characterization of biosorbents
   - Factors influencing the sorption performance
   - Instrumental tools used in the research of biosorption
5. Utilization and regeneration of spent biosorbents.
Introduction

- Thousands of publications show that materials of biological origin (i.e., biosorbents) can be used as effective material to remove different substances, such as, heavy metals, nutrients, drugs and dyes from aqueous solutions.

- The use of biosorbents has been considered as an alternative to traditional wastewater treatment methods, such as chemical precipitation.
What is biosorption? (1/2)

- "Biosorption may be simply defined as the removal of substances from solution by biological material" (Gadd, 2009).

- It seems that virtually every article dealing with biosorption has its own definition of term „biosorption”.
What is biosorption? (2/2)
Definitions. Some [not so good] examples.

- "The term biosorption commonly refers to the passive binding of metal ions or radioactive elements by dead biomass" (Naja et al., 2010).

- "Microorganisms such as bacteria, fungi, yeast, algae, and plant can remove some pollutants from aqueous solutions, and such biological phenomena are called biosorption" (Lin and Juang, 2009).

- "The uptake of both metal and non-metal species by biomass, whether living or denatured, is commonly termed biosorption" (Ma and Tobin, 2004).
Why biosorption?

- The use of biosorbents is one of the alternative options, when traditional wastewater treatment methods, such as biological treatment or chemical precipitation, cannot be used because of:
  - the high costs;
  - low removal efficiency;
  - large amount of chemicals used or sludge produced.

- Biosorption offers the advantages of low cost and good efficiency.
Title = biosorption OR biosorbent OR biosorbents; Scopus database
Practical application of biosorption (1/3)

Biosorbents can be used as:

- Material in water treatment systems
- Absorbents for chemical / oil spills
- Permeable reactive barriers
- Waste basin liners

✔ Leachate from landfills
✔ Mine drainage
✔ Industrial effluents
✔ Municipal wastewater
✔ Drinking water?

Millions of people are drinking water that is contaminated with heavy metals!
Practical application of biosorbents (2/3)

Wastewater treatment systems

- Packed bed reactor (also called column reactor)
- Suspended biomass biosorption system - stirred tank reactor is used. Simple process, but it is necessary to add additional biomass-liquid separation unit (clarifier, filter or membrane).
Practical application of biosorbents

Biosorbents as media in constructed wetlands

Grismer, 2011
Types of biosorbents

Some examples.

Dried water hyacinth roots
Oil-palm fibers
Tea leaves
Seaweed
Olive stones
Yeast biomass
Soybean hulls
Sawdust
Rice hulls
Chitin
Bacteria
Fish scales
Fungi
Animal bones
Peat is a light brown to black organic material formed under waterlogged conditions from the partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs or trees.

All peatlands, such as bogs and fens, are composed primarily of peat.
Peat as a biosorbent (2/2)

Peat is a material with unique characteristics:

- large specific surface area
- high water holding capacity and high porosity
- it is easy to handle, process, grade and blend it
- it is widely available in many parts of the world and is considered as a relatively cheap material

... therefore the use of peat in the treatment of polluted water has significant advantages compared to other biosorbents.
Biosorption of metals

There are at least three major points to consider, when choosing the metal for biosorption studies:

- metal toxicity (direct health threat)
- metal costs (recovery interests)
- how representative the metal may be in terms of its behavior (scientific studies)
Calcium, Titanium, Zirconium, Barium, Chromium, Iron, Manganese, Cobalt, Nickel, Copper, Zinc, Aluminum, Lead, Silver, Cadmium, Mercury, Thallium
Due to the complexity of biomaterials used, it is possible that different mechanisms are acting simultaneously to varying degrees depending on the biosorbent and the solution environment (Volesky, 2001)
Sorption performance of biosorbents has been evaluated...

- ... in their natural environment, for example, a lot of research has been devoted to study ability of peat to sorb heavy metals in bogs and fens.
- ... in so called laboratory scale batch experiments.
- ... in laboratory scale column studies.
- ... in pilot scale studies.
- ... in full scale systems, such as constructed wetlands.
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Laboratory scale batch experiments

+ Simple and quick method.
- Batch adsorption tests cannot simulate or predict dynamic performance.
- There is not a standard procedure for batch experiments, therefore it is difficult to compare results.

