Catalytic polymer-clay composite for enhanced removal and degradation of diazinon

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HIGHLIGHTS

• The bi-functionality of the HPVPcoS-MMT polymer-clay composite, e.g. adsorption and catalysis, was explored.
• Diazinon filtration by HPVPcoS-MMT was more efficient than by granular activated carbon.
• The HPVPcoS-MMT composite catalyzed acidic hydrolysis of diazinon.
• Regeneration and reuse of HPVPcoS-MMT columns were demonstrated.

GRAPHICAL ABSTRACT

ABSTRACT

It is well established that organophosphate pesticides, such as diazinon, pose environmental and health risks. Diazinon is prone to rapid acidic hydrolysis, forming the less toxic compound 2-isopropyl-6-methyl-4-pyrimidinol (IMP). In this study, diazinon surface catalyzed hydrolysis was achieved by its adsorption to a composite, based on protonated poly(4-vinyl-pyridine-co-styrene) (HPVPcoS) and montmorillonite (MMT) clay. The adsorption affinity and kinetics of diazinon to HPVPcoS-MMT were significantly higher than those obtained to the deprotonated PVPcoS-MMT, emphasizing the importance of hydrogen bonding. Correspondingly, diazinon filtration by HPVPcoS-MMT columns was highly efficient (100% for 100 pore volumes), while filtration by columns of PVPcoS-MMT or granular activated carbon (GAC) reached only 55% and 85%, respectively. Regeneration of HPVPcoS-MMT by pH increase was demonstrated and sorbent reuse was successful, whereas regeneration and reuse of GAC and PVPcoS-MMT were inefficient. Proton transfer from HPVPcoS-MMT to diazinon, investigated by FTIR analysis, supports the suggested mechanism of surface catalyzed hydrolysis. These findings demonstrate the applicability of such bi-functional sorbents, to adsorb and degrade pollutants, for efficient water treatment.

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1. Introduction

Organophosphates are a broad group of toxic compounds which include pesticides, flame retardants and nerve agents.
Due to the prevalence of these hazardous compounds in various environments, different approaches of treatment are constantly being investigated [1–3]. Organophosphate pesticides have largely replaced organochlorine pesticides because of the persistence and accumulation of the latter in the environment. Diazinon (O,O-diethyl O-[6-methyl-2-{(1-methylethyl)-4-pyrimidinyl}] phosphorothioate), an organophosphate insecticide, is used to control foliage and soil pests of many vegetable and ornamental crops. Diazinon is classified by the World Health Organization as class II (moderately hazardous). Its acute toxicity to aquatic organisms, insects, birds and mammals is achieved by inhibiting acetylcholinesterase [4]. Diazinon has also been recently classified as a class 2A carcinogen (probably carcinogenic to humans). These concerns have led to a phase out, commenced in the early 2000’s, of residential and agricultural use of diazinon in the USA and the EU. However, diazinon is still being intensively used in other parts of the world [5,6].

Diazinon has recently been detected in surface waters [7–9], urban waters [10], wastewaters [11,12] and groundwaters [13,14], although a sharp decline in measured concentrations, attributed to its phase out, was observed. Once in the aquatic environment, the fate of diazinon depends on its volatilization, photolysis, sorption to sediments and hydrolysis. Abiotic hydrolysis is one of the main degradation pathways of diazinon in water [15]. Rapid hydrolysis occurs in acidic and alkaline conditions, with half-lives of 0.5, 171, and 6 days at pH 3.1, 7.3, and 10.4 (at 20 °C), respectively [16]. At acidic pH, protonation of the pyrimidine nitrogen (pKa 2.4–2.6) [17] activates a rapid nucleophilic attack of the phosphorus group and subsequent cleavage of the bond between phosphorus and oxygen linked to the ring [18]. While at extremely high acid concentrations, protonation of the sulfur, phenoxy oxygen or second pyrimidine nitrogen as the initial step, may take place [18,19]. The hydrolysis products in all cases are 2-isopropyl-6-methyl-4-pyrimidinol (IMP) and diethylthiophosphoric acid [15,20]. IMP is considered more persistent [21], yet less toxic than its parent compound [20,22]. Consequently, several treatment methods, which include the degradation of diazinon, have been suggested. Efficient degradation of diazinon by chlorination [23], ultrasonic irradiation [24], and by several advanced oxidation processes (AOPs), such as UV/H2O2, UV/O3, Fenton’s reagent, photo-Fenton and nanoparticle photo catalysts [20,25–27] has been reported. The disadvantages of these methods include high energy and chemical consumption as well as formation of oxidation products such as diazoxon, an acetylcholinesterase inhibitor which is more potent than its parent compound. In addition, natural waters contain inorganic species and dissolved organic matter which compete with the oxidation reactions of the target pollutant and greatly reduce their efficiency [28,29].

