

Conference paper

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Targeted catalytic degradation of organophosphates: pursuing sensors

<https://doi.org/10.1515/pac-2018-0104>

Abstract: Chemical security has been a hot topic over several years, especially involving organophosphates (OP), which are related to organophosphorus chemical warfare and pesticides. The main challenges are to develop efficient ways to destroy stockpiles of these materials and also to monitor their presence in the field or food. A promising approach in this sense is the targeted design of catalysts that can react with OP and degrade them. Herein, we present a summary of some recent advances towards OP detoxification and monitoring that involves four different approaches: (i) How? Understanding the mechanism: thorough mechanistic elucidation and design of an ideal catalytic scaffold; (ii) Nanocatalysts and sensors: rational functionalization of carbon nanomaterials leading to nanocatalysts as powder and thin films. A surface-enhanced Raman scattering (SERS) sensor for OP was also obtained combining the functionalized material with silver nanoparticles; (iii) Catalysts from waste: reuse of rice husk waste as well as waste derived from the cheap gum arabic for developing biocatalysts that have high added-value and are environmentally friendly; (iv) A simple sensor: a simple, cheap and compact homemade colorimeter that can be used as a colorimetric sensor for detecting quantitatively various compounds, including pesticides.

Keywords: catalysis; Chemical Weapons Convention 2017; imidazole; organophosphorus chemistry.

Introduction

In the context of chemical security, an important class of toxic agents that comprise numerous pesticides and chemical warfare agents are the organophosphorus compounds, especially the phosphate esters (OP), which present high toxicity and can be fatal when people are exposed to them. The use of OP is illegal in many countries, although OP are still present in many agrochemicals, and their potential use for chemical attacks constitutes a risk to modern society [1]. Consequently, there are some initiatives focused on the peaceful use of toxic chemicals and overall chemical security, many sponsored by the Organization for the Prohibition of Chemical Weapons [2] that received the Peace Nobel Prize in 2013. OP are known for their highly stable P–O bond, hence one of the problems with their use is related to the fact that they can be potentially active in the environment for a long time. Thereby, it is of great interest to study ways of detecting them, in order to assist

Article note: A special issue containing invited papers on Innovative Technologies for Chemical Security, based on work done within the framework of the Chemical Weapons Convention.

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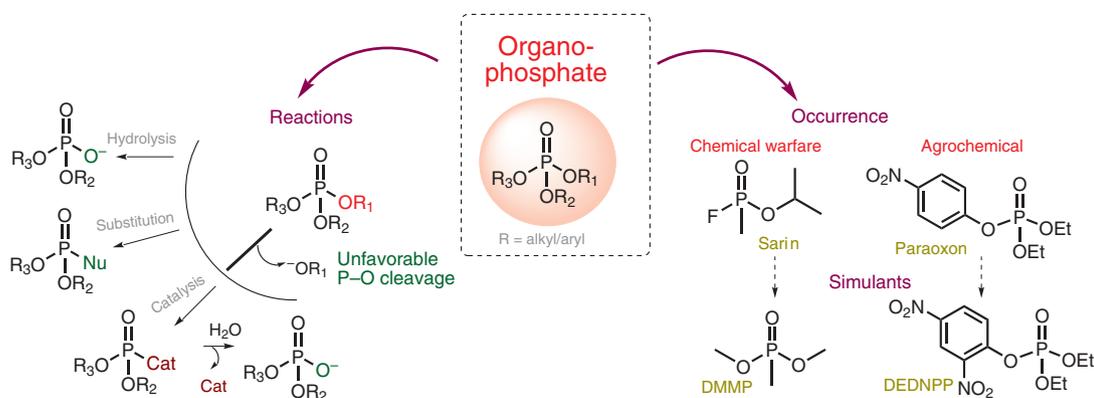


Fig. 1: Occurrence and reactions of OP.

the combating of chemical terrorism, help prevent the abusive usage of agrochemicals, and promote efficient destruction of any unnecessary stockpiles worldwide (by accelerating their degradation). Figure 1 presents the structures of some known OP, showing sarin as an example of a chemical warfare agent, and paraoxon as an example of an agrochemical [3]. Due to their high toxicity, many studies have been conducted with lower toxicity simulants for example diethyl 2,4-dinitrophenyl phosphate (DEDNPP) and dimethyl methylphosphonate (DMMP). In addition, there are presented some reactions that can enable the very unfavorable P–O cleavage, such as hydrolysis, nucleophilic substitution and catalytic processes. The latter has been greatly pursued due to its promising efficiency and recycling, requiring relative low amounts of catalyst in the presence of water to achieve effective P–O cleavage [1].

