



N-methylcarbamate pesticides and their phenolic degradation products: hydrolytic decay, sequestration and metal complexation studies

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ABSTRACT

We report on the rates of decomposition of a group of *N*-methylcarbamate (NMC) pesticides (carbaryl, carbofuran and propoxur) under pre-determined tropical field conditions. Rates of decomposition for three NMCs were determined at pH 7.08 and $T = 20^\circ\text{C}$ and pH 7.70 and $T = 33^\circ\text{C}$ respectively, as follows: carbaryl (78 days and 69 days); carbofuran (143 days and 83 days) and propoxur (116 days and 79 days). Investigation on methods for removal of NMCs and their phenolic decomposition products shows that activated charcoal outperforms zeolite, alumina, diatomaceous earth, cellulose and montmorillonite clay in the removal of both NMCs and phenols from aqueous solution. Furthermore, metal complexation studies on the NMCs and phenols showed that Fe (III) forms a complex with isopropoxyphenol (IPP) within which the Fe:IPP ratio is 1:3, indicative of the formation of a metal chelate complex with the formula $\text{Fe}(\text{IPP})_3$.

KEYWORDS

N-methylcarbamate pesticides; tropical aquatic systems; alkaline hydrolysis; metal chelates; sequestration

Introduction

The *N*-methylcarbamates (NMCs) are an important class of organic pesticides that have been used globally for crop protection as insecticides since 1958.^[1] The compounds are acetylcholinesterase inhibitors and are active against organophosphate-resistant pests. Importantly, NMCs are chlorine-free and non-ozone-depleting, and are thus favored for their relatively low atmospheric contamination.^[2] Despite these benefits and with increased application over the past six decades, NMCs pose risks to human and ecosystem health due to contamination of ground and surface water. NMCs are deposited into aquatic systems through leaching from soils, surface runoff or deposition from aerial mist.^[3–7] The compounds degrade in water under alkaline conditions to form toxic phenols via an E_{1cb} mechanism (Scheme 1).^[8,9]

Research in our group has focused on the aquatic chemical fate of NMCs under tropical conditions because of the importance of the tropics in global agricultural production.^[10] Most studies on hydrolytic decay of NMCs are reported for temperate zones, and relatively few studies conducted under tropical conditions have been published.^[11–13] Yet, tropical conditions significantly differ from those in temperate zones and factors such as sunlight, temperature, and frequency of pesticide application may alter rates and mechanisms of NMC decomposition. Therefore, investigating the chemical behavior of NMCs in tropical environments is needed, and may help inform recommendations for

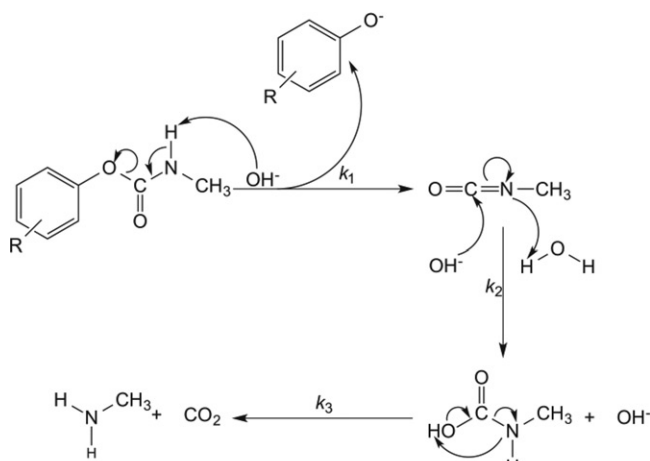
application protocols and remediation methods in tropical areas.^[14–16]

We recently reported on relative rates of alkaline hydrolysis for three NMC pesticides: carbaryl, carbofuran and propoxur.^[17] Our results showed that rates of NMC degradation largely depend on the molecular electronic properties of the compounds, and that more electron-deficient NMCs degrade faster. Herein, we report on NMC degradation rates under pre-determined tropical conditions, as well as on the investigation of possible methods for sequestration of both the NMCs and their phenol degradation products using a series of metal systems and adsorption materials.

