STUDY OF THE REMOVAL OF 4–NITROPHENOL FROM AQUEOUS MEDIA BY ADSORPTION ON DIFFERENT MATERIALS

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ABSTRACT

The removal of 4–Nitrophenol (4–NP) from aqueous media by adsorption is studied in a batch system using different porous materials: activated carbon, zirconia, alumina, sepiolite, natural zeolite and 13X zeolite. Depending on their adsorption capacities, the best adsorbent was chosen to be impregnated with different levels of nickel (Ni) in order to study the adsorption by π-complexation in batch and continuous systems. The samples of Ni(x)/support (x= 2, 4, 6%) were prepared by wet impregnation and were characterised using the same method as with all the materials, by N₂ adsorption-desorption using the BET method, surface acidity and Z potential measurements by electrophoretic migration. The samples were measured in a UV-Vis spectrophotometer at a wavelength of 318 nm, while the adsorption capacity of the material in the batch system was calculated by making the difference in concentration once the adsorbent became saturated after an initial concentration of ~20 ppm, and in the continuous system this was done by integrating the area under the adsorption curve. The results suggest that adsorption capacity depends on the specific BET area, apparent acid strength and the IEP of each support, and that it varies with the addition of Ni.

Keywords: Adsorption, 4–Nitrophenol, supports, π-complexation.

1. INTRODUCTION

In Chile, agriculture and forestry are highly productive economic activities involving anthropogenic factors that affect the quality of surface water courses and bodies through the use of fertilisers and pesticides. This is because approximately 90% of farming fields have these components added, mainly in the form of organophosphate pesticides, which are known to be less persistent than organochlorines¹. However, partial degradation of this type of pesticide generates by-products of higher toxicity than the initial compound². This is the case with methyl-parathion (commercial name: Nitrox-80) which is moderately adsorbed onto surface soil particles, whereupon it may degrade naturally by biodegradation or chemical photolysis or hydrolysis³, thus creating the by-product 4–Nitrophenol (4–NP).

Considering that different natural degradation processes can simultaneously act on the degrading compound and on different points on its structure, knowledge of these transformation reactions remains in its initial stages. However, more than 50% of the initial compound of 4–NP is degraded in approximately three weeks by any natural process acting upon it⁴.

Nitroaromatic compounds are generally highly toxic and are classified as hazardous⁵ due to their mean lethal concentration (LC₅₀). They therefore belong to the group of the eleven most pollutant phenols described by the EPA⁶. Their removal from the environment poses a risk of exposure via the food chain or the lungs through inhalation of fine droplets⁷. Their removal from the body is slow and the half-life in humans has been documented at 5 to 14 days⁸.

Several methods have been reported for the degradation or removal of 4-NP in aqueous media, giving high levels of purity to the waters. They are known as Advanced Oxidation Technologies (AOT)⁹. Though these technologies lead to the formation of an oxidising radical, each of these processes requires various conditions in order to remove the compound effectively. An example of this is Fenton’s Process¹⁰ which requires strict pH control. These oxidation processes are of importance in this work due to their mean lethal concentration (LC₅₀) and that of the samples (C₅₀) and that of the samples (C₅₀) and that of the samples (C₅₀)

2. MATERIALS AND METHODS

2.1 Preparation of the adsorbents.

For the study of Ni impregnation, the adsorbents were prepared by impregnation in excess solvent using Ni(NO₃)₂ x 6H₂O (Merck pa.) as the precursor salt. The percentage metallic content was set at 2, 4 and 6% Ni. This was achieved by dissolving the necessary quantity of the precursor salt. Once the supports had been impregnated, the adsorbents were dried at 100°C for 12 hours and then calcined at 300°C for 4 hours in a muffle furnace.

2.2 Characterisation of the adsorbents.

In order to determine the BET area, 200 to 400 mg of each sample was degassed at 120°C for 18 hours, attaining a final pressure of 1 x 10⁻³ mm Hg. The subsequent analysis was carried out in a glass flask at the temperature of liquid nitrogen (-196°C) using a Micromeritics ASAP-2010 nitrogen adsorption/desorption volumetric instrument.

The surface acidity of the materials was measured by potentiometric titration¹¹. An amount of 100-150 mg of support sample with 100 mL of pure acetonitrile was mixed with 0.05 mL of titration solution, 0.05N butylamine in acetonitrile. The mixture was shaken for three hours and the first reading was taken with a calibrated potentiometer. Neutralisation of acidic sites was obtained by adding 0.05 mL of titration solution per minute until no appreciable variation was seen in the potential readings.

