Removal of Phenoxyacetic Acid Based Herbicides by Crosslinked Poly(N-vinyl pyrrolidone)

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ABSTRACT

In this study, binding of herbicides such as p-chlorophenoxyacetic acid, 2,4-dichlorophenoxyacetic acid and the ammonium salt of 2,4-dichlorophenoxyacetic acid onto poly(N-vinyl pyrrolidone) and the adsorption of these herbicides to crosslinked poly(N-vinyl pyrrolidone) are investigated. It is shown that there are electrostatic interactions between anionic sites of the herbicides with cationic sites of poly(N-vinyl pyrrolidone). The adsorption of these herbicides to crosslinked poly(N-vinyl pyrrolidone) shows Type III adsorption isotherms. The values of percentage sorption of the low concentrations of herbicides are higher than those at the high concentrations of herbicides.

Key Words: crosslinked poly(N-vinyl pyrrolidone), herbicide, phenoxyacetic acid, adsorption, hydrogels

INTRODUCTION

Herbicides may enter the water ecosystem in different ways such as through direct application, movement of surface and underground water drainage or rain water, improper disposal of waste from the herbicide industry directly into water resources and soil, and the dumping of herbicide waste into water or soil [1].

When water resources become contaminated with herbicides, they not only become unsafe for human and animal consumption, their use for recreation may also be endangered. Water which has become contaminated with herbicide residues may be harmful to plants, thus having adverse effects on the food chain cycle, which is of vital importance to fish, birds, other animals and, eventually, human beings.

After herbicides have entered the body of an aquatic organism, they may remain there a long time without undergoing any changes, thus destroying the health of the animal or plant. Some of the substances thus produced may be even more toxic than the original contaminate.

As a general rule, when a herbicide enters a water ecosystem, it affects the flora and fauna. Aside from the purposes for which they are generally used, herbicides also have side effects on the organisms. If these side effects are not excessive, or if the organisms affected are unimportant, the situation is ignored. If, on the other hand, the effect on the plants or animals is rapid or destructive, certain problems are recognized to exist. In the long run however, the ecosystem may undergo
Removal of Phenoxyacetic Acid Based Herbicides

Phenoxyacetic acids have been commonly applied in agriculture as herbicides. Many chemical and biological investigations have been conducted on these herbicides. Under experimental conditions, the oral, dermal and cumulative toxicities of phenoxyacetic acids are moderate. Uptake of formulations is caused both by inhalation of the aerosol and by dermal contact. They are strong irritants of skin, eyes and upper respiratory passages. The suggestion has been made that their rapid excretion from the affected organism contributes to their lack of acute toxicity. They are distributed in nearly all organs but show relatively higher concentrations in the kidney where they are transported actively by renal tissue for elimination. Phenoxyacetic acids inhibit oxidative phosphorylation and oxygen uptake in the liver mitochondria.

Many peripheral adverse effects such as myotonia, disturbed cerebral electrical activity, degenerative changes in the spinal cord, liver and kidney and thyroid gland dysfunction have been reported in experimental animals. The herbicides have embryotoxic and teratogenic effect in several animal species.

Crosslinked hydrophilic polymers capable of imbibing large volumes of water (i.e., >20%) are termed hydrogels. Hydrogels are polymers that absorb water and swell with a significant proportion of water without any dissolution taking place. Hydrogels have widespread applications in the bioengineering, biomedicine, pharmaceutical, veterinary, food and agricultural industries and related fields. They are used as controlled release systems of drugs and some physiological body fluids, production of artificial organs, manufacture of contact lenses, and as an adsorbent for removal of certain unwanted agent in environmental application. They are used also, in the study of enzyme kinetics in bioengineering and as a carrier of water and pesticides in agriculture.

Poly(N-vinyl pyrrolidone), a water-soluble synthetic polymer shows a resemblance to serum albumin in many respect. For example just like serum albumin, this polymer forms complexes with small molecules such as iodine, azo dyes and amino acid. Molyneux and Vekavakanyanonda have reported studies on interactions of aromatic compounds with poly(N-vinyl pyrrolidone) in aqueous solution for binding of some organic substances to polymer chains.

In this study, binding of some herbicides such as p-chlorophenoxyacetic acid, 2,4-dichlorophenoxyacetic acid and the ammonium (amine) salt of 2,4-dichlorophenoxyacetic acid onto poly(N-vinyl pyrrolidone) and the adsorption of these herbicides to crosslinked poly(N-vinyl pyrrolidone) have been investigated.