Another important demand is monitoring OP with the use of sensors, which have been described in the literature, for example using surface enhanced Raman spectroscopy (SERS) [4–6], fluorescent sensors [7–10], electronic tongue [11], colorimetric sensing [12] and electrochemical detection [13–15], among others [1]. Herein, we summarize some recent advances of our research group (group of catalysis and kinetics) in the field of OP degradation and monitoring that will be underlined by four central interests: (i) How? Understanding the mechanism: evidencing the importance of elucidating the reaction mechanism; (ii) Nanocatalysts and sensors: rational design of novel catalysts derived from carbon nanomaterials and their application as SERS sensors; (iii) Catalysts from waste: reuse of rice husk waste for developing biocatalysts as well as waste derived from other cheap biopolymers such as gum arabic; (iv) A simple sensor: a homemade colorimeter that can be easily used for following reactions and detecting quantitatively various compounds such as pesticides.

Recent advances

How? Understanding the mechanism

Whenever seeking to promote a reaction, undoubtedly understanding the mechanism is essential. Specifically for destroying toxic agents such as OP, the reaction must lead to less toxic products and possible side reactions should be known in order to effectively guarantee chemical detoxification. Moreover, the reactants chosen should contain functional groups that are efficient in cleaving the P–O bond, either by directly attacking the phosphoryl moiety or by catalyzing its cleavage in the presence of other species, even with water, for example. Interestingly enough, biological systems can inspire some of these processes, since there are many important phosphoryl transfer reactions that occur mediated efficiently by enzymes. For example, the amino acid histidine is present in several enzymatic active sites [16] with the imidazole (IMZ) group acting as catalyst in dephosphorylation reactions, like the cleavage of RNA (in the case of ribonuclease) [17]. Indeed, IMZ displays interesting chemical versatility in living organisms, acting as acid/base catalyst or even as a nucleophile [18].

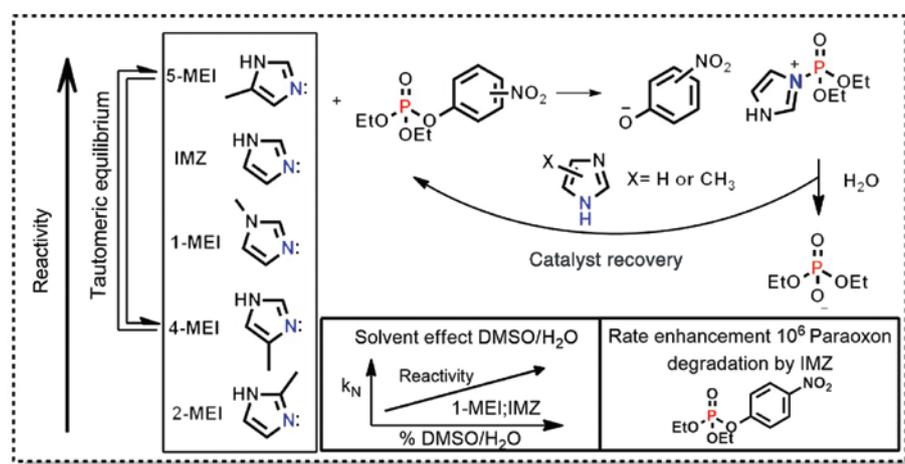


Fig. 2: Summary of reactions involving IMZ organocatalysts.

The enhanced reactivity of IMZ in biological processes has encouraged its investigation toward phosphoryl transfer reactions *in vitro*, in order to develop even more efficient catalysts for the detoxification of pesticides and chemical warfare agents [19, 20]. Figure 2 presents an overall summary of our results in this context.

A former study evaluated the catalytic activity of IMZ itself in the cleavage of a series of phosphate esters, including the triester DEDNPP [18]. In fact, a remarkable rate enhancement of over 10^5 -fold was observed in the cleavage of DEDNPP by IMZ, compared to its spontaneous hydrolysis. These results also motivated the evaluation of the catalytic activity of IMZ in the reaction with the pesticide Paraoxon [21]. Results once more indicated impressive rate enhancements in the order of 10^6 -fold in comparison to the spontaneous hydrolysis of Paraoxon, even under mild conditions (Fig. 2). Nuclear magnetic resonance (NMR) analysis and mass spectroscopy (MS) shed light on the concerted mechanism consisting in the nitrogen lone pair of IMZ attacking the phosphorus atom and leading to the phosphorylated-IMZ intermediate, which is hydrolyzed restoring the catalyst, as shown. Henceforth, the P–O bond is rapidly cleaved by IMZ, by one pathway, leading to less toxic products and the recovery of IMZ.