Materials and methods

General considerations

Unless otherwise specified, reagents were purchased from commercial suppliers and used without further purification. All glassware was pre-washed with 1 M sulfuric acid, and thoroughly rinsed with deionized water and allowed to dry. All pH measurements were conducted using a Fisher Scientific AB15 pH meter. UV-vis spectroscopy was conducted on an Agilent Technologies Cary 60 UV-Vis spectrometer using UV-grade methacrylate cuvettes. Buffers used were potassium monobasic solutions at pH 7 and 10. Activated charcoal used was Darco® Activated G-60 grade purchased from Fisher Scientific.



Scheme 1

Spectroscopic characterization of carbamates and phenols

Samples of each NMC or phenol [carbaryl (5.0 mg, 25 μmol); carbofuran (5.5 mg, 25 μmol); propoxur (5.0 mg, 25 μmol); 2,3-dihydro-2,2-dimethyl-7-benzofuranol (4.0 mg, 25 μmol); 2-isopropoxyphenol (3.6 mg, 25 μmol); 1-naphthol (3.8 mg, 25 μmol)] were transferred into 25 mL volumetric flasks and fully dissolved in 2 mL of methanol. The volumetric flask was then filled to the mark with deionized water to obtain 1×10^{-4} M solutions. An automatic pipette was used to transfer 2 mL of the NMC or phenol solution into 4.5 mL capacity cuvettes for analysis by UV-visible spectroscopy.

NMC degradation studies under pre-determined conditions

Into a 500 mL beaker was measured 450 mL of stock pH 7.00 phosphate buffer and the pH adjusted to 7.08 by addition of 1 M NaOH. This procedure was repeated to prepare a 450 mL buffer solution of pH 7.70. Both solutions were left to equilibrate overnight and, as necessary, the pH was re-adjusted using NaOH prior to use. Into three 50 mL volumetric flasks were weighed separately each NMC [carbaryl (1.0 mg, 5 μmol); carbofuran (1.1 mg, 5 μmol); propoxur (1.0 mg, 5 μmol)]. The solids were dissolved in pH 7.08 buffer, and the same buffer solution was added to the mark to make up 1×10^{-4} M solutions of each NMC at pH 7.08. This procedure was repeated with pH 7.70 buffer. One 20 mL sample was drawn from each of the six flasks and transferred to clean and dry scintillation vials, then tightly capped and wrapped in parafilm. Three vials containing each NMC at pH 7.08 were placed in a water bath maintained at 20 $^{\circ}\text{C}$, and another three vials at pH 7.70 were placed in a water bath at 33 $^{\circ}\text{C}$. Each of the six samples was analyzed by UV-Vis spectroscopy every 2–3 days by transferring 2 mL of the solution into 4.5 mL cuvettes and measuring the λ_{max} values of the parent NMCs.

Metal-NMC/phenol complexation studies

Stock solutions (0.1 M) of the metals under analysis [Cu(NO₃)₂, Zn(NO₃)₂, Fe₂(NO₃)₃, Al(NO₃)₃, Mn(NO₃)₂] were prepared in 250 mL volumetric flasks using a 1% methanol aqueous solution. NMC or phenol stock solutions (0.1 M) in methanol were prepared in 25 mL volumetric flasks. Metal and ligand (NMC or phenol) mixtures were first prepared in a 1:1 metal:ligand ratio. UV-vis spectroscopy was used to monitor disappearance of metal and ligand peaks as well as to probe for the appearance of new peaks. For a metal:ligand ratio of 1:1, 20 μL of ligand stock solution and 20 μL metal stock solution were mixed in a 4.5 mL capacity cuvette and diluted to the 2 mL mark with de-ionized water and gently swirled to yield a solution with metal and ligand concentrations of 1×10^{-3} M. Only Fe (III) and isopropoxyphenol (IPP) showed a detectable interaction and further analysis was conducted for this pair. For a 1:2, 1:3 and 1:4 Fe (III) to IPP ratio, 40 μL , 60 μL and 80 μL of IPP stock solution, respectively, were used while the volume of Fe(III) stock solution was kept constant at 20 μL .