Degradation of isocarbophos (an organophosphate similar to diazinon) by acidic hydrolysis has also been reported [30]. However, a significant amount of pollutants or byproducts remain in solution unless they are physically removed from the water. To that end, employing bifunctional sorbents which efficiently adsorb and catalyze (acidic hydrolysis) organophosphates are advantageous [31] and offer a promising strategy for diazinon treatment. Few studies have addressed the removal of diazinon by sorbents such as granular activated carbon (GAC) [32], NH4Cl-activated GAC [33] and organo-zeolites [34]. The investigations of surface catalyzed hydrolysis of diazinon, are even fewer, and include goethite [35] or Cu-montmorillonite [36] surfaces.

Polymer-clay composites are considered efficient, low cost sorbents which can be applied to water treatment [37–39]. We have designed and employed polymer-clay composites, based on polyvinyl-pyridine-co-styrene (PVPCS) and montmorillonite (MMT) clay, for the removal of micropollutants [40–43] and effluent derived organic matter [44]. The filtration of atrazine by PVPCS-MMT composite was significantly enhanced at acidic pH, due to hydrogen bonding between the triazine ring and the positively charged, protonated PVPCS-MMT (HPVPCS-MMT) [40,41].

In the current study, the bi-functionality of the HPVPCS-MMT composite, e.g. adsorption and catalysis, was explored. The removal of diazinon and IMP by the HPVPCS-MMT composite was addressed and the potential of the composite surface, an H-donor, to induce the hydrolysis of diazinon was investigated. The Langmuir coefficients, deduced from the adsorption isotherms of diazinon and IMP to MMT, PVPCS-MMT and HPVPCS-MMT, were determined. Kinetic parameters of diazinon adsorption to HPVPCS-MMT and GAC were calculated and compared. Diazinon removal and hydrolysis by filtration with HPVPCS-MMT and GAC columns was compared. Furthermore, the feasibility of regenerating the spent HPVPCS-MMT filters by increasing the pH was tested.

2. Materials and methods

2.1. Materials

Wyoming Na-montmorillonite SWy-2 (MMT) was obtained from the Source Clays Repository of the Clay Mineral Society (Columbia, MO). Poly (4-vinylpyridine-co-styrene) (PVPCS) with a molecular weight of 120–150 KDa and pyridine to styrene ratio 1:9, analytical grade diazinon and IMP (2-isopropyl-6-methylpyrimidin-4-ol) (Fig. 4), and all other reagents were purchased from Sigma Aldrich. Granular activated carbon (GAC) was Hydrafine 30N.

2.2. Analytical methods

Polymer concentration was determined by UV−vis spectrophotometry (Thermo Scientific, Evolution 300, Waltham, MA, USA) at an excitation wavelength of 256 nm. A standard calibration curve was fitted and the amount of polymer adsorbed to the clay was calculated accordingly. FTIR spectra were obtained by KBr pellets (100 mg) and recorded at room temperature in the range of 600–4000 cm−1 using an FTIR spectrometer (Nicolet Magna-IR-550, Madison, WI, USA). Surface area of the GAC and polymer−clay composite was 856 and 39 m2/g, respectively, as determined from N2 adsorption−desorption isotherms at 77 K (Quantachrome Instruments, Boynton Beach, FL, USA). Point of zero charge (pzc) of the GAC, determined by the method of mass titration [45], was 8.4. The isoelectric point (IEP) of the composite was 4.1, as determined by measurement of the zeta potential of 0.1% (w/w) composite suspensions with a Zetasizer Nano ZS (Malvern Instruments, Southborough, MA) as a function of pH (2.6–10) with NaOH 0.1 N. See Supplementary Material (Fig S1) for surface charge analysis results.