The batch tests are used mainly to examine the mechanism of sorption and to compare sorption capacity of different sorbents.
Pretreatment of biosorbent

Modification of biosorbent

Determination of sorption capacity, depending on:
- Type of biosorbent used
- Initial metal concentration
- Contact time between sorbent and sorbate
- pH of the solution
- Ionic strength
- Temperature

Characterization of biosorbent (before and after the sorption)
1 g of peat was mixed with 80 ml of aqueous solution containing different concentrations of phosphate ions, using capped bottles (100 ml).

Samples were shaken on a rotary shaker with a constant speed of 140 rpm for 24 h.

The suspensions were filtered and the concentration of phosphates in the filtrates as well as in the initial solutions was determined.
In many cases little or no information is given about chemical and physical parameters of the tested biosorbent...
Overview of studies
Pretreatment of biosorbent

In most cases relatively simple pretreatment of biosorbent has been performed.

- Drying > sieving (most often)
- Drying > grinding > sieving (often)
- Drying > grinding > sieving > rinsing with distilled H₂O
- Drying > homogenization > grinding > sieving
- Drying > sieving > homogenization
- Sieving
- Homogenization > drying > grinding
Characterization of biosorbent (1/2)

Example of peat. Why it is so important?

Peat with a low degree of decomposition for the production of sorbents should be used, because it exhibits higher porosity, specific surface area, and more developed structure.
### Characterization of biosorbent

#### Peat type

<table>
<thead>
<tr>
<th>Peat type</th>
<th>Raw peat</th>
<th>Modified peat</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Sphagnum fuscum</em> peat</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### pH (in H₂O)

<table>
<thead>
<tr>
<th></th>
<th>Raw peat</th>
<th>Modified peat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.31</td>
<td>5.15</td>
</tr>
</tbody>
</table>

#### Organic matter, %

<table>
<thead>
<tr>
<th></th>
<th>Raw peat</th>
<th>Modified peat</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>96.6</td>
<td>83.4</td>
</tr>
</tbody>
</table>

#### Decomposition degree, %

<table>
<thead>
<tr>
<th></th>
<th>Raw peat</th>
<th>Modified peat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22</td>
<td>-</td>
</tr>
</tbody>
</table>

#### C, %

<table>
<thead>
<tr>
<th></th>
<th>Raw peat</th>
<th>Modified peat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>46.57</td>
<td>32.98</td>
</tr>
</tbody>
</table>

#### H, %

<table>
<thead>
<tr>
<th></th>
<th>Raw peat</th>
<th>Modified peat</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>5.52</td>
<td>4.48</td>
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</table>

#### N, %

<table>
<thead>
<tr>
<th></th>
<th>Raw peat</th>
<th>Modified peat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.96</td>
<td>0.66</td>
</tr>
</tbody>
</table>

#### S, %

<table>
<thead>
<tr>
<th></th>
<th>Raw peat</th>
<th>Modified peat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt; 0.5</td>
<td>0.0</td>
</tr>
</tbody>
</table>

#### Specific surface area BET, m²/g

<table>
<thead>
<tr>
<th></th>
<th>Raw peat</th>
<th>Modified peat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.02</td>
<td>43.80</td>
</tr>
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</table>

#### Zero point of charge

<table>
<thead>
<tr>
<th></th>
<th>Raw peat</th>
<th>Modified peat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.43</td>
<td>3.68</td>
</tr>
</tbody>
</table>

#### Concentration of iron, mg/kg

<table>
<thead>
<tr>
<th></th>
<th>Raw peat</th>
<th>Modified peat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>789</td>
<td>125000</td>
</tr>
</tbody>
</table>

#### Particle size distribution (after modification), % w/w

<table>
<thead>
<tr>
<th></th>
<th>&lt;0.05 mm</th>
<th>0.05 - 0.125 mm</th>
<th>0.125 - 0.250 mm</th>
<th>0.25 - 0.50 mm</th>
<th>0.5 - 1.0 mm</th>
<th>1.0 - 2.0 mm</th>
<th>&gt; 2.0 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Raw peat</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 %</td>
<td>6.5 %</td>
<td>8.6 %</td>
<td>14.6 %</td>
<td>22.3 %</td>
<td>36.1 %</td>
<td>10.8 %</td>
<td></td>
</tr>
<tr>
<td><strong>Modified peat</strong></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
The factors that influence the biosorption process can be grouped as:

