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THIN FILMS AND COATINGS FOR ABSORPTIVE REMOVAL OF ANTIMICROBIALS, ANTIBIOTICS, AND OTHER PHARMACEUTICALS

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Abstract

The US EPA regards “emerging pollutants” as new unregulated chemicals which impact the environment and human health. Many chemicals such as analgesics, anti-inflammatories, beta-blockers, antibiotics, and antimicrobials are not being effectively removed in water treatment. Triclosan, a ubiquitous antimicrobial that is widely used in antibacterial products and in clinical situations is of growing concern as it has been found to degrade human health with potentially devastating promotion of cancer and autoimmune diseases. In this study we are exploring the removal of triclosan using molecular modeling and absorptive/adsorption experiments on modified clays monitored by Tandem Liquid Chromatography – Mass Spectrometry (LCMS). Thin films and coatings offer the opportunity to build complex structures, save materials and engineer hybrid systems. Manual coating (brushing, dipping and air spraying) as well as 3D printing has been explored.

Introduction

Since the large increases in the use of polychlorinated aromatic antimicrobials there is increasing evidence of these chemicals negatively impacting the environment[1] and the immune systems of human populations via immune and inflammatory dysfunction. [2]. This supports not only questioning the effect of triclosan on the human immune system but to find more efficient ways of removing triclosan at the source and from the biota.

Triclosan is classified as a broad-spectrum antimicrobial agent as it is effective against a wide range of microbes including: bacteria, parasites, fungi, and virus [3].Triclosan is effective at low concentrations against bacteria. It has been used in soaps, mouthwashes, face washes, deodorants, toothpastes, and many other household products. In 2012 it was estimated that approximately 1500 t of TCS was being produced annually worldwide with up to up to 96% being washed down drains and into the sewerage systems [4]. It is becoming the main example of emerging new environmental pollutants. Consequently, describing the mechanisms, whereby triclosan produces its toxicity, is necessary for the full evaluation of the ecological damage that might result from triclosan in the biota. Understanding its structure–activity relationships [5] and molecular dynamics [6] in relation to the mechanisms can have broad consequences in amelioration of its effects as well as finding biomedical uses. It is a chlorinated aromatic compound, polychlorophenoxy phenol, that has halogen, ether and phenol functional groups. The toxic effects of a phenol depends on many molecular structural factors. Two obvious ones are the pKa (i.e. the phenols dissociation constant) and log P (where P is the octanol-water partition coefficient). The larger the value of pKa, the smaller the extent of dissociation at any given pH (see Henderson–Hasselbalch equation)—that is, the weaker the acid. Here chlorine is expected to increase hydrophobicity and the value of logP and increase membrane penetrability whereas, if it decreases the pKa value (becomes more acidic), membrane penetration is decreased but if it increases pKa the opposite may occur depending on its surrounding pH. Its molecular structure is shown in Figure 1.

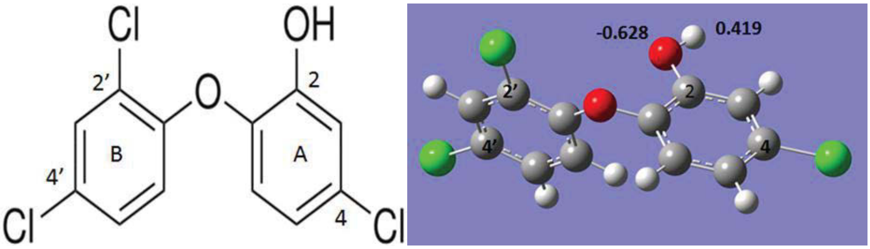

Figure 1 Triclosan from Avogadro and Gaussian (level of theory: B3LYP/6-31G(d)). The fractional numbers indicate the Mullikan charge of phenolic oxygen and hydrogen atom.