Adsorption studies

Into 50 mL volumetric flasks were transferred NMC or phenol dissolved in 2 mL of methanol [carbaryl (0.010 g, 0.050 mmol); carbofuran (0.011 g, 0.05 mmol); propoxur (0.010 g, 0.05 mmol) 2,3-dihydro-2,2-dimethyl-7-benzofuranol (0.008 g, 0.05 mmol); 2-isopropoxyphenol (0.0072 g, 0.05 mmol); 1-naphthol (0.0076 g, 0.05 mmol)] and the resultant solution diluted to the mark with deionized water to make up 1×10^{-3} M stock solutions. For the adsorption study for each NMC/phenol, activated charcoal was weighed out in seven batches: 10, 20, 30, 40, 50, 60 and 70 mg. Each batch was transferred into a separate glass pipette containing a small cotton plug at the base. An automatic pipet was used to deliver 5 mL of NMC or phenol stock solution onto the adsorbent. The eluent was collected in 20 mL glass scintillation vials and analyzed by UV-vis spectroscopy. This procedure was repeated for the other adsorbing materials (zeolite, alumina, diatomaceous earth, cellulose and montmorillonite clay). If a decrease in NMC/phenol concentration in the eluent was detected by UV-vis spectroscopy, then a fresh column was similarly prepared using the same mass of adsorbent, and the analyte added to the column in 2 mL increments. The eluent was analyzed by UV-vis spectroscopy until breakthrough from the column was observed.

Results and discussion

Our group recently reported on the kinetics of alkaline (pH 9) hydrolysis of the NMCs carbaryl, carbofuran and propoxur.^[17] Carbaryl (Sevin) is a broad spectrum pesticide^[18] that is moderately toxic to aquatic organisms and highly toxic to many non-target insects, such as honeybees.^[19] The compound has the potential to migrate to groundwater ($K_{\text{ow}}=71$).^[18,19] Propoxur (Baygon) possesses tumorigenic activity in experimental animals,^[20] and is moderately

soluble in water ($K_{ow}=33.11$).^[21] Carbofuran (Furadan), an insecticide and nematocide, is classified as a restricted-use pesticide in temperate zones.^[22,23] It is highly toxic to mammals, has been shown to be mutagenic after metabolic activation,^[24,25] and is partially soluble in water ($K_{ow}=209$).^[22]

Research in our group showed that all three NMC compounds decay to yield phenol products via first-order kinetics in an E_{1cb} mechanism (Scheme 1). The half-life values decreased in the order: carbofuran ($t_{1/2}=57.75$ h) > propoxur ($t_{1/2}=38.5$ h) > carbaryl ($t_{1/2}=19.25$ h) translating into increased decomposition rates in the order: carbaryl > propoxur > carbofuran. The rates of decomposition reflect the acidity of the *N*-bound proton, and are governed by the electron density of the aromatic ring. Thus, the longest-lived NMC, carbofuran, bore the most electron-rich aromatic ring with two electron-donating substituents, and therefore possessed the least acidic proton. Conversely, the most electron poor NMC, carbaryl, degraded the fastest. We have extended this study to explore methods for sequestration of the three NMCs and their phenol hydrolysis products because both NMCs (themselves persistent under neutral pH) and their phenol degradation products are toxic toward organisms. The structures of the NMCs and their corresponding phenol

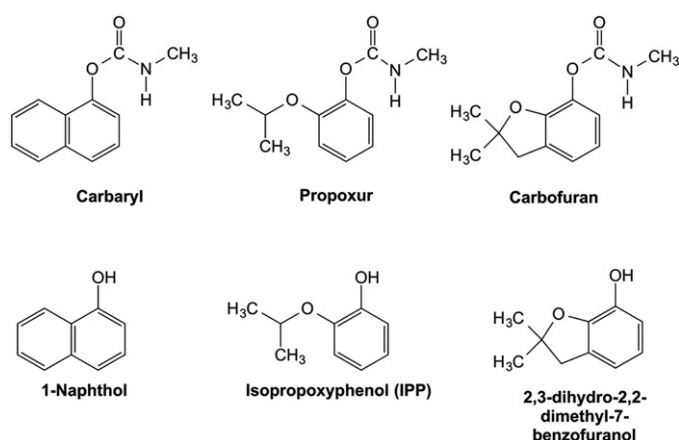


Figure 1. NMCs and phenols used in this study.

degradation products are presented in Figure 1, and the UV-vis spectra for the three NMCs and their corresponding phenol products are presented in Figure 2.