In light of the interesting catalytic activity presented by IMZ in dephosphorylation processes [17, 18], we have also been assessing the substituent effects on IMZ derivatives, seeking the discovery of ideal catalysts. Considering that electron donating groups usually act by increasing the nucleophilicity/basicity [22], a detailed investigation of the methyl positioning on IMZ ring reactivity was carried out [23]. Based on pH-rate profiles, the monosubstituted methyl-IMZ derivatives (x-MEI where x equals the position of the methyl group on the ring, Fig. 2) 1-methylimidazole (1-MEI), 2-methylimidazole (2-MEI) and 4(5)-methylimidazole (4(5)-MEI) presented outstanding catalytic activities in the cleavage of DEDNPP. The highest reactivity was shown by 4(5)-MEI, followed by 1-MEI and 2-MEI with rate enhancements of 1.9×10^5 , 8.9×10^4 and 3.0×10^4 , respectively. Curiously, these results are not related to the basicity of the species (pK_{aH} values: 2-MEI = 7.85, 4(5)-MEI = 7.69, 1-MEI = 7.21 and IMZ = 6.95) [23], which is often taken as an indication of nucleophilicity [24]. The proposed reaction pathway was analogous to the reaction with IMZ and confirmed by NMR analysis. In contrast to IMZ and other x-MEI, 4(5)-MEI consists of a pair of different tautomers featuring distinct reactivity. In fact, we observed two concomitant reactions by monitoring the simultaneous formation of the different phosphorylated-x-MEI using ^{31}P NMR spectroscopy. Results indicated 5-MEI as the main tautomer responsible for the high reactivity of 4(5)-MEI, while 4-MEI presented lower reaction rate, similar to 2-MEI. Calculation results using B3LYP [25, 26]/6-31 + G(d,p) level of theory revealed that steric hindrance is the main factor controlling the nucleophilic activity of x-MEI. The weakest nucleophiles 4-MEI and 2-MEI present the methyl group vicinal to the nucleophilic center, which disfavors the attack to phosphorus atom of DEDNPP. On the other hand, calculations evidenced that the highest reactivity presented by 5-MEI is due to the highly energetic nonbonding sigma orbital

– among the non-steric hindered species – compared to 1-MEI and IMZ. Consequently, despite the electron donating character of the methyl group, its effect on the IMZ ring is antagonistic, since it acts by increasing the nucleophilic activity only in 5-MEI.

Another aspect that has been investigated is the solvent effect on the catalytic activity of potential detoxification agents. Specifically, although 1-MEI and IMZ present similar reactivity in water toward DEDNPP, varying DMSO/H₂O compositions reveals another behavior [27]. Quantitative analysis of the reactions was performed by multiple regression curve fitting of the second-order rates and related to the acidity (SA), basicity (SB) and polarizability (SPP) of the medium according to the Catalan's scale [28]. Statistical results evidenced that SA, SB and SPP solvation has a stabilizing role in both nucleophiles, lowering the bimolecular reaction rates with DEDNPP. IMZ presented higher nucleophilic activity in all compositions evaluated and a more intense solvation effect, since IMZ acts as a donor/receptor of hydrogen bonding, while 1-MEI acts only as receptor (Fig. 2). By decreasing the composition of the protic polar solvent, the IMZ reactivity is enhanced compared to 1-MEI, since DMSO is only a hydrogen bonding acceptor. Therefore, a lower capacity of hydrogen bond interaction by the medium leads to a subtle increase in the reactivity of IMZ (in comparison with 1-MEI), evidencing the modulator character of the medium on reaction rates [27].

In summary, regarding mechanistic aspects, we have showed that understanding the reaction is fundamental for guaranteeing the proper detoxification. In addition, such studies with small molecules (i.e. IMZ derivatives) surely delineate studies towards more complex systems, such as nanomaterials. Thus, we must first understand how a specific functional group reacts in order to further apply in sensors, for example. Finally, the combination of experimental and theoretical approaches enables the design of novel highly efficient scaffolds for catalysts. More recently, other IMZ derivatives have been proposed theoretically by strategically positioning substituents that enhance their reactivity. Experimentally, some IMZ derivatives have already preliminary shown high reactivity such as 4(5)-hydroxymethylimidazole, in which the neighboring hydroxyl group assists the reaction by hydrogen bonding.