Another factor that determines a phenol's toxicity is its reactivity with a cell's biomolecules and the participation in oxidative processes. Reactive oxygen species (ROS) play a pivitol role in human health and disease via biochemical physiological and pathophysiological processes [7] and probably in aging [8].

In this work, we investigated the adsorption of triclosan on three types of cloisites, and calculated the relative removal efficiency. We are also beginning to explore their thin films and coatings that will offer the opportunity to build complex structures, save materials and engineer hybrid systems.

There are two major removal technologies for phenolic compounds: chemical oxygenation processes with reagents such as hydrogen peroxide [9,10],and the second and the subject of this paper absorption and extraction processes [11-14]. Clays and clay minerals acting as chemical adsorbents are important systems in the removal of these chlorinated organic compounds and in some ways may be more desirable than polymers and activated carbon [11, 15-19]. Clay minerals have large specific surface areas, cation exchange capacity, and low cost as well as very low toxicity [17, 19-20]. The adsorption of organic molecules to these minerals is affected by various parameters, such as the exchangeable cations, the distance between the clay mineral layers, and the existence of water molecules between the layers [20, 21-24] and are aided by the inclusion of organic entities in the interlayers and in the case of cloisite. Recently it has been demonstrated that self-assembled layers of polymer and montmorillonite clay nanoparticles can be produced as a 3-D layer on various substrates [25]. These 3-D printed highly ordered structures are easily produced with conventional ink jet printing technology. Figure 2 contains an x-ray diffraction pattern of such a film that illustrates the high degree of order and self-assembly by the number of orders of reflection and the sharpness of the peaks.

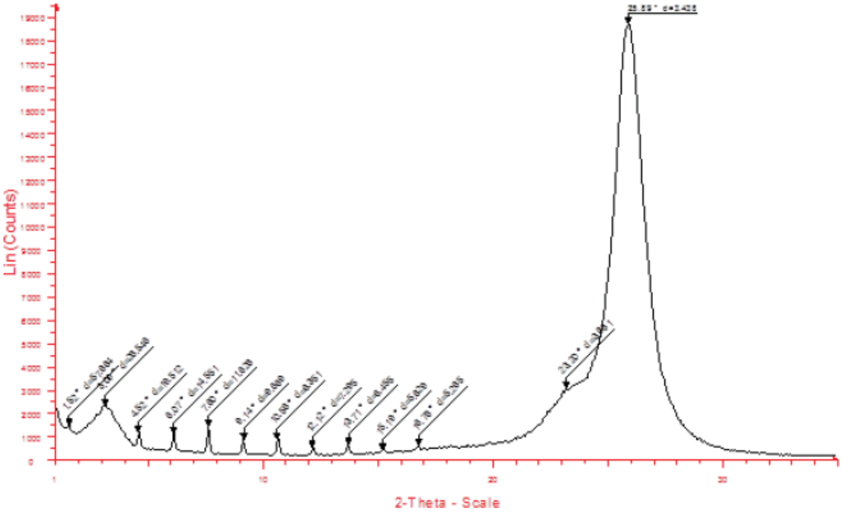

Figure 2 X-ray diffraction pattern of self-assembled nanocomposite 3-D film of polyvinylpyrrolidone and montmorillonite nanoparticles.

Figure 3 shows the layered structure of cloisite 30B, where interlayers are organoclays that contain quaternary ammonium cations bonded with one methyl group, two hydroxyethyl groups, and one tallow group. Figure 3 shows the Avogadro-optimized structure of the organoclay.