The zeta potential was measured using a Zeta Meter Inc. instrument, model 3.0, with an automatic sample transfer unit. Approximately 30 mg of support with 300 mL of KCl 10⁻¹⁰M solution were added. The pH was adjusted for each support with solutions of NaOH or 0.1M HCl, as required.

2.3 Determining adsorption capacity.

2.3.1 Batch system.

Approximately 500 mg of support were added to 100 mL of synthetic aqueous solution containing ~20 ppm of 4-NP. The solution was shaken mechanically at room temperature for eight hours (until saturation of the adsorbent). During this time, a sample was taken every 40 minutes, with cycles of 10 minutes, rest and 15 minutes in the centrifuge. The 4-NP feed and the samples were measured in quartz cells using a UV-Vis spectrophotometer with a wavelength of 318 nm. The amount of compound adsorbed was calculated by converting the measured absorbency into units of concentration using a simple calibration curve, taking into account that the difference between the initial concentration of the feed solution (Cᵢ) and that of the samples (Cₑ) (i.e. Cᵢ – Cₑ) is the amount of compound adsorbed onto the material.

2.3.2 Continuous system.

Approximately 500 mg of the best adsorbent in terms of the adsorption capacity measured in the batch system was placed into a Pyrex tube with a frit to hold the adsorbent. The sample was dried for an hour at 100°C with a flow of...
Activated carbon clearly has the largest area by far with 690 m² g⁻¹ and it doesn’t have high pore volume and pore diameter, as shown by the type of N₂ adsorption isotherm. As with the other supports, activated carbon presented a type IV isotherm, characteristic of mesoporous solids (diameter between 2 nm and 50 nm). However, it was the only material with a clear trend towards microporosity, given the volumes of the meso and micro-pores, which are responsible for this classification. With regard to the other supports, which all possess relatively similar specific BET, zirconia (258 m² g⁻¹) showed highly varied textual properties depending on the calcination temperature, with higher calcination temperatures decreasing the specific BET area and the pore size. This support has higher total pore volume (the sum of meso and micro-pores), which it does not have high pore diameter, as do natural and 13X zeolites. This is related to the hysteresis loop, which was of the H₁ type for the zirconia and for the zeolite and sepiolite. Though the zeolites have pore diameters of the same size, 36 nm, due to their similar nature, they differ in area and in pore volume as a result of the different molar Si/Al ratio between the two. The alumina has the fourth highest specific BET area and a high pore volume, and also has the second highest pore diameter after the zeolites.

For the apparent acid strength, the activated carbon has very weak acidic sites and its acidic site density shows that there are few potentially acidic groups on this support. The sepiolite has an acid strength corresponding to strong sites, which is expected considering that this metallic oxide contains silicon (Si), which forms oxides that are more acidic than those formed by the aluminium (Al) in the alumina. The latter support has an apparent acid strength corresponding to weak sites due mainly to the lower electro-negativity of the Al atoms in comparison to Si atoms. The difference in acidic site density between the sepiolite and the alumina is due to the fact that alumina is formed not only of metal atoms but also surface hydroxyl groups. For the aluminosilicates, the natural zeolite has higher apparent acid strength (weak sites) than the 13X zeolite (very weak sites) due to the difference in the molar Si/Al ratio, which is lower for the 13X zeolite. This can also be seen with the acidic site density, which is lower for 13X zeolite due to the increased Al in its structure and to the rapid neutralisation of the few acidic sites present. The zirconia has a potential that corresponds to very strong sites, which is directly related to the calcination temperature: 300°C in this case. Under this condition, the highest degree of acidity and the highest acidic site density are obtained.

Finally, with regard to the surface charge of the materials, at pH levels below 3.1 Effect of the nature of the support. The results for specific area (Sₐ), pore volume (Vₚore), pore diameter (Dₚore), acid strength, density of acidic sites and IEP for each of the materials in question are shown in Table 1.