Nanocatalysts and sensors

One way to take a step beyond the previous studies is by anchoring different functionalities on various complex supports for example nanomaterials, seeking synergistic effects, optimized activity, feasible “processability” (e.g. powder, film: can be easily separated, washed and reused) and for sensing purposes. Functionalization is a powerful tool to extend the applicability of nanomaterials by rational design. The insertion of functional groups on the nanomaterial backbone can greatly change the properties, hence extending novel applications such as: electrical, mechanical, reactivity and/or biological [29]. In general, functionalization can be carried out by covalent or non-covalent means [30]. While in the first, a chemical bond is formed, for the latter van der Waals interactions, electrostatic interaction and hydrogen bonding predominate. Thus, in non-covalent functionalization there is a weaker interaction, hence the groups can be leached from the surface (i.e. washed away) [29]. Highly exploited materials in this area of functionalization are carbonaceous nanomaterials such as graphene oxide (GO), which is composed of a two-dimensional sheet the thickness of an atom formed by sp² and sp³ carbons. In contrast to bare graphene, GO comprises a surface with several oxygenated groups such as hydroxyl, carboxylate, epoxide and ketone. Indeed, the surface characteristics of GO materials makes them capable of functionalization with different molecules. These modifications may occur by nucleophilic, electrophilic, condensation and addition reactions [29–31]. Recently, we reported various condensation reactions under mild conditions (low/room temperature, aqueous) between terminal amine groups and the carboxylate groups of GO using the coupling and activating reactants N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide (EDC) and N-hydroxysuccinimide (NHS), respectively, [32–34]. Specifically, IMZ and thiol groups were anchored on GO by the highly stable amide bond, as shown in Fig. 3, leading to GOIMZ and GOSH, using the precursors 1-(3-aminopropyl)imidazole (API) and cysteamine. These materials have been processed as powder and thin film, and further applied as nanocatalysts towards OP destruction by a heterogeneous process [32, 34, 35]. When the synthesis is conducted starting from a GO

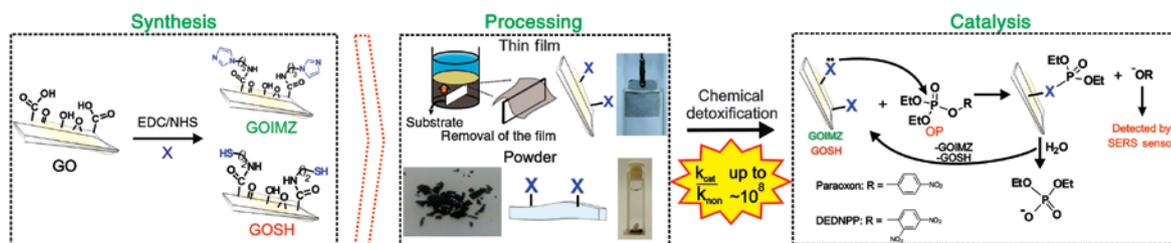


Fig. 3: Summary of the recent advances with nanocatalysts.

aqueous dispersion, the final functionalized material precipitates and is easily separated [32, 33]. Another approach is interfacial liquid-liquid functionalization [36], in which a self-assembled film is formed in the interface water/toluene and can be deposited on various substrates, such as glass. This film can be easily handled and adheres favorably to the substrates [32, 34]. Figure 3 summarizes some of the results involving the nanocatalysts.

The nanocatalysts GOIMZ and GOSH, both in powder [32, 35] and thin film [32, 37] were evaluated in the degradation of DEDNPP and the pesticide Paraoxon, by monitoring the formation of the phenolic products. The powdered materials (GOSH1 and GOIMZ1; ~ 1.0 mg) were maintained under magnetic stirring during the reaction and the solid decanted easily for measuring the reaction product in solution. In the case of the thin films (GOSH2 and GOIMZ2; $\sim 5.0 \times 10^{-5}$ mg), it was deposited on a glass substrate and immersed in the reaction medium and maintained under stirring. Interestingly, even upon many cycles and strong magnetic stirring, the films maintained adherence to the substrate and no trace of the nanomaterials were observed in the solution (evidenced by various techniques). All reactions obeyed pseudo-order kinetics, giving pseudo-first order rate constants (k_{obs}), that were converted to second-order constants by dividing " k_{obs} " by the mass of catalysts used, in order to facilitate comparison (i.e. normalize). First, considering the results just with the simulant DEDNPP, among the nanocatalysts evaluated, the powdered ones presented lower activity than thin films. Both powdered material had similar activity, hence GOIMZ1 and GOSH1 had k_{cat} values 0.11 and $0.14 \text{ g}^{-1} \text{ min}^{-1}$, respectively. For the thin films, significantly higher k_{cat} were observed: 12.50 and $9.60 \text{ g}^{-1} \text{ min}^{-1}$ for GOIMZ2 and GOSH2, respectively. Comparing with the spontaneous reaction of DEDNPP with water, rate enhancements of 10^5 and 10^7 -fold were observed with the powdered and thin film catalysts, respectively. Albeit, with the toxic pesticide Paraoxon (much less reactive), the thin film imidazole-derived catalyst (GOIMZ2) presented significantly greater activity with $k_{\text{cat}} = 0.18 \text{ g}^{-1} \text{ min}^{-1}$ (4.60×10^{-3} and $5.8 \times 10^{-2} \text{ g}^{-1} \text{ min}^{-1}$ for GOIMZ1 and GOSH2, respectively). This implies impressive rate enhancements of up to 10^8 -fold. Non-functionalized materials, i.e. GO, did not present any significant activity with both OP. In addition, reaction of the OP solely with the functional groups unanchored (IMZ and thiol in homogenous reactions) presented significantly lower rate constants than the nanocatalysts. Overall, rate enhancements with DEDNPP and Paraoxon are among the highest reported for OP degradation. The heterogeneous medium guarantees easy recovery and reuse, especially in the case of thin film, which can be deposited on a plastic surface that can be immersed into contaminated samples to destroy (in the case of stocks) or detect the presence of OP through the cleavage reaction that is promoted. All catalysts were reused and maintained their catalytic activity for over three cycles. Various post-reaction characterizations confirmed that the functional groups remain intact throughout all reaction cycles.