Diazinon and IMP concentrations were measured by an Agilent 1200 series HPLC instrument equipped with a G1315D diode-array detector. HPLC column was Waters XBridge Shield RP18 3.5 μm, 4.6 mm × 100 mm. Diazinon and IMP were monitored at wavelengths of 210 and 234 nm, respectively. The mobile phase was composed of acetonitrile and double distilled water. The flow rate for was 1 mL/min with a mobile phase gradient starting at 10% acetonitrile and increasing to 95% at the 4 min mark. The flow rate decreased to 0.8 mL/min at the 6 min mark while maintaining 95% acetonitrile. Both flow rate and acetonitrile decreased to 1 mL/min and 10%, respectively after 7.5 min and maintained for an additional minute. Column temperature was set to 30 °C. Limit of quantification was 3 × 10⁻⁵ and 1.5 × 10⁻⁴ mM for diazinon and IMP, respectively.
2.3. Experimental methods

2.3.1. Composite preparation

Preparation of protonated PVPCoS (HPVPCoS) and polymer-clay composites was carried out as described [41]. Briefly, PVPCoS (3 g/L) was protonated by adding H$_2$SO$_4$ (95%; 0.65 mL/L) at stoichiometric concentrations (100% of pyridine monomers). MMT clay suspension (1.67 g/L 4 mL) was added to HPVPCoS solutions (0.03–0.56 g/L, 8 mL) in 12 mL Teflon-capped glass vials. The pH was adjusted, if necessary, to 3.5 ± 0.1 with dilute H$_2$SO$_4$. The clay-polymer suspensions were agitated for 2 h (equilibrium was reached within 1 h) using a shaker, centrifuged, and supernatants were separated from the settled HPVPCoS-MMT composites. The supernatants were washed with deionized water (12 mL) to remove excess polymer and electrolytes and centrifuged again. The absorbance of the supernatants was measured using UV–vis spectrophotometer. PVPCoS-MMT composites (i.e., deprotonated HPVPCoS-MMT) were prepared by washing HPVPCoS-MMT composites with deionized water and adjusting solution pH to 8 ± 0.1 with dilute NaOH. For adsorption studies, composites were prepared in larger batches and freeze-dried prior to further use.

2.3.2. Diazinon and IMP adsorption to MMT and composites

Diazinon and IMP stock solutions were prepared first in methanol followed by transfer to distilled water (0.1% v/v). The stock solutions (0.13 mM or 0.2 mM) were vigorously stirred for 24 h before experiments. Stock solutions were analyzed with HPLC and compared to more dilute solutions to confirm a linear response, which verified the complete dissolution of diazinon. In preliminary experiments, the hydrolysis of diazinon (0.13 mM) at pH 3.5 ± 0.1 was determined (Fig. S2) and the data was fitted to the pseudo-first order rate equation, obtaining the rate constant (5 × 10$^{-4}$ 1/min), as reported [17,18,20]. Half-life was approximately 23 h, however, kinetic studies indicated that adsorption pseudo equilibrium between HPVPCoS-MMT and diazinon was reached within 30 min (see below), after which less than 2% was hydrolyzed (Fig. S2). In order to ensure equilibrium at all concentrations, yet minimize the hydrolysis of diazinon in solution, batch experiments with HPVPCoS-MMT at pH 3.5 were extended to 4 h (unless stated otherwise), after which approximately 13% was hydrolyzed (Fig. S2). To account for diazinon hydrolysis in experiments carried out at pH 3.5, adsorption was calculated based on the concentration of both diazinon and IMP detected in solution. Furthermore, the total concentration of diazinon and IMP decreased during hydrolysis (Fig. S2) (approximately 15% after 4 h), possibly due to volatilization. All experiments included controls to account for losses other than adsorption to sorbents.