### Table 1. Results for Sₐ, Vₚore, Dₚore, acid strength, density of acidic sites and IEP for each material.

<table>
<thead>
<tr>
<th>Support</th>
<th>Sₐ (m² g⁻¹)</th>
<th>Vₚore (cm³ g⁻¹)</th>
<th>Vₚore (cm³ g⁻¹)</th>
<th>Dₚore (nm)</th>
<th>Acid Str. (mV)</th>
<th>Density of acidic sites (meq g⁻¹)</th>
<th>IEP (pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon</td>
<td>690</td>
<td>0.03</td>
<td>0.30</td>
<td>3.5</td>
<td>-152.2</td>
<td>1.67</td>
<td>3.67</td>
</tr>
<tr>
<td>13X zeolite</td>
<td>186</td>
<td>0.02</td>
<td>0.08</td>
<td>36</td>
<td>-105.4</td>
<td>0.39</td>
<td>3.10</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>245</td>
<td>0.16</td>
<td>0.11</td>
<td>4.1</td>
<td>-40.6</td>
<td>0.86</td>
<td>2.60</td>
</tr>
<tr>
<td>Alumina</td>
<td>205</td>
<td>0.05</td>
<td>0.09</td>
<td>6.8</td>
<td>-51.8</td>
<td>1.62</td>
<td>8.14</td>
</tr>
<tr>
<td>Natural Zeolite</td>
<td>36</td>
<td>0.02</td>
<td>0.03</td>
<td>36</td>
<td>-40.3</td>
<td>0.68</td>
<td>3.05</td>
</tr>
<tr>
<td>Zirconia</td>
<td>258</td>
<td>0.35</td>
<td>0.12</td>
<td>3.7</td>
<td>176.5</td>
<td>2.63</td>
<td>5.65</td>
</tr>
</tbody>
</table>

Figure 1. Adsorption curves for all supports using a batch system (left) and the adsorption capacity for each support (right).
The materials that showed a trend towards microporosity (BET analysis), such as activated carbon, sepiolite and 13X zeolite, also showed the highest adsorption capacities in the same order (see right-hand graph in Figure Nº1). This can be explained by the dimensions of the 4-NP compound (0.48 nm x 0.62 nm). The low adsorption capacities shown by the alumina and the zirconia are mainly due to their trend towards mesoporous volumes, and in the case of natural zeolite, this is principally due to the low specific BET area.

3.2 Effect of adsorbent mass.

Table Nº2 presents a comparative analysis of the masses and adsorption capacities obtained in the batch system, considering the initial mass of the adsorbent and the saturation time as parameters.

<table>
<thead>
<tr>
<th>Support</th>
<th>Ads Mass (g)</th>
<th>Saturation time (min)</th>
<th>Ads Capacity (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon</td>
<td>0.5013</td>
<td>160</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>0.2508</td>
<td>280</td>
<td>7.67</td>
</tr>
<tr>
<td></td>
<td>0.2007</td>
<td>280</td>
<td>9.66</td>
</tr>
<tr>
<td></td>
<td>0.1460</td>
<td>320</td>
<td>12.42</td>
</tr>
</tbody>
</table>

The masses were studied in order to select the optimal mass of activated carbon for impregnation with Ni given that activated carbon adsorbs around 20 ppm when using ~500 mg. Therefore, there is no reason to use a transition metal with this amount of mass, since the initial sample concentration was 20 ppm.

The 4-NP adsorption capacity results onto activated carbon using different masses clearly show that at lower mass there is higher adsorption capacity in terms of mg g⁻¹, though this is obtained at higher saturation times. This deviates from expectations, since adsorption capacity should normalise per g of adsorbent and should therefore be independent of the adsorbent mass used. This unexpected result is mainly due to diffusion problems, such as shaking, meaning higher efficiency is obtained when lowering the diffusion resistance in batch systems, leading to a more homogenous distribution of the 4-NP solution with the decrease in mass increasing contact between the solution and the adsorbent.

Figure Nº2 shows the effect of mass on the adsorption curves for activated carbon, justifying the use of a lower mass when conducting the Ni study to analyse possible changes in adsorption capacity and saturation times using this material.