Regarding the mechanism, based on previous studies with IMZ and thiol molecules with OP (using kinetic, NMR, MS and theoretical studies), we propose a similar pathway. Firstly, the OP could be adsorbed on the backbone of GO by hydrophobic attraction, followed by the nucleophilic attack of the functional group (nitrogen and sulfur atom for IMZ and thiol groups, respectively) on the phosphorus atom. A phenolic product (RO^-) and intermediate are generated. The latter readily hydrolyses, restoring the initial nanocatalyst and forming a phosphoric acid derivative. Therefore, the OP is efficiently degraded, without side reactions and leading to products of much lower toxicity.

Another interesting aspect that has been exploited is combining functionalized GO containing thiol groups with metallic nanoparticles (NPs), ideal for modulating the size, shape and distribution of nanoparticles [33, 38–40]. Moreover, due to its characteristic plasmonic resonance, noble NPs (e.g. Ag-NPs) are widely employed as substrates for SERS, in which the inherently weak Raman scattering signals of targeted molecules are impressively boosted [41]. SERS signals from graphene/metal NP-based materials have shown superior capabilities in the detection of some probe molecules, e.g. rhodamine reaching detection of up to nanomolar (nM) [42]. In this context, we synthesized thin film nanocomposites of GOSH with Ag-NPs leading to rGOSHAg and employed this material as a SERS sensor for the detection of 4-aminothiophenol, detecting up to 10^{-8} mol L⁻¹ [37]. Also, for the purpose of inferring a potential multifunctionality for the rGOSHAg thin film, we have employed it against DEDNPP degradation. Although, its catalytic activity was lower than without NPs (~10-fold lower than GOSH1, GOSH2), it was still satisfactory and among the highest reported for analogous systems. The highlight in this study is that rGOSHAg was not only catalytic but also presented promising performance as a SERS substrate for detecting the degradation product (phenol), hence a dual function. The film was employed for DEDNPP degradation, removed from the reactive medium and directly analyzed by Raman spectroscopy. The characteristic band for the nitrophenol formed in low concentration was easily detected, which was not possible using common glass substrates without the rGOSHAg film, confirming its SERS effect with the phenolic product. Surprisingly, total OP degradation was attested through the detection of the characteristic band of the product and the absence of an initial DEDNPP band, proving that rGOSHAg can be employed as a SERS sensor for OP such as pesticides and possibly some organophosphorus nerve agents, by relying on the detection of the product by the promoted reaction.

Overall, many nanocatalysts have been rationally designed that rely on chemical functionalization. These results are promising since these nanomaterials have intrinsic properties that enable their optimized catalytic activity as well as their application as sensors (SERS, electrochemical). Previous basic science studies with bare IMZ and various OP are essential for guaranteeing the successful development of the nanocatalysts. These, on the other hand are more closely aligned with real applications, due to their electrical and mechanical properties, for example. We have extended our approach to functionalizing carbon nanotubes with IMZ that contain magnetic Fe₃O₄ inside the nanotubes, which favors its easier magnetic separation in catalytic reactions. Analogously, we have obtained polymeric nanocomposites covalently linked, specifically GO with polypyrrole [43]. Finally, other functionalities that are reactive towards OP degradation are being designed and combined on nanomaterials, for example, containing two different groups on the same backbone, mimicking enzymatic sites.