Adsorption of diazinon or IMP (10 mL) to MMT, PVPCoS-MMT and HPVPCoS-MMT was tested in triplicates in 12 mL Teflon-capped glass vials. The pH of MMT and PVPCoS-MMT suspensions was maintained at 8 ± 0.1 while that of HPVPCoS-MMT at 3.5 ± 0.1. The vials were agitated for 24 h at 25 °C (for MMT and PVPCoS-MMT composites) or 4 h (for HPVPCoS-MMT composites). In some cases, PVPCoS-MMT and HPVPCoS-MMT were agitated with diazinon or IMP for 4, 24 and 72 h. The samples were centrifuged (16000 RCF; 20 min), decanted and filtered through 0.45 μm PTFE syringe filters. Supernatants from vials containing HPVPCoS-MMT (pH 3.5 ± 0.1) were neutralized to pH 7 ± 0.1 with a phosphate buffer to halt acidic hydrolysis.

In preliminary experiments, diazinon (0.13 mM) adsorption to HPVPCoS-MMT (0.5 g/L composite) with various HPVPCoS loadings (0.009–0.13 g/g clay) (Fig. 1b) was determined. Diazinon adsorption did not significantly increase at HPVPCoS loading above 0.06 g/g clay (see discussion below), and therefore this composite was chosen for the following experiments. Adsorption isotherms of diazinon or IMP (0.007–0.2 mM) to MMT, PVPCoS-MMT or HPVPCoS-MMT (0.5 g/L) were constructed, fitted to the Langmuir equation using the Curve Fitting Toolbox in MATLAB 8.5 and the adsorption affinity ($K_L$) and capacity ($Q_{\text{max}}$) coefficients were extracted.

2.3.3. Diazinon adsorption kinetics to composites and GAC

The adsorption kinetics of diazinon (0.13 mM) to HPVPCoS-MMT or GAC (0.5 g/L) was tested in triplicates in 180 mL Teflon tubes. Adsorption to GAC was determined at both pH 8 ± 0.1 and 3.5 ± 0.1. Aliquots (1 mL) were taken at timed intervals, filtered through a 0.45 μm PTFE syringe filters, their pH neutralized to pH 7 ± 0.1 as described above and the concentrations of diazinon and IMP determined with HPLC. The acidic hydrolysis of diazinon in the timeframe of the experiment (125 min) was 6%. Removal was based on the total concentration of diazinon and IMP in solution.

The kinetics of adsorption was analyzed with the time dependent Langmuir equation as follows [46]:

$$\frac{dC_t}{dt} = -C_t \cdot C_e (t) \cdot R (t) + D (R_0 - R (t))$$

$R_0$ is the molar concentration of sorbent surface sites. Kinetic parameters $C$ (L/mol-min), forward coefficient of adsorption, and $D$ (1/min), rate coefficient of desorption, satisfy the relation $K = C/D$ ($R_0$ was determined by the adsorption isotherm). $R (t)$ denotes the molar concentration of unoccupied sites of the sorbent at time $(t)$. $C_t$ is the pollutant molar concentration, $C_e (t)$ relates to the pollutant molar concentration at time $(t)$. This set of equations was solved by a Taylor series, as described previously [47].

2.3.4. Diazinon filtration by composites and GAC

Column experiments were conducted in glass columns (20 cm length, 1.6 cm diameter), each containing 1.4 g of sorbent (composite or GAC) and mixed with quartz sand (grain size 0.8–1.5 mm) to achieve a weight ratio of 1:50 (w/w) and sorbent bed height of 20 cm. Composites were mixed with excess quartz sand to enable a high flow rate through the column. Experiments were carried out in duplicates at 25 °C. The columns were slowly saturated from the bottom to prevent channeling. Diazinon solutions (0.04 mM) were prepared with distilled water at pH 3.5 (for HPVPCoS-MMT column) or 8 (GAC and PVPCoS-MMT columns) and pumped through the columns with a peristaltic pump at a flow rate of 6 mL/min, obtaining a filter velocity of 1.8 m/h and an empty bed contact time of 6.7 min. The experiment was terminated after passing 110 pore volumes of diazinon solution, after which 10 pore volumes of distilled water (pH 3.5 or 8) were passed through the columns to remove the pore solution which contained diazinon or IMP (verified with HPLC).

