Abstract

Carbon - based nanomaterials. Environmental applications

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Section 1 Scientific achievements

In this thesis, some environmental applications of carbon nanomaterials, natural and engineered as sorbents are presented. These materials unite the properties of \( \text{sp}^2 \) hybridized carbon bonds with the characteristics of physics and chemistry at the nanoscale. The most common properties cited in environmental applications are size, shape and surface area, molecular interactions and sorption properties and electronic, optical and thermal ones. This work treats the applications of engineered carbon-based nanomaterials as sorbents for environmental contaminants and possible applications of natural carbon-based nanomaterials in the same purposes.

NPs in the environment are divided into natural and anthropogenic particles, which can be separated into carbon-containing and inorganic NP. Both C-containing natural NPs and inorganic ones are divided into biogenic, geogenic, atmospheric and pyrogenic, NPs mostly appearing from combustion processes. Natural inorganic nanoparticles NPs are present everywhere in air, soils and geologic systems. NPs are also ubiquitous aerosols in the atmosphere and represent the precursors for the formation of larger particles, influencing global climate and global transport of pollutants. Primary atmospheric NPs can be soil dust and sea salt.

The environmental applications of engineered carbonaceous nanomaterials are both proactive (preventing environmental degradation, improving public health, optimizing energy efficiency) and retroactive (remediation, wastewater reuse, pollutant transformation). Carbon unique hybridization properties and the sensitivity of carbon’s structure to perturbations in synthesis conditions allow for tailored manipulation to a degree not yet achieved by inorganic nanostructures\(^1\).

In the first part of the study\(^2\) we reported first data on exfoliated graphitic nanoplatelets (xGnP) as a sorbent for phenol removal and preliminary evaluated the ability of different type of natural organic matter (NOM) to effectively disperse exfoliated graphitic nanoplatelets.
Phenol adsorption was found to increase with increase of adsorbent loading, contact time and phenol concentration on as-grown xGnP. The optimum adsorbent loading was found to be 400 mg/L when 72.25 % of phenol removal was achieved. The obtained adsorption data were best represented by Langmuir model and maximum monolayer adsorption capacity exceeded phenol adsorption to other sorbents. In the present work $q_e$ value for phenol sorption on as-grown xGnP was calculated to be 213.85 mg/g after 30 hrs of contact, this value indicating possible future uses of xGnP in environmental removal of pollutants and also the suitability of xGnP for waste water treatment application, taking into account the very low amounts needed in comparison with the activated carbon and the potential easy routes to control the functionalized groups on the xGnP surface for increasing the selectivity vs. several other contaminants.
In the second part of our study, xGnP were oxidized with KMnO$_4$ and HNO$_3$ and characterized in terms of Boehm’s titration and pH of the point of zero charge pH$_{PZC}$. The Pb(II) adsorption isotherms of the as-grown and the three kinds of oxidized xGnP were studied, the pH and xGnP dosage effects on the Pb(II) sorption being also evaluated. The effect of solution conditions such as metal ion concentration on their sorption behavior was investigated.

Batch adsorption experiments were carried out in 50 mL glass tubes at room temperature and the filtrates were electrochemically measured using ion-selective electrodes for lead, the amount of lead adsorbed on xGnP being determined by the difference between the initial Pb(II) and the equilibrium Pb(II) concentration. The metallic species were analyzed by electrochemical methods like in.\(^4\),\(^5\),\(^6\).

It was observed that the lead adsorption on xGnP depend on many factors, such as the surface functional groups, the specific surface area and the composition of the solution, the most important factor being the surface functional groups. It is already known that the oxidation treatment by nitric acid can cause a modification in the ion-exchange capacity, different functional groups with acidic nature on the surface dissociating at different pH values. Adsorption characteristics of the lead by carbon material are influenced by several factors such as: the pH, adsorbate concentration and adsorbent dosage. Here only preliminary results are presented which suggest that xGnP might be interesting sorbents for lead having possible very interesting environmental applications.

The two models for the adsorption isotherms of Pb(II) were compared in Table 7. Both models are applicable since the correlation coefficients present very close values higher than 0.9990. It was also observed that Freundlich and Langmuir models fit the adsorption isotherms of metal ions on activated carbon, Langmuir isotherm fitting the data better in single component systems, whereas the Freundlich one fitting better in multicomponent system.

<table>
<thead>
<tr>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>q$_m$ (mg/g)</td>
<td>333.3</td>
</tr>
<tr>
<td>K$_a$ (L/mg)</td>
<td>0.003</td>
</tr>
<tr>
<td>r$_m^2$</td>
<td>0.9994</td>
</tr>
<tr>
<td>K$_F$</td>
<td>13.592</td>
</tr>
<tr>
<td>n</td>
<td>1.142</td>
</tr>
<tr>
<td>r$_F^2$</td>
<td>0.9996</td>
</tr>
</tbody>
</table>

Table 7 Parameters of Freundlich and Langmuir adsorption isotherm models for Pb(II) on xGnP
It can be observed from Table 7 that both Langmuir and Freundlich models show good agreement with the experimental data with the correlation coefficient values of 0.9996 and 0.9994, respectively. The parameters $q_m$ and $K_F$, related to the adsorption capacity presented the biggest values at a pH value of 6.