Water quality studies were conducted by our group on the Ruiru River (1.1457° S, 36.9649° E, 1800 m above sea level) located in the central highlands of Kenya, and on the estuary of the Guayas River (1.9575° S, 79.9193° W, 6 m above sea level) in Ecuador.^[17,26] Both field sites lie within commercial and subsistence agriculture areas near important rivers, and are representative of heavily cultivated and productive tropical zones where pesticide use is prevalent. The average values of pH and temperature of the Ruiru River, Kenya were 7.08 and 20 °C, and the average values of the Guayas River were 7.70 and 33 °C, respectively.^[17,26]

Kinetic studies were conducted on the three NMCs under the predetermined conditions. Solutions of each NMC (1.0×10^{-4} M) were prepared at pH 7.08 and 7.70 in the appropriate buffer and stored at 20 °C and 33 °C respectively. Each NMC sample was analyzed under the two sets of conditions periodically by measuring the λ_{max} values of the NMC. The linear first-order plots are presented in Figures 3 and 4. Half-life values were determined from the rate constants obtained from the first-order plots, and are shown in Table 1.

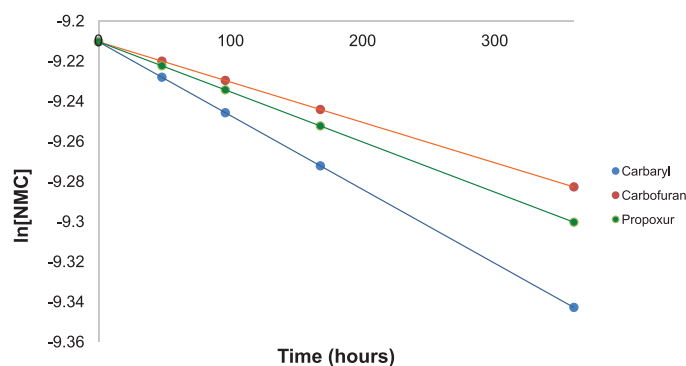


Figure 3. Linear first-order decay plot for NMCs at pH 7.08 and $T = 20$ °C representative of conditions in the Ruiru River, Kenya.

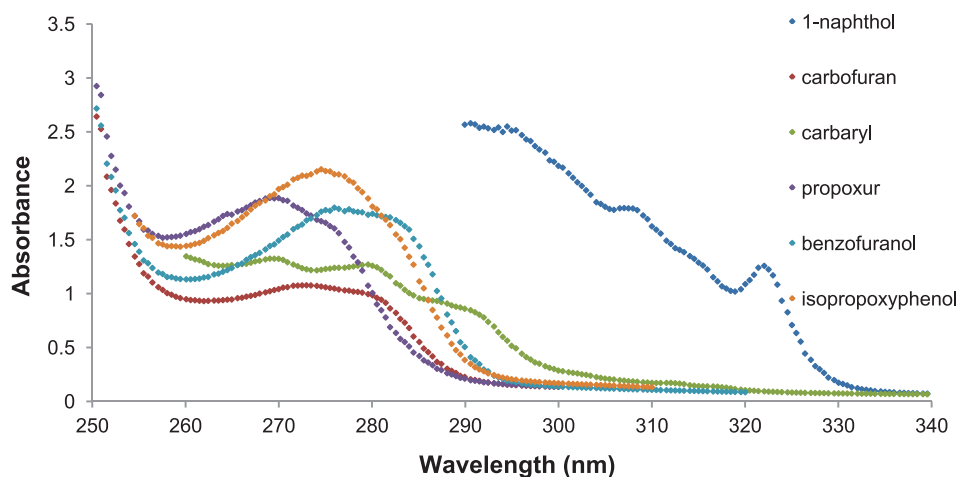


Figure 2. UV-vis spectra of the carbamates: carbofuran, carbaryl and propoxur and their respective phenols. The λ_{max} values monitored were carbofuran, ~275 nm; propoxur, 271 nm; carbaryl, 270 nm; 2,3-dihydro-2,2-dimethyl-7-benzofuranol, 278 nm; 2-isopropoxyphenol, 276 nm; 1-naphthol, 322 nm.

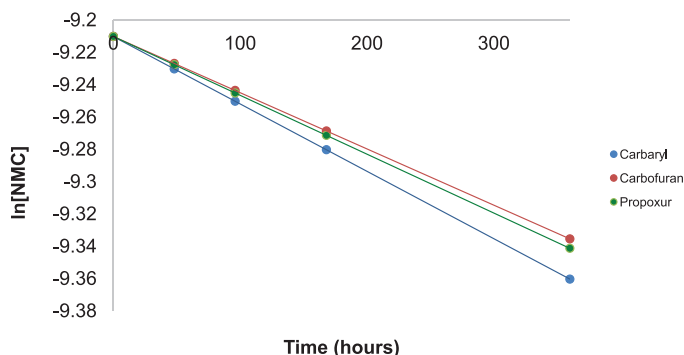


Figure 4. Linear first-order decay plot for NMCs at pH 7.70 and $T = 33\text{ }^{\circ}\text{C}$ representative of conditions in the Guayas River, Ecuador.