2.3.5. Regeneration and reuse of composite and GAC Filter

The columns were stop cocked and left for 72 h. Next, distilled water was adjusted to pH 10 ± 0.1 and pumped through the columns for an additional 100 pore volumes to extract bound diazinon and IMP. A diazinon solution was again pumped through the columns (as described above).

In each stage (filtration and regeneration) the eluent from each column was collected at timed intervals and their pH and diazinon and IMP concentrations were determined. Hydrolysis reached approximately 18% at pH 3.5 (no hydrolysis at pH 8) after 6 h. The IMP adsorbed by HPVPCoS-MMT was calculated accordingly and subtracted from the eluted IMP concentration. Control columns containing only quartz sand were included to account for loss (30–50%) due to volatilization, adsorption to pipes, plastic connections etc. Diazinon removal by the sorbents was calculated based on the concentration of diazinon which eluted from the sand columns.
3. Results and discussion

3.1. Diazinon and IMP adsorption to MMT and composites

Diazinon adsorption to MMT followed a Langmuir like curve (Fig. 1a). The relatively high adsorption to the bare clay, was attributed to specific interactions, between the exchangeable clay cations and the P=S group [48,49]. Accordingly, IMP, which lacks the phosphorus group, did not appreciably adsorb to MMT.

Diazinon adsorption increased upon modification with HPVPcoS (Fig. 1b) indicating that P=S-cation interaction are not involved in diazinon adsorption to the composite. Diazinon adsorption (pH 3.5, 0.13 mM) as a function of HPVPcoS loading on clay (0.01–0.13 g/g clay) was complete even at a low polymer loading of 0.06 g HPVPcoS/g clay. Hydrogen bonding may play a major role since the diazinon pyrimidine and the protonated pyridine of HPVPcoS-MMT are hydrogen acceptors and donors, respectively. To test the role of hydrogen bonds, adsorption isotherms of diazinon and of IMP to PVPcoS-MMT and HPVPcoS-MMT (0.06 g polymer/g clay) were constructed (Fig. 2) and Langmuir coefficients extracted (Table 1).

The adsorption capacity (Qmax) and affinity (Kc) of diazinon were higher for HPVPcoS-MMT, in comparison to the PVPcoS-MMT composite. Likewise, IMP showed higher adsorption towards the protonated composite, suggesting that hydrogen bonding with diazinon involved the nitrogen atom of the pyrimidine ring. Diazinon adsorption to the PVPcoS-MMT was not negligible and may have involved other non-specific interactions, whereas the enhanced adsorption to HPVPcoS-MMT may be through a combination of specific interactions (e.g. H-bonding) as well as non-specific interactions. In the case of natural aqueous environments, competition by other solutes for the specific interaction may decrease pollutant adsorption [50]. However, in a previous study, the removal of atrazine by HPVPcoS-MMT composites (governed by H-bonding) was not affected by the presence of natural organic matter, possibly due to the high pollutant-composite affinity. The increased adsorption to the protonated composite may have also been a result of a possible conformational change of the polymer, which may have offered additional non-specific adsorption sites on HPVPcoS-MMT. The adsorption affinity of diazinon to HPVPcoS-MMT was in the same order of magnitude, though slightly higher, as that of triazine herbicides to HPVPcoS-MMT [40] and of diclofenac to QPVPcoS-MMT (methylated poly vinyl-pyridinium-co-styrene-MMT composite) [43].

3.2. Diazinon and IMP adsorption kinetics to composites and GAC

The kinetics of diazinon adsorption is of great importance especially when considering non-equilibrium systems such as column filtration. The kinetics of diazinon removal by HPVPcoS-MMT, PVPcoS-MMT and a commercial GAC is presented in Fig. 3. The reduction in diazinon concentration as a result of acidic pH was negligible, thus, adsorption to the sorbents was the dominant process. Adsorption kinetics to GAC was not affected by solution pH (3.5 or 8) (Fig. S3). Diazinon removal by GAC and PVPcoS-MMT (at pH 8) reached only 40 and 30%, respectively, while a removal of 80% was obtained by HPVPcoS-MMT (at pH 3.5) (Fig. 3a). In addition, adsorption to HPVPcoS-MMT reached equilibrium within only 30 min while adsorption to GAC and PVPcoS-MMT did not (Fig. 3b). These results correspond to the less rapid rate of partitioning and migration to micropores characteristic of GAC.