The results of pH and xGnPs dosage on the Pb(II) adsorption show that the increase of Pb(II) adsorption capacity for HNO$_3$ oxidized xGnP is greater than for as-grown and KMnO$_4$ oxidized ones they were used in further sorption preliminary experiments.

The third part of the dissertation has the goal to evaluate the effect of burning treatment of soils on their toxicological properties and on their sorption properties for PAHs, in this purpose choosing for modeling naphthalene and considering that the behavior of burned and not-burned soils vs. naphthalene will be similar for the others PAHs. Electrochemical methods were used in analysis. The burned and not burned soils were separated into several fractions on the basis of size using membranes with different pore size, batch experiments being conducted to test the impact of operating parameters (initial concentration of contaminant – naphthalene, initial concentration of soil, pH, soil structure and composition, soil characterization).

Soils were also investigated regarding their toxic effectiveness (a) as extracts of the respective samples in small-scale test systems on acute cytotoxicity, embryo toxicity and dioxin-like activity, to evaluate the influence of soot particles on the extractability of environmental contaminants, and (b) in whole-sample assays on bacteriotoxicity and embryo toxicity with respect to the actual availability for sediment-dwelling organisms.

Another direction of our research activity concerned the effect of particles in the nano range from the air. Aerosols are of climatic interest because they act as cloud condensation nuclei and scatter and absorb solar radiation. In the fourth part of the thesis, we examined rural background aerosols, which were collected during a 2003 summer field campaign. Emphasis was given to the chemical analysis of polar organic compounds, i.e., polyols, mono- and dihydroxydicarboxylic acids and saccharidic compounds. Valuable information could be obtained on SOA components as well as on primary organic aerosol components. Fine size aerosols ($<2.5$ $\mu$m) collected on quartz fibre filters were extracted with an organic solvent mixture. The extract was derivatised into trimethylsilyl derivatives and analysed by gas
chromatography with flame ionisation detection (GC-FID) and gas chromatography/mass spectrometry (GC/MS), according to previously developed analytical procedures. Fig.35 shows a typical GC/MS total ion chromatogram obtained for the trimethylsilylated extract of the fine size fraction of a day time and a night time aerosol sample.

![GC/MS TIC](image)

Major peaks in the chromatogram correspond to the 2-methyltetrols, 2-methylthreitol (3) and 2-methylerythritol (4). These polyols have been reported for the first time in forest aerosols from Amazonia and have been explained by gas-phase photo-oxidation of isoprene.

Overall, the carbon content of the organic species quantified by GC/MS accounted for an average of only 3.2% of the OC in the fine aerosol fraction. Individual organic compounds insoluble in CH$_3$OH or not amenable to GC/MS analysis due to their low volatility (including naturally occurring humic acids) would constitute a significant fraction of the unidentified material. However, an important majority of the remaining OC was likely in the form of complete or fragmented primary biological structures, such as spores, pollen, algae, bacteria, leaves and insect parts. Because a major fraction of the OC is blocked in cellular structures, either as biopolymers like proteins, cellulose and other polysaccharides or as low-molecular-weight compounds inside
cells, techniques as GC/MS can never be expected to explain more than a small fraction of the organic aerosol mass. Many of the compounds identified by the GC/MS method are highly polar, multifunctional compounds that are highly soluble supporting the notion that these aerosols are a source of water-soluble compounds.

In conclusion, this dissertation presents some environmental applications based on our original result in efficient use of soil resources (nanoparticles in soil in situ remediation, absorption and release of contaminants in soils; nanosensors in monitoring of heavy metals and organic pollutants) and in efficient use of water resources (nanotechnology in desalination and water purification; nanoporous membranes for filtration; nano-sponges in the absorption of toxic metals)

Section 2 Future research directions

Our approaches will involve the following actions in order to improve the quality of the research work and of the lectures:

- to conduct research and produce and diffuse information on how nanotechnology applications can be used to improve environmental quality and agricultural yields;
- to develop and to encourage the use of possible nanotechnologies applications to support agricultural policies (for example to create soil maps by using data from nanotechnology based sensors;
- to conduct research on the critical issues related to nanotechnology and to help the overcoming of funding, access, risk and possible regulatory challenges;
- to lead debates on aspects of nanotechnologies applications in connections with a positive public perception

Future directions of research will envisage the applications of engineered and of natural carbon-based nanomaterials as sorbents for environmental contaminants and further on their applications in controlled deliver of pesticides and fertilizers in agriculture and sensors based on engineered carbon-based nanomaterials with environmental and agricultural applications.
Section 3 Selected references