1. **Physical and chemical properties of metal ions** (e.g., molecular weight, ionic radius, oxidation state)
2. **Properties of the biosorbent** (e.g., the structure of the biomass surface)
3. **The experimental conditions** (e.g., pH, temperature, concentration of biosorbent, the concentration of sorbate, contact time, etc.)
Overview of studies

Factors influencing sorption performance

![Graph showing phosphates sorbed over time for different masses (m=0.2 g and m=1.0 g).](chart.png)
A wide range of modern analytical tools are used in the research of biosorption, for example:

- Fourier transformed infrared spectroscopy (FTIR)
- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- Energy dispersive X-ray spectroscopy (EDS)
- X-ray diffraction (XRD) analysis
- Electron spin resonance spectroscopy (ESR)
- Nuclear magnetic resonance (NMR)
- X-ray photoelectron spectroscopy (XPS)
- X-ray absorption spectroscopy (XAS)
- Thermogravimetric analysis (TGA)
- Differential scanning calorimetry (DSC)
**Instrumental tools used in the research of biosorption (2/2)**

<table>
<thead>
<tr>
<th>Description</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visual confirmation of surface morphology of the biosorbent</td>
<td>Scanning electron microscope (SEM)</td>
</tr>
<tr>
<td>Crystallographic structure and chemical composition of metal bound on the biosorbent</td>
<td>X-ray diffraction (XRD) analysis</td>
</tr>
<tr>
<td>Determine active sites of the biosorbent</td>
<td>Fourier transformed infrared spectroscopy (FT-IR)</td>
</tr>
</tbody>
</table>
Utilization and regeneration of spent biosorbents

- Any biosorbent sooner or later has to be replaced, therefore it is important that saturated biosorbent can be handled with low costs and regeneration does not negatively affect the environment.

- Taking into account the environmental and economic aspects, it is desirable to use biosorbents which can be used for several sorption / desorption cycles.
Modification of biosorbents

- Biosorbents can be modified in order to reduce several deficiencies, which are:
  - Low sorption capacity
  - Poor chemical stability
  - Low mechanical strength
  - Tendency of biosorbent particles to expand or shrink

- It should be noted that the modification reagents or equipment used leads to additional costs. However, it should be strongly emphasized that the costs of modification are never mentioned in research papers, as well as cost evaluation in general.
If the biosorbent is in the form of powder, it is possible to granulate (or to pelletize) it, therefore reducing the possibility to clog the system. In addition, hydraulic conductivity is increased.

If biosorbent is granulated, it is recommended by Volesky (2001) to have size of these granules to be between 0.7 to 1.5 mm, as the ion exchange resins used in waste water treatment is of the same size.
Granulation of biosorbents (2/2)

► It must be pointed out that granulation provides not only the optimum particle size, but also provides mechanical strength, rigidity and porosity (Wang and Chen, 2009).

► It seems that granulation offers significant advantages, however it should be pointed out that “granulation is more of a trial-and-error task making it difficult for academic researchers to make a significant contribution” (Volesky, 2001), therefore relatively low number of researchers have used granulated biosorbent in their studies.
Immobilization of biosorbents

- Term „immobilization” is with a broader meaning - it can include granulation, as well as:
  - entrapment of biosorbent particles in a strong but permeable matrix
  - encapsulation within a membrane-like structure
  - grafted onto an inorganic support material such as silica

- According to Wang and Chen (2009), “immobilization technique is one of the key elements for the practical application of biosorption”. 
Future directions

- Economic analyses are required to obtain the overall cost of the sorbent and biosorption process.

- The fate of exhausted biosorbent remains relatively unanswered.

- Cooperation between scientists would be advisable, as multidisciplinary skills are needed.

- There is a need to reduce the “gap” between laboratory experiments and application of tested biosorbents in full scale systems, such as constructed wetlands.
References


Thank you for your attention!