Catalysts from waste

For the last two decades, the principles of green chemistry are becoming increasingly applied by industry and academia. Two of these principles are the utilization of sustainable and non-toxic compounds and the pursuit of new reactions or routes to already known processes, under mild conditions, such as in aqueous medium [44]. In this context, the use of cheap precursors or residues to produce new materials with high added-value is key for sustainable and economic development. Two particularly interesting classes of substances are gum arabic (GA) and rice husk (RH). GA is a biopolymer obtained from Acacia tree exudates, which is biocompatible and mainly composed of polysaccharides and protein fractions. It is widely used in food industries, among others, and can be obtained commercially for a very low price. Moreover, it is a residue from the tannin industry, hence it can be considered a waste product [45]. In this context, RH also stands out, since it comprises a lignocellulosic residue that is one of the main worldwide agricultural waste materials [46]. One green and noble destination for these residues can be achieved by its chemical functionalization for catalytic purposes, as pursued with the nanocatalysts. The functionalization approach for these residues is still poorly explored and recently we have reported the functionalization of commercial GA and RH waste with IMZ groups, as shown in Fig. 4a [45, 46]. Both functionalizations are analogous to the previously shown

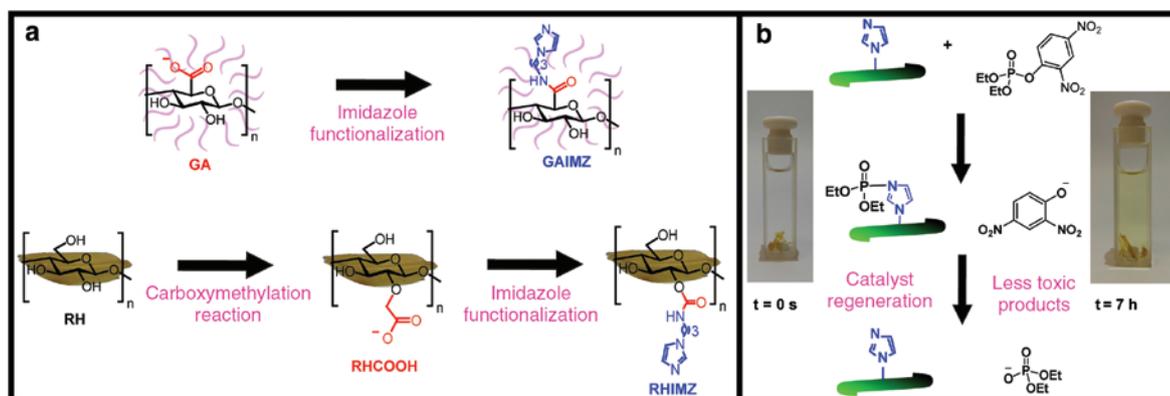


Fig. 4: Summary of the most relevant results regarding the development of sustainable catalysts derived from waste (RH) and biopolymers (gum arabic). Firstly, the functionalization process is shown, where the imidazole groups are covalently anchored (a). The reaction with the OP which is followed in the presence of these catalysts is then shown in (b), together with photos at the beginning and end of the reaction.

nanocatalysts. In the case of GA, its uronic acid groups are directly functionalized via an amide bond (using API, EDC and NHS), giving freely available IMZ groups (GAIMZ), with nearly 12% degree of functionalization of all available acid groups [45]. For RH, which does not present inherent carboxylate groups, we carried out a carboxymethylation reaction to enable the placement of acid groups that were then functionalized (~11% of the carboxylate groups) giving RHIMZ [45].

The functionalized materials were evaluated towards the OP cleavage reaction. With DEDNPP, rate constants of $k_{\text{cat}} = 2.42$ and $0.30 \text{ g}^{-1} \text{ min}^{-1}$ (considering the total amount of catalysts) were obtained for RHIMZ and GAIMZ, respectively. It should be noted that the reaction with GAIMZ is homogenous, while with RHIMZ is heterogeneous. This gave up to a 10^6 -fold rate enhancement, compared to the spontaneous reaction. The mechanism proposed is shown in Fig. 4, analogous to that put forward for the nanocatalysts. Hence, the catalysts are recovered at the end of the reaction and in fact their recycling feature has been evaluated, their catalytic activity being maintained for over three consecutive cycles [45, 46]. Given the feasible separation and waste-nature, RHIMZ was chosen for the degradation of the toxic pesticide Paraoxon, showing a catalytic activity of 10^7 -fold enhancement, an outstanding performance for a heterogeneous reaction [46]. Furthermore, GAIMZ was availed as an artificial nuclease in the plasmid DNA cleavage and surprisingly it efficiently cleaved the DNA strands, comprising an artificial enzyme. This is promising for future studies towards genetic therapy for example [45].