EXPERIMENTAL

The polymer poly(N-vinyl pyrrolidone), PVP, (M<sub>a</sub> 10,000–700,000), and crosslinked poly(N-vinyl pyrrolidone), CPVP, were obtained from BASF (Germany). The herbicides p-chlorophenoxyacetic acid, CPA, 2,4-dichlorophenoxyacetic acid, 2,4-D, and the amine salt of 2,4-dichlorophenoxyacetic acid, 2,4-D amine, were purchased from Sigma (USA). The chemical formulas, molar masses and the wavelength maximum of these herbicides are shown in Table 1.

The herbicide 2,4-D amine salt (250 mg) was dissolved in distilled water and made up to 1 liter. The herbicides CPA (250 mg) and 2,4-D (250 mg) were each dissolved in 2% ethyl alcohol and they were made up to 1 liter.

For examination of the interaction of PVP with herbicides, 100 mgL<sup>-1</sup> of PVP solution was mixed with 250 gL<sup>-1</sup> of herbicide solutions in equal volume and these systems were allowed to equilibrate for 24 h at 25 °C in a water bath.

Spectrophotometric measurements of these solutions were carried out using a UV-VIS double beam spectrophotometer, Shimadzu A160, at ambient temperature. The solvent systems were chosen as a reference.

Experiments of Adsorption

The herbicides solutions were prepared in concentration range of 25–250 mgL<sup>-1</sup> in the suitable
Table 1. Chemical formulas, molar masses and $\lambda_{\text{max}}$ of used herbicides.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Molar mass (g mol$^{-1}$)</th>
<th>$\lambda_{\text{max}}$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Chlorophenoxyacetic acid (CPA)</td>
<td>![Chemical structure]</td>
<td>186.60</td>
<td>278.1</td>
</tr>
<tr>
<td>2,4-Dichlorophenoxyacetic acid (2,4-D)</td>
<td>![Chemical structure]</td>
<td>221.04</td>
<td>282.6</td>
</tr>
<tr>
<td>Amine salt of 2,4-dichlorophenoxyacetic acid (2,4-D amine)</td>
<td>![Chemical structure]</td>
<td>238.04</td>
<td>283.4</td>
</tr>
</tbody>
</table>

solvent systems. CPVP (100 mg) was transferred into 50 mL of the solutions of herbicides and it was allowed to equilibrate for 24 h at 25°C in water bath. Supernatants of these solutions were separated by decantation and centrifugation from CPVP. The absorbances of these solutions were measured by spectrophotometry at the wavelengths shown in Table 1. The solvent systems were chosen as a reference. The equilibrium concentrations of solutions were calculated by using the calibration curves.

RESULTS AND DISCUSSION

Binding of Herbicides onto PVP
The absorption spectra of herbicides and herbicides-PVP are shown in:
Figure 1 for CPA and CPA-PVP, in Figure 2 for 2,4-D and 2,4-D-PVP, and in Figure 3 for 2,4-D amine and 2,4-D amine-PVP.

The absorption spectra of herbicides have $\lambda_{\text{max}}$, and when polymer solutions are added, the wavelength of maximum absorbance is constant with increase in absorbance.

It is evident from the structural formulas that the herbicides have a number of groups capable at forming electrostatic interaction like, hydrogen bonds, ion-dipole, dipole-dipole and hydrophobic interactions.

To explain the binding between PVP and the herbicides, let us consider the nature of PVP. Although at pH = 7, PVP is a neutral polymer, the tertiary nitrogen in the pyrrolidone ring acquires a positive charge as shown in Scheme 1 [8,11].

A and B type units are probably binding sites. Since the herbicides have phenoxyacetate groups (PA$^-$) in solution, there should be electrostatic interaction between PA$^-$ and PVP.

The binding of one PA$^-$ ion to B unit is shown Scheme 2.

Furthermore, if PA$^-$ ions bind to A type
units, the concentration of binding sites constituted by A type is very high, and the bound PA\(^{-}\) ions may come closer to each other. Hence, there would be anionic repulsions between the bound PA\(^{-}\) ions.

Phenyl rings of herbicides may be expected to show hydrophobic bonding to the nonpolar portions of polymer. But these hydrophobic groups are surrounded by strong hydrophilic groups and so the contribution of hydrophobic bonding can be expected only to a limited extent.

**Adsorption**

In the second stage of experiments, adsorptions of herbicides within CP hydrogels were investigated.

The graphs of the herbicides mass per unit polymer mass (q\(e\), mg herbicide/g polymer) against equilibrium concentrations of herbicides (C, mg herbicide/L) are shown in Figure 4 for CPA, in Figure 5 for 2,4-D and in Figure 6 for 2,4-D amine.

**Scheme I.** Kato-enol tautomersism in pyrrolidone ring [8].

Scheme II. Binding of the herbicides based phenoxyacetic acid onto PVP.

Figures 4, 5 and 6 show that adsorption of herbicides within CPVP hydrogels corresponds to isotherms of Type III [12-15].