Table 1. Half-life values of *N*-methyl carbamates under varying pH and temperature (T , $^{\circ}\text{C}$) conditions.

pH and T , $^{\circ}\text{C}$	Carbaryl	Carbofuran	Propoxur
7.08, $20\text{ }^{\circ}\text{C}$	78 dys	143 dys	116 dys
7.70, $33\text{ }^{\circ}\text{C}$	69 dys	83 dys	79 dys

Our results showed that half-life values of the NMCs decreased with increase temperature and pH. The $t_{1/2}$ value decreased by 12% for carbaryl, 43% for carbofuran and 32% for propoxur. This result is expected as reaction rates generally increase with temperature and alkaline hydrolytic decay is accelerated at higher pH. As with previous findings, the trend in half-life values decreased in the order $t_{1/2}$ carbofuran (143 days and 83 days) $>$ $t_{1/2}$ propoxur (116 days and 79 days) $>$ $t_{1/2}$ carbaryl (78 days and 69 days) at pH 7.08/ $20\text{ }^{\circ}\text{C}$ and 7.70/ $33\text{ }^{\circ}\text{C}$ respectively, reflecting an increase in the acidity of the *N*-bound proton. This trend has been observed in other studies where at pH 8.0 and $25\text{ }^{\circ}\text{C}$ $t_{1/2}$ carbofuran (50 days) $>$ $t_{1/2}$ carbaryl (10 days).^[27]

Metal-pesticide complexation has been investigated by others as a possible method for either decomposing bound pesticides or for their capture. For example, a study by Strathmann and Stone on the carbamate pesticides oxamyl and methomyl found that these two compounds bind Fe (II) and Cu (I), and are reduced by the metals under anaerobic conditions.^[28] In another study, Cu (II) ions were proposed to complex the carbamate aldicarb through either chelation of the metal ion to an imine and carbamate nitrogen atom, or through the imine nitrogen and carbonyl oxygen.^[29] Cu (II) has also been found to bind the imidazolinone herbicide imazapyr to form a square-based pyramidal structure with two imidazolinone molecules chelating the metal and an aqua ligand occupying the apex of the pyramid.^[30]

Our group is also interested in metal sequestration of NMCs and their phenolic decomposition products. As a first step in exploring possible sequestration protocols, we surveyed a group of metals (selected for their relatively low toxicity and high earth abundance) for binding to the NMCs and their corresponding phenols. All metal cations surveyed were obtained from the respective nitrate salts to ensure consistency in anions added to the samples, as well as to guarantee complete solubility of the added salts. UV-vis spectroscopy was used to probe for binding by Cu (II), Zn (II), Fe (III), Al (III) and Mn (II) via monitoring changes in

Table 2. Reactions between select metal ions and NMCs/phenols.

NMCs/phenols	Metal ions screened for complexation				
	Cu(II)	Zn (II)	Fe (III)	Al (III)	Mn (II)
Carbofuran	–	–	–	–	–
Propoxur	–	–	–	–	–
Carbaryl	–	–	–	–	–
1-Naphthol	–	–	–	–	–
2-Isopropoxyphenol	–	–	x	–	–
Benzofuranol ^a	–	–	–	–	–

a2,3-Dihydro-2,2-dimethyl-7-benzofuranol abbreviated as benzofuranol.

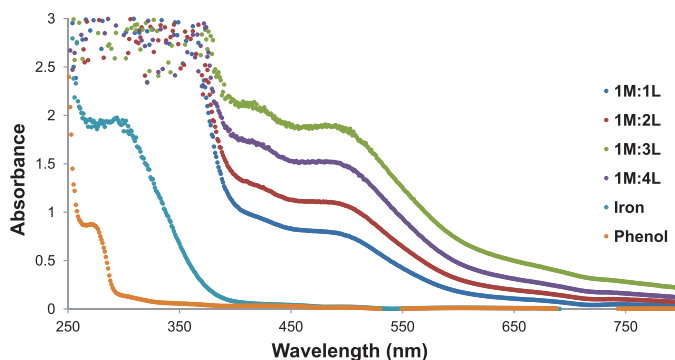


Figure 5. UV spectral analysis of binding between Fe (III) (M) and isopropoxyphenol (L) showing the absorbance of the 1:4 mixture (purple) as lower than that of the 1:3 (green) mixture.