Overall, we have shown that we can also obtain prominent catalysts for OP degradation derived from cheap and waste materials such as GA and RH. This is interesting in the sense that the reuse of waste greatly cheapens the process and helps to solve a serious worldwide waste matter. Some preliminary results have also been obtained with GA waste from Brazilian tannin industries, evidencing that it can also be reused to obtain biocatalysts. In addition, the functionalization process is carried out aqueous medium, which is desirable. These results could be extended to other residues as well as other functional groups. Ideally, we are projecting detoxification media for OP (pesticide and chemical warfare agent simulants) using these waste-derived catalysts.

A simple sensor

Another important approach in the monitoring of OP is enabling a simple and cheap method for detecting these agents. In fact, there are many known analytical methods for this detection, such as mass spectrometry, ion mobility spectrometry, NMR and UV-Vis spectroscopy [47–49]. Although these techniques are classical for qualitative and quantitative determinations, they are also expensive, and unpractical for field

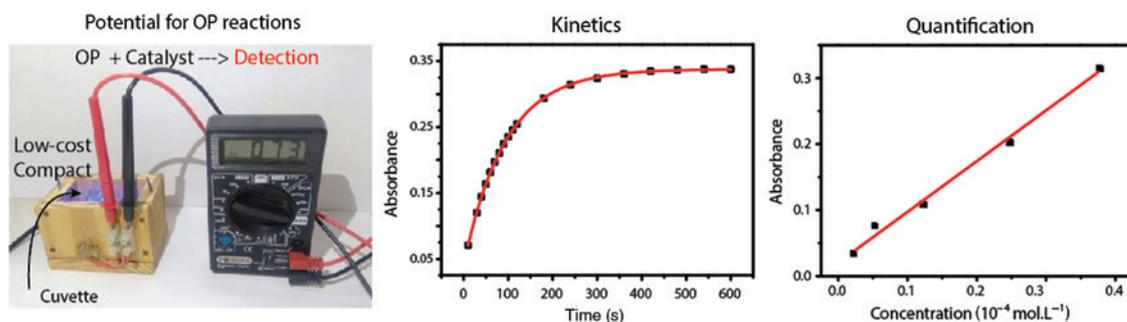


Fig. 5: Compact homemade colorimeter using a LED as light source.

analysis. Colorimetric detection is promising for use in the field. Nowadays there are several studies of agrochemical detection by colorimetric and fluorimetric methods [7, 12, 50–52]. We have recently reported the construction of a compact homemade colorimeter (Fig. 5) and its validation for following reaction products. A LED is used as a light source, that passes through a sample, reaching the detector, which is another LED working as a photodetector, that can convert the light arriving, into electrical energy [53]. The color of the LED (emitting wavenumber) should be compatible with the absorbing wavenumber of the substance that will be detected. For example, blue LEDs are ideal for substances that have maximum absorbance near 430 nm [53]. So, it is possible to use this equipment for simple quantitative analysis, since it can measure absorbance indirectly. The amount of light that passes through the sample and reaches the detector is proportional to the measured potential, which gets lower when the concentration of the sample rises, since less light is reaching the detector. This equipment is inexpensive (under US\$ 10.00 without the multimeter) and compact, interesting characteristics to use directly in field to monitor OPs. Figure 5 shows an optimized version of this colorimeter using wood, along with the analytical curve of p-nitrophenol, evidencing the expected linear behavior predicted by the Beer-Lambert law. A kinetic profile is also shown in Fig. 5 for the model deacylation reaction of p-nitrophenyl acetate with IMZ, with a first-order kinetic behavior giving nearly the same rate constant as that obtained using commercial UV-Vis equipment (less than 10 % deviation) [53]. Therefore, this is an interesting way for quantitative determination of various OP (possibly chemical warfare agents and agrochemicals) for field analysis with low resources. Using our homemade colorimeter, it is possible to use the catalysts developed herein in the cleavage reaction with OP, leading to a colored product that can then be converted to determine the amount of toxic agent present. Some initial studies have been carried with pesticides, showing that we can detect OP agents in less than 10 min. A commercial spectrophotometer could be used for this purpose, but would demand a laboratory. In war zones or crop environments, a rapid response is necessary, which would be viable with the proposed homemade colorimeter, since it is a simple, cheap and small which presents results similar to those obtained by the commercial spectrophotometer.