The adsorption (C) and desorption (D) coefficients, which can describe the adsorption affinity coefficient (K), were determined by relating the data from the kinetic experiments to the time dependent Langmuir equation (Table 2). Since the removal of diazinon by the HPVPcoS composite reached equilibrium the values for the adsorption affinity coefficient (K) (4.5·10^4 L/mol) as well as R0 (molar concentration of adsorption sites) were in good agreement with the Langmuir adsorption affinity coefficient (Kc) and adsor-
The adsorption coefficient ($C$) of HPVPcoS-MMT is an order of magnitude higher than that of GAC while the desorption coefficient ($D$) and $R_0$ (molar concentration of adsorption sites) are similar. Since the adsorption coefficient ($C$) is dominant in the first stages of adsorption, it is most likely that diazinon filtration by HPVPcoS-MMT columns will be superior to filtration by GAC columns. The adsorption coefficient ($C$) and $R_0$ of PVPcoS-MMT are similar to the GAC coefficient, however, the high desorption coefficient ($D$) indicates poor filtration by this composite (Fig. 5).

In addition to the enhanced adsorption properties, the pH dependency of HPVPcoS-MMT may provide two complementary advantages: (1) Surface catalyzed acidic hydrolysis of diazinon bound to the HPVPcoS composite (Fig. 4) and (2) pH controlled column regeneration and reuse.

### 3.3. Diazinon filtration by composites and GAC

The filtration of diazinon by columns of GAC, PVPcoS-MMT and HPVPcoS-MMT and their regeneration is depicted in Fig. 5. To account for diazinon loss not due to adsorption by the sorbents,
control columns filled with sand (i.e. no sorbent) were included. Diazinon removal by the sorbents was calculated based on the corrected concentration of diazinon which eluted from the sand columns.

The filtration by GAC columns was relatively efficient, reaching 80%. Removal by PVPcoS-MMT columns was initially high but rapidly declined as predicted by the high desorption coefficient (Table 2). Diazinon removal by filtration with HPVPcoS-MMT columns was 100% throughout the experiment with low concentrations of IMP detected in the effluent, after the filtration of 50 pore volumes (expressed by a decrease in filtration to 93%). The highly efficient filtration of diazinon by the HPVPcoS-MMT column corresponds to its rapid adsorption kinetics (Table 2) and high affinity (Table 1).

The columns were regenerated by a NaOH solution (110 pore volumes; pH 10) and the concentrations of diazinon and IMP in the eluent were monitored (Fig. 6). Throughout the regeneration analytes were not detected in the eluent from the GAC columns. In comparison, the eluted diazinon and IMP from the PVPcoS-MMT and HPVPcoS-MMT columns accounted for approximately 22 and 64% of the initially adsorbed diazinon, respectively, emphasizing the regenerability of the HPVPcoS-MMT sorbent. The degree of regeneration can be explained in terms of the adsorption mechanisms to the different sorbents. Adsorption to GAC and PVPcoS-MMT is mainly attributed to hydrophobic interactions [51,52]. Obviously, a change in solution pH does not trigger significant desorption. In contrast, diazinon adsorption to HPVPcoS-MMT is dominated by hydrogen bonding, as well as non-specific hydrophobic interactions. Thus, deprotonation led to a reduction in adsorption affinity (Table 1 and Fig. 2) and subsequent desorption.

Following regeneration the columns were reused. Filtration efficiency of the regenerated HPVPcoS-MMT columns remained very high, where as that of PVPcoS-MMT and GAC declined due to gradual depletion of available adsorption sites.

3.4. Surface catalyzed hydrolysis of diazinon

The hydrolysis of diazinon in acidic solution, in which IMP is the principal product is well known and established in the literature [17–20]. In the current study, we hypothesized that hydrolysis of bound diazinon may be catalyzed by HPVPcoS-MMT and aimed to demonstrate this.