In the adsorption experiments, Type III adsorptions were found. Type III isotherms are characterized by convexity toward the concentration axis, and is characteristic of weak solute/solid interactions. The Type III isotherm is being given by a nonporous and mesoporous materials.

The weakness of the adsorbent-adsorbate forces will cause the uptake at low concentrations to be small, but once a molecule has become adsorbed, the adsorbate-adsorbate forces will promote the adsorption of further molecules into a cooperative process so that the isotherm will become convex towards the concentration axis.

Type III isotherms may originate through the adsorption of either nonpolar molecules or polar molecules, always provided that the adsorbent-
adsorbate force is relatively weak.

A polar adsorbate of particular interest in this context is water, because dispersion contribution to its overall interaction energy is unusually small compared with the polar contribution. Not surprisingly, water provided many examples of Type III isotherm.

The most straightforward case is given by organic high polymers (e.g., polytetrafluoroethylene, polyethylene, polymethylmethacrylate or polyacrylonitrile) which give rise to a well defined Type III isotherm with water, as a consequence of the weak dispersion interactions. In some cases the isotherms have been measured at several temperatures so that \( q_H \) (isosteric enthalpy of adsorption) could be calculated. The value is somewhat below the molar enthalpy of crystallization (\( q_c \)) and rises to \( q_H \) as adsorption proceeds. So, \( \Delta H \), (net heat of adsorption) is zero or negative.

The strength of dispersion interaction of solid with a solute molecule is determined not only by the chemical composition of the surface of solid, but also by the surface density of force centres. If therefore, this surface density can be sufficiently reduced by the pre-adsorption of a suitable substance, the isotherm may be converted from Type II to Type III. Once, the hydrogel is covered with a layer of adsorbed water, however, the adsorbent/adsorbate interaction would be reduced to the weak dispersion energy of water with herbicides, so that a Type III isotherm should result. In a system which gives rise to a Type III isotherm, however, the multilayer is being built up on some parts of the surface while the monolayer is still incomplete on others [13].

On the other hand, some authors have demonstrated that adsorption of 2,4-D and some derivatives of anionic phenoxacyclic acids to certain clay minerals has been negative [16].

The percentage sorption of herbicides based phenoxacyclic acid is presented in Table 2.

Table 2 shows that the values of percentage sorption of 2,4-D in all concentrations are about constant while these values of CPA and 2,4-D amine in low concentrations are relatively higher than in high concentrations of herbicides.

CONCLUSION

The herbicides based on phenoxacyclic acid such as p-chlorophenoxyacetic acid, 2,4-dichlorophenoxyacetic acid and amine salt of 2,4-dichlorophenoxyacetic acid can bind onto poly(N-vinyl pyrrolidone) by electrostatic interactions.

The adsorptions of these herbicides to crosslinked poly(N-vinyl pyrrolidone) exhibit Type III adsorption isotherms. The values of percentages sorption of the low concentrations of herbicides were higher than the high concentrations of herbicides.

As a result, it was shown that crosslinked poly(N-vinyl pyrrolidone) hydrogels could be used as a sorbent for water pollutants such as herbicides and so immobilize some organic contaminants within the hydrogels, to facilitate cleaning of waste water which is an important problem facing environmental chemists.
Table 2. Sorption percentage of herbicides.

<table>
<thead>
<tr>
<th>$C_{\text{initial}}$ (mg L$^{-1}$)</th>
<th>CPA</th>
<th>2,4-D</th>
<th>2,4-D Amine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{\text{equilibrium}}$ (mg L$^{-1}$)</td>
<td>Sorption (%)</td>
<td>$C_{\text{equilibrium}}$ (mg L$^{-1}$)</td>
</tr>
<tr>
<td>20</td>
<td>9.2</td>
<td>54</td>
<td>16.9</td>
</tr>
<tr>
<td>30</td>
<td>18.3</td>
<td>39</td>
<td>26.2</td>
</tr>
<tr>
<td>40</td>
<td>28.0</td>
<td>30</td>
<td>34.2</td>
</tr>
<tr>
<td>50</td>
<td>37.3</td>
<td>26</td>
<td>43.6</td>
</tr>
<tr>
<td>100</td>
<td>80.7</td>
<td>19</td>
<td>85.3</td>
</tr>
<tr>
<td>160</td>
<td>135.9</td>
<td>15</td>
<td>134.8</td>
</tr>
<tr>
<td>200</td>
<td>171.4</td>
<td>14</td>
<td>168.2</td>
</tr>
<tr>
<td>250</td>
<td>217.0</td>
<td>13</td>
<td>207.2</td>
</tr>
</tbody>
</table>

REFERENCES