Concluding remarks

In summary, we described four approaches for accomplishing effective OP degradation that are directly aligned with the interest of destroying and monitoring OP that could be applied to agrochemicals or chemical warfare agents. First, we thoroughly studied reactions of various IMZ derivatives with OP in order to understand how they undergo P–O bond cleavage, aiming to confirm the mechanism and that a degradation process was being undertaken. The substituent on the IMZ ring as well as the medium solvent are crucial for modulating the catalytic activity that shed light towards the design of ideal highly efficient catalysts. Seeking complex systems, we took advantage of the optimal inherent properties of nanomaterials such as graphene and equipped them with catalytic properties by rationally functionalizing the materials with reactive groups. Nanocatalysts containing IMZ and thiol groups were obtained as powder and thin films, which presented

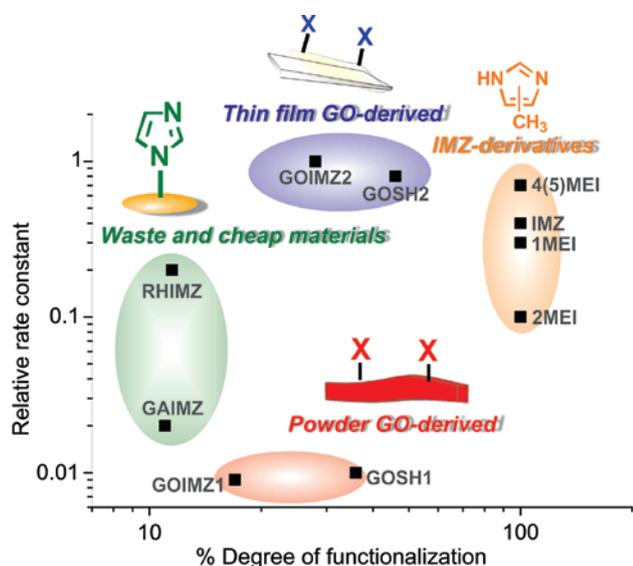


Fig. 6: Summary of the catalytic results shown herein for the DEDNPP degradation reaction. The degree of functionalization is given in relation to the amount of carboxylate groups that were functionalized. For the nanocatalysts, this was estimated from thermogravimetric analysis [32, 33] and for GAIMZ and RHIMZ, was obtained from titration results [45, 46]. For the IMZ derivatives, this degree was considered 100 % for analysis purposes. The relative rate constants were obtained by comparing all k_{cat} of the materials ($\text{g}^{-1} \text{min}^{-1}$).

high rate enhancements. A SERS sensor was also obtained by this means, targeted for the phenolic degradation product. Hence, a bifunctional material was obtained with catalytic and sensing properties. The feasibility in handling these materials is promising for their multiple reuse, especially with the thin film, since it can be deposited on cheap substrates (e.g. plastic). From the sustainable point of view, we also pursued cheap catalysts, derived from waste, for example. Commercial GA, cheap and biocompatible, was functionalized leading to GAIMZ, which not only was very efficient for OP degradation but also comprised an artificial enzyme since it was able to cleave plasmid DNA. RH, a major agricultural waste, was also architected for catalysis leading to RHIMZ. This comprised an environmentally friendly approach to efficiently degrade OP. Finally, we showed a cheap homemade colorimeter than can be easily carried and very effective in following various reactions, presenting similar results to a commercial UV-Vis spectrometer. This apparatus might be designed for field analysis of agrochemicals and chemical warfare, enabling a prompt response as a sensor. Overall, the recent advances have shown that the targeted catalytic degradation of OP and therefore the design of catalysts is promising for promoting chemical security possibly for stockpile destruction and also for pursuing sensors that detect these toxic OP substances, alerting to their misuse.

Finally, in order to compare all catalysts presented herein, Fig. 6 summarizes the relative rate constant of all the materials in relation to the degree of functionalization for their reaction with DEDNPP. This degree is calculated considering the amount of carboxylate groups that are functionalized. For the IMZ-derivatives, this value is considered 100 %. Analyzing the comparison in Fig. 6, four distinct regions are noticeable. The least reactive class comprise the powdered nanocatalysts, followed by the waste and biocatalysts, which although have intermediate catalytic activity, present the lowest degree of functionalization (~10 %) and the advantage of a sustainable approach. The IMZ derivatives have a high catalytic activity, albeit, they undergo through homogenous reactions. Thus, their study is important for understanding the mechanism and designing ideal catalysts but they are more difficult to recover than other heterogeneous catalysts. Finally, the most efficient class is the thin film nanocatalysts, i.e. they are the most effective in promoting the degradation of the DEDNPP, per mass of catalyst used. In addition, their degree of functionalization is under 50 %, hence, functionalization further might enhance the catalytic activity. Indeed, this class of materials is highly promising for developing sensors due to their easy “processability”.

Authors acknowledge financial support from UFPR, CNPq, CAPES, L'Oréal-UNESCO-ABC, Fundação Araucária, and National Institute of Science and Technology of Carbon Nanomaterials (INCT-Nanocarbon).

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