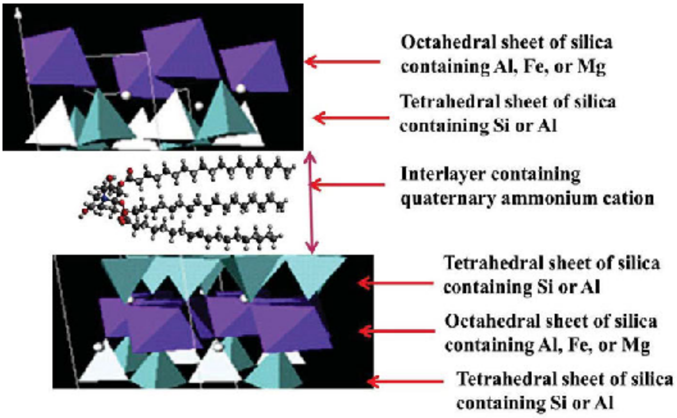

Figure 3.Structure of cloisite30B.In the interlayer, there are one methyl group,two hydroxyethyl groups, and one tallow group bonded to central nitrogen or quaternary ammonium cation. The diagram was modified after [26].

Experimental

Theoretical Simulation

Avogadro visualization platform [27] was used to draw triclosan, cloisite and their adducts and these models were optimized using molecular mechanics that are imbedded in Avogadro software. The outputs were used as inputs for running Gaussian 03W simulation [28]. We used at the beginning ab initio theory with a basis set of STO-3-21G. Later on, the ab initio optimized structures were further modified using Density functional Theory (B3LYP) with 6-31G(d) basis set.

Absorption Experiment

100 mg triclosan and 100 mg cloisite (15a,20A,30B) was dissolved into 25mL of Acetonitrile solution to make a 4000ppm solution. The solution was then run for 20 minutes for stirrer with magnetic stirrer for adsorption of triclosan in cloisite. Later this solution run for centrifuge and for filtration to get the triclosan-cloisite adduct precipitate. The centrifuged solution run for filtration by using micro filter and obtained solution was ready for getting data in LC-MS (Agilent, 6460C, 1290 infinity LC with triple quadruple MS).

The precipitated triclosan-cloisite adduct precipitate was run in TGA (TA-Q-500) hypernated with Hiden MS (HPR 20) instrument.

Results and Discussion

Table 1 shows the results of the adsorption experiments. According to Table 1, closite 15A adsorbs the highest amount of triclosan in comparison to cloisite 20A and closisite 30B. Since the d-spacing in cloisite 15A is maximum, the result was expected. Figure 4 shows the calibration curve for measuring triclosan in the treated water. Figure 5 shows the residual MS peaks with respective MS peak areas when different kinds of cloisite were used to treat triclosan contaminated water. As mentioned in Table 1, cloisite 15A was found to have least redual MS area.

Figure 6 shows the thermogravimetric analysis of trilcosan-cloisite adduct. It shows the slow degradation of triclosan when mixed with closite 30B. It also indicates that when thermally degraded, triclosan will probably degrade slowly. Our MS results did not show any indication of release of toxic components that one might expect otherwise.

Table 1.Removal of triclosan by different types of closites.

Name	Properties	d-spacing (Å)	Residual area	Relative removal efficiency (%)
Cloisite 15A	Weight loss percencentage in ignition is more	31.5	1177	94
Cloisite 20A	Low mass loss, broader peaks in derivative peak in thermal analysis	24.2	25128	54
Cloisite 30B	Off white color additive for plastics improve plastics physical properties	18.5	29127	47