the λ_{max} values of the NMC and phenols. Solutions of the metals (1×10^{-3} M) in methanol/water were added to methanol solutions of the NMCs (1×10^{-3} M) and phenols (1×10^{-3} M) and the λ_{max} values for NMCs and phenols monitored. Under our experimental conditions, dissolution of NMCs and phenols in small quantities of methanol was required for homogeneity of solutions.

The results of the coordination studies are presented in Table 2. The data revealed that of the possible metals pairings, only Fe(III) and isopropoxyphenol (IPP) showed a change in the UV-vis spectrum. Upon addition of an equimolar amount of the 1×10^{-3} M solution of Fe(III), the 1×10^{-3} M IPP solution changed from clear and colorless to bright orange-red. The UV-vis spectrum revealed two new peaks at 420 nm and 485 nm that were distinct from free Fe (III) or free IPP (Fig. 5). We investigated the change in these absorbances at Fe (III):IPP ratios of 1:2, 1:3 and 1:4. For all three ratios, the only peaks observed were again those at 420 and 485 nm indicating that the same complex is likely generated with Fe (III):IPP ratios of 1:2, 1:3 and 1:4. Importantly, we observed an increase in the values of these absorbances with Fe:IPP ratios of 1:2 and 1:3. Conversely, a decrease in these absorbance values was observed at Fe:IPP = 1:4. Our data are consistent with the formation of a Fe(IPP)_3 complex within which the Fe (III):IPP ratio is 1:3. The decrease in peaks when the Fe (III):IPP ratio was increased to 1:4 can be attributed to the dilution of the Fe(IPP)_3 complex by addition of excess IPP.

Octahedral complexes of Fe (III) with bidentate oxygen containing ligands are well known and structurally characterized.^[31,32] For example, the crystal structure of *tris*(catecholate) iron (III) reveals that the compound adopts a pseudo-octahedral geometry.^[33] We postulate a similar

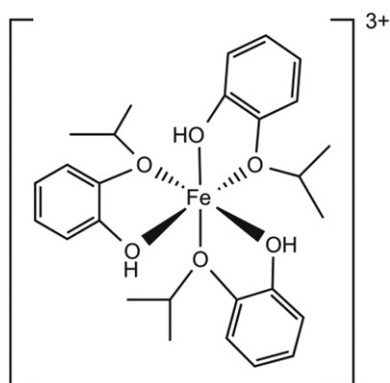


Figure 6. Proposed structure of the $\text{Fe}(\text{IPP})_3$ complex.

octahedral structure for the $\text{Fe}(\text{IPP})_3$ complex within which the IPP ligand chelates the Fe (III) via both the phenolic and the ether oxygen atoms (Fig. 6). We rationalize that IPP is more favored for coordination to Fe (III) than the other phenols because, unlike 1-naphthol, it is capable of chelation. Furthermore, IPP is less sterically restricted than benzofuranol, another possible chelating ligand. Future studies will focus on confirming the electronic and steric properties of the ligands as well as characterizing the $\text{Fe}(\text{IPP})_3$ by X-ray crystallography.

Remediation methods such as ozonation, photodegradation, use of nanofiltration membranes, coagulation and adsorption onto activated carbon have been assessed and used for pesticide removal from aqueous solutions.^[34] However, many of these techniques are either impractical or cost-prohibitive for treating polluted water, especially in lower- and middle-income countries where our field work is conducted. Thus, there is a need to explore affordable, readily available materials for the treatment of contaminated water.