The degree of hydrolysis on composite surfaces was estimated by monitoring the composition of the solution eluting from the columns during regeneration (Fig. 6). Following diazinon filtration, deionized water (10 pore volumes of pH 3.5 or 8) was passed through the columns to remove the pore solution which contained diazinon and IMP (verified with HPLC). This rinse was followed by column regeneration with a NaOH solution. The concentration of IMP and diazinon in the eluent generated after more than 5 pore volumes was measured. Any eluting IMP is therefore directly attributed to surface-catalyzed hydrolysis of diazinon.

A total (IMP and diazinon) of 2.7 µmol/g composite eluted from the PVPcoS-MMT column while 4 µmol/g composite eluted from the HPVPcoS-MMT column. In the case of PVPCoS-MMT, IMP constituted 1.6 µmol/g composite from the total eluent, indicating that the composite catalyzed diazinon hydrolysis at a neutral pH as well (bare MMT does not catalyze diazinon hydrolysis [36]), as previously reported for diisopropyl fluorophosphate [53]. While the IMP that eluted from the HPVPcoS-MMT columns reached 6.1 µmol/g composite. This clearly indicates that acidic hydrolysis on HPVPcoS-MMT surfaces generated a significant amount of IMP.

Since diazinon in the column was only present at the adsorbed state, IMP could not have been the result of acidic solution hydrolysis. The eluting solution contained only diazinon and IMP and no other degradates, clearly indicating the surface enhanced acidic hydrolysis was the only process of diazinon degradation taking place.

We suggest that the protonation of the diazinon pyrimidine nitrogen, reported as the first step in acidic hydrolysis at this pH is the [17,18], is achieved by transferring of protons from HPVPcoS-MMT to diazinon. Proton transfer is supported by FTIR analysis of HPVPcoS-MMT and PVPcoS-MMT before and after diazinon adsorption (0.13 mM) in batch (4, 24 and 72 h contact time). The protonation of diazinon or the bond cleavage that is a result of the hydrolysis, unfortunately, could not be monitored by FTIR since these characteristic bands of diazinon are screened by those of the composite. However, the protonation of diazinon could be monitored through the change in the bands assigned to the composite. In the case of HPVPcoS-MMT, the increase in the pyridine assigned band (1607 cm−1) on account of the pyridinium assigned band (1639 cm−1) [43,44] with increasing contact time, was attributed to deprotonation of pyridinium groups (Fig. 7a). These results indicated that pyridinium deprotonation was coupled to the protonation of the diazinon pyrimidine nitrogen, which activated its acidic hydrolysis [17,18]. This trend was not observed in the case of diazinon adsorbtion to PVPcoS-MMT (Fig. 7b) or IMP adsorption to HPVPcoS-MMT (Fig. S4), thus reaffirming that these observations were a result of the proposed mechanism.

4. Conclusions

In the current study, the bi-functionality e.g. adsorption and catalysis of diazinon by a polymer-clay composite, was explored. The adsorption of diazinon to the protonated PVPCoS-MMT composite (HPVPcoS-MMT composite) was rapid and high with respective affinity and capacity coefficients of Kd 5.6·10^4 L/mol and Qmax 5.8·10^-4 mol/g. Diazinon filtration by columns of HPVPcoS-MMT composite was more efficient than by GAC or PVPcoS-MMT columns. The regeneration of the HPVPcoS-MMT columns by increasing pH, was demonstrated, whereas GAC did not respond to a pH change. Furthermore, the reuse efficiency of the regenerated HPVPcoS-MMT columns was high. The catalytic properties of the HPVPcoS-MMT composite induced IMP generation and elution from the column. Surface enhanced hydrolysis, brought about by proton transfer from HPVPcoS-MMT to diazinon, was indicated by FTIR spectroscopy. Thus, protonation of the composite enabled high diazinon filtration, column regeneration and induced the catalytic surface reaction. Such bi-functional polymer-clay composites may offer an efficient method for removal and detoxification of various classes of pollutants.
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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2017.04.017.

References