![Figure Nº2](image)

3.3 Effect of Ni content on the adsorption capacity in batch and continuous systems.

The characterisation results for acid strength, acidic site density, isoelectric point (IEP), point of zero charge (PZC) and coated fraction (X_M) for the best adsorbent and its respective metallic content and adsorption capacities are shown in Table Nº3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Acid Str. (mV)</th>
<th>Density of acidic sites (meq g⁻¹)</th>
<th>IEP (pH)</th>
<th>PZC (pH)</th>
<th>X_M</th>
<th>Adsorption Capacity (mg (g ads)⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Batch</td>
</tr>
<tr>
<td>AC</td>
<td>-152.2</td>
<td>1.65</td>
<td>3.67</td>
<td></td>
<td></td>
<td>12.42</td>
</tr>
<tr>
<td>Ni(2)/AC</td>
<td>-109.6</td>
<td>1.93</td>
<td>4.50</td>
<td>0.12</td>
<td></td>
<td>12.45</td>
</tr>
<tr>
<td>Ni(4)/AC</td>
<td>-104.6</td>
<td>2.17</td>
<td>5.76</td>
<td>0.31</td>
<td></td>
<td>12.48</td>
</tr>
<tr>
<td>Ni(6)/AC</td>
<td>-57.1</td>
<td>1.12</td>
<td>7.92</td>
<td>0.62</td>
<td></td>
<td>11.99</td>
</tr>
<tr>
<td>AC: Activated carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Ni(X)/AC: Activated carbon impregnated by X% of Ni (X= 2, 4,6%).

For all the activated carbon adsorbents containing different levels of Ni, an increase in acid strength from very weak sites to weak sites was seen with the increase in metal content. This is because Ni impregnation increase Lewis acidity, producing an increase in total acidity (Bronsted and Lewis), which is in turn identified by this method. It can also be deduced that the PZC values increase along with metal content, seen in the increase in coated fraction values, going from 12% of the surface covered in Ni on the activated carbon to 62% of the surface covered when the Ni content is raised to 6%. It was also seen that above this percentage, the Ni is homogeneously spread over the surface of the activated carbon. These results are in agreement with those for acidic site density, which increase along with the metal content and only decrease with Ni content of 6%, thus discarding the possibility that the metal is agglomerating on the surface. Therefore, the decrease can only be due to the metal covering the active sites.
Analysing the adsorption capacities in the batch system (Figure Nº3 left), it can be seen that the addition of metallic Ni did not increase adsorption capacity or reduce saturation times (~320 minutes) for any of the content levels, though this was observed in the continuous system (Figure Nº3 right). This is because in the latter system type diffusion phenomena were not observed due to the controlled sample flow of 1.5 mL min$^{-1}$, clearly improving contact time between the sample and the adsorbent.

Considering this, in a continuous system the activated carbon without impregnated metal has an adsorption capacity of 5.45 mg of 4-NP (g ads)$^{-1}$, which is very low in comparison with the value obtained with the activated carbon impregnated with 2% Ni (Figure Nº4), reaching 31.26 mg 4-NP (g ads)$^{-1}$. This increase can be attributed to the contribution of Ni to the adsorption through π-complexation. It can also be seen that with 4% metal content, the adsorption capacity does not increase from the value found with lower Ni content, which should have occurred based on all the previous characterization, since the Ni content was homogenously distributed over the activated carbon, as was verified by the increase in acid strength and the density of acidic sites. However, this leads to the conclusion that it is not necessary to apply higher Ni content levels when using a continuous system, since with the higher Ni content the saturation time and the negative surface charge of the adsorbents both decreased. The lower adsorption capacity for the 6% metal content level may be because the Ni blocks up active sites. This was also verified by the characterizations. With this level of metal content, the surface of the adsorbent has a positive charge and therefore the adsorption is no longer planar but axial along the 4-NP molecule. This is because the 4-NP compound concentrates higher electron density in the nitro group, and therefore adsorption cannot occur with this group, thus explaining the planar adsorption, due to the surface groups and the surface charge of the adsorbent. These results are in agreement with those presented by Kwon in a previous study$^{19}$.

4. CONCLUSIONS

The study of adsorption capacity showed that though all the materials used in the study presented some degree of adsorption, the activated carbon was the best adsorbent, as it possesses a higher specific BET area, lower acid strength, and a surface that is negatively charged under the condition of this study, all of which contributes to planar adsorption of the 4-NP compound. In addition, impregnation with Ni leads to increased adsorption capacity by π-complexation in the continuous system. The level of metal content also plays an important role in the adsorption capacity for the best adsorbent, with an optimal content level that depends on the $X_{M}$.

Finally, removal of 4-NP by adsorption is shown to be a good alternative for the removal of priority phenolic compounds.

5. ACKNOWLEDGEMENTS

This work has been financed under FONDECYT project 1140808. Donation of hydrous zirconium by MEL Chemicals is gratefully acknowledged and DI 125.760 Pontificia Universidad Católica de Valparaíso.

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