More inexpensive methods include the use of activated carbon, generated by treating carbon with oxygen resulting in a highly porous material widely used for purification of wastewater due to its high surface area, vast network of pores and surface reactivity.^[34] Synthetic zeolite powder is also a promising inexpensive adsorbent and is cheaper than activated carbon. Readily available alumina has been proven to be an effective adsorbent in the removal of heavy metals such as iron, chromium, lead, cadmium, copper and zinc, and cellulose in the form of cotton has been modified to absorb pesticides.^[35,36] Diatomaceous earth can remove the herbicide paraquat from aqueous solution,^[37] and montmorillonite clay has a high affinity and sorption capacity for some carbamate pesticides.^[38]

To investigate the sequestration capabilities of readily available adsorbents, the following materials were assayed for potential adsorption of NMC/phenol: activated charcoal, zeolite, alumina, diatomaceous earth, cellulose and montmorillonite clay. The minimum mass of activated charcoal (loading capacity) required to reduce the concentration 1×10^{-3} M NMC/phenol eluent from a glass column was first determined. The minimum mass of adsorbent required for breakthrough from the column at the loading capacity

Table 3. Loading requirements (mg activated charcoal) and adsorption capacities (mol NMC/phenol per mg activated charcoal) of activated charcoal.

NMC/phenol	Loading requirement (mg activated charcoal)	Adsorption capacity (mol NMC or phenol/mg activated charcoal)
Carbofuran	50	2.60×10^{-7}
Propoxur	30	2.70×10^{-7}
Carbaryl	60	1.33×10^{-7}
1-Naphthol	40	6.25×10^{-7}
2-Isopropoxyphenol	50	$>4.80 \times 10^{-7}$
Benzofuranol ^a	50	1.20×10^{-7}

a2,3-Dihydro-2,2-dimethyl-7-benzofuranol abbreviated as benzofuranol.

was then determined and used to calculate the adsorption capacity of the adsorbent (Table 3).

Of the six materials, only activated charcoal showed any activity with the NMCs and phenols. The adsorption capacities of NMCs on activated charcoal are presented in Table 3 and were determined to increase in the order: 1.33×10^{-7} mol carbaryl/mg activated charcoal $< 2.6 \times 10^{-7}$ mol carbofuran/mg activated charcoal $< 2.7 \times 10^{-7}$ mol propoxur/mg activated charcoal. The adsorption capacities for phenols increased in the order: 1.2×10^{-7} mol benzofuranol/mg activated charcoal $< 4.8 \times 10^{-7}$ mol isopropoxyphenol/mg activated charcoal $< 6.25 \times 10^{-7}$ mol 1-naphthol/mg activated charcoal.

Other groups have reported the use of activated charcoal in fixed adsorption columns for removal of aqueous phenols.^[39,40] In our easy-to-assemble fixed columns, structurally similar carbofuran and propoxur had similar adsorption capacities (2.60×10^{-7} mol/mg activated charcoal and 2.70×10^{-7} mol/mg activated charcoal, respectively). This indicated that structural and electronic properties may be predictive of adsorption by activated charcoal. In addition, carbaryl had the lowest adsorption capacity (1.33×10^{-7} mol/mg activated charcoal) of all the compounds assayed, and is likely the most intractable NMC. However, since previous kinetics studies on NMCs showed that carbaryl was hydrolyzed most rapidly, targeting sequestration of 1-naphthol (6.25×10^{-7} mol/mg activated charcoal) may be a better approach than attempts to remove the parent NMC.

Conclusion

We have reported on kinetic studies of the hydrolysis for three NMCs (carbaryl, carbofuran and propoxur), and on cost-effective remediation techniques for the removal of NMCs and their phenolic degradation products. The rates of NMC alkaline hydrolytic decay are consistent with electronic properties of the compounds and reveal that the longest-lived NMC, carbofuran, with a half-life of 83–143 days is also the most toxic. Thus, developing sequestration protocols for this NMC over the other compounds will be prioritized. Metal complexation studies revealed likely chelation of isopropoxyphenol (IPP) to Fe (III) to form an octahedral complex, $\text{Fe}(\text{IPP})_3$, thus making Fe (III) a promising sequestration agent for isopropoxyphenol. Our future work will focus on elucidation of the structure of the complex using X-ray diffraction, as well as the exploration of iron-doped

materials as possible sequestration agents for IPP. Furthermore, the visible color change observed in the formation of Fe(IPP)₃ is a promising built-in indicator of Fe-IPP binding. This possible detection mode will be further investigated. The performance of different solid adsorption materials (activated charcoal, zeolite, alumina, diatomaceous earth, cellulose and montmorillonite clay) to remove NMCs and their phenols showed that the inexpensive activated charcoal outperformed all other materials. Compounds with similar electronic properties appeared to display similar adsorption to activated charcoal. Future studies will focus on scaling this technique to develop targeted and cost-effective protocols for NMC and phenol removal from aqueous solutions.

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