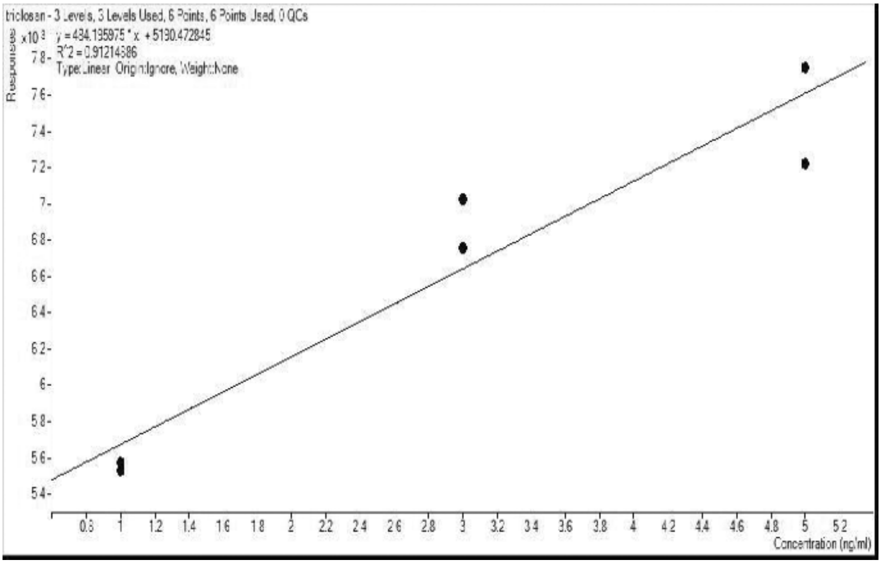

Figure 4. A calibration curve of triclosan measurement using LC/MS. R2 is found to be 0.91.

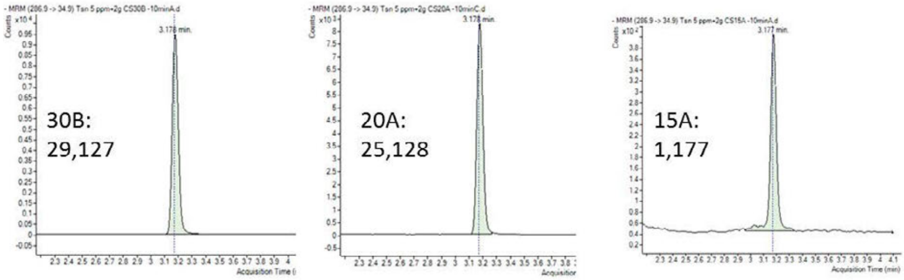

Figure5. Residual Mass Spectrometer (MS) peak areas for remaining triclosan in closites-treated water. 30B, 20A, and 15A indicate three types of closites.

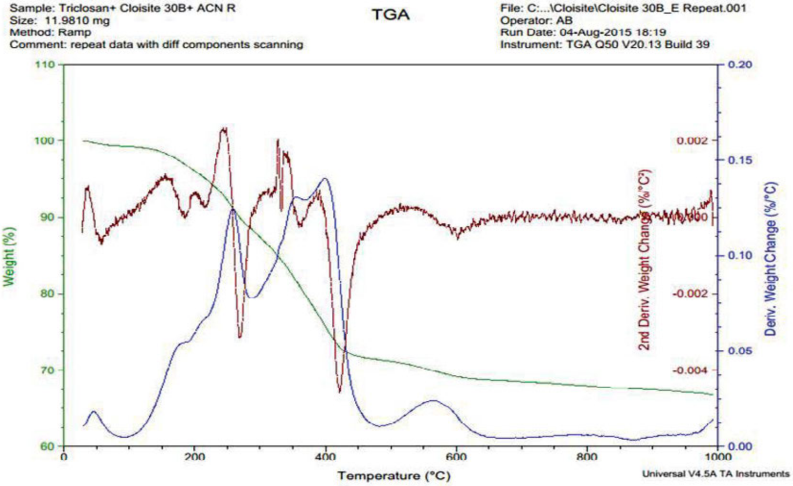

Figure 6. TGA plot for triclosan-cloisite 30B adduct. The green curve is for TGA, the blue curve for differential of TGA, and the pale red curve double differential of TGA.

Conclusions

Optimized structures of triclosan, and triclosan-cloisite adduct were calculated using Density Functional Theory with Gaussian 03 program. Closite 15 A was found to have the highest adsorption capability of triclosan compared to those with cloisite 20A and 30B. Thermal decomposition triclosan-cloisite adduct may create lower toxic products compared to triclosan. As demonstrated for the polymer and montmorillonite clay nanoparticles system, new highly structured clay layers can be produced by 3D ink jet printing which we are currently exploring with cloisite layers.

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