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RESEARCH ARTICLE

Pesticide removal from waste spray-tank water by organoclay adsorption after field application to vineyards

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Abstract
Purpose The main objective of this work was to develop and test a pilot scheme for decontaminating pesticide-containing water derived from pesticide mixtures used to protect vineyards, in which the scheme comprises adsorption by an organoclay and includes a system where an enhanced or rapid microbial degradation of the adsorbed residues can occur.
Methods In laboratory experiments, the Freundlich adsorption coefficients of formulations of two fungicides, penconazole and cyazofamid, onto the organoclay Cloisite 20 A were measured in order to predict the efficiency of this organoclay in removing these fungicides from the waste spray-tank water. Subsequently, the adsorption tests were repeated in the pilot system in order to test the practical operation of the depuration scheme.
Results The adsorption tests with the pilot system show 96% removal of both fungicides over a few hours, similar to the efficiency of removal predicted from the laboratory adsorption tests. The formulation type may influence the efficiency of clay recovered after adsorption. Regarding the waste disposal, for instance, the organoclay composted after the treatment, cyazofamid showed significant dissipation after 90 days, whereas the dissipation of penconazole was negligible.
Conclusion The depuration scheme developed showed to be efficient for decontaminating pesticide-containing water derived from vineyards, but additional treatments for the adsorbed residues still appear to be necessary for persistent pesticides. However, future decontamination research should be attempted for water contaminated with pesticides containing antifoaming agents in their formulations, in which case the present pilot system could not be applied.

Keywords Pesticide · Point source contamination · Depuration · Waste water · Modified clays

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1 Introduction

With the coming into force of the new European directive 2009/128/EC (The European Parliament and the Council of the European Union 2009), the sustainable use of pesticides becomes a duty for all the European Member States. The directive establishes a framework to achieve sustainable use of pesticides by reducing the risks and impacts of pesticide use on human health and the environment and by promoting the use of integrated pest management.

Particular attention is accorded to pesticide contamination of surface and groundwater; appropriate measures to reduce exposure of water bodies to nonpoint sources (spray drift, drain flow, and runoff) and point sources (pesticide handling procedures) should be adopted (EU 2009/28/EC). Recent field surveys and measurement campaigns demonstrated that 40–90% of surface-water contamination is due to point sources (Decoin 2003; Kreuger and Nilsson 2001; Jaeken and Debaer 2005). Several studies have shown that the use of a low-cost system known as a biobed can minimize the risk of contamination or pollution due to point sources (Fait et al. 2007; Vischetti et al. 2004; Castillo et al.

2008). In its simplest form, a biobed system consists of a biologically active matrix which retains the pesticides onto organic matter or soil particles and where enhanced or rapid microbial degradation or bioremediation of the pesticides then occurs (De Wilde et al. 2008, 2010). However, due to the temperature and organic matrix dependence of the pesticide sorption in the system, its use in the field can sometimes be restricted (Castillo et al. 2008).

Several other techniques have been developed for the removal of pesticides from water. Sorption on activated carbon is one of the most extensively used technologies to purify water contaminated by pesticides and other hazardous chemicals (Hamadi et al. 2004; Hameed et al. 2007). However, the high cost of active carbon together with the expensive process for its regeneration has led to the search for new inexpensive materials (Gupta et al. 2006), such as the potential use of complexed organoclay adsorbents investigated at the laboratory scale (Suciu and Capri 2009; Rodriguez-Cruz et al. 2008; Cruz-Guzman et al. 2005; Polubesova et al. 2005). The current paper aims at validating the practical applications of the laboratory findings and at testing a possible approach to dispose of the adsorbed residues. Recent studies have shown that irradiation simulating sunlight could represent a suitable technique to photodegrade pesticide adsorbed on natural and modified clays (Tajeddine et al. 2010). As an alternative, Kupper et al. (2008) demonstrated that the composting of 28 pesticides, adsorbed on an active biomix, was successful in full-scale composting plants, with a dissipation rate of more than 50% for more than two thirds of the pesticides after 112 days of treatment. The objectives of this study were (1) to assess the adsorption of representative formulated pesticides on an organoclay and (2) to assess the mass balance in batch studies. The findings were then used (3) to test a pilot depuration system that could be utilized on farms. The depuration scheme comprises, beside the pilot plant for adsorption, a system where enhanced or rapid microbial degradation of the adsorbed residues can occur.

2 Materials and methods

2.1 Pesticide selection

The pesticides selected were cyazofamid (4-chloro-2-cyano-*N*,*N*-dimethyl-5-p-tolylimidazole-1-sulfonamide) and penconazole (1-[2-(2,4-dichlorophenyl)pentyl]-1*H*-1,2,4-triazole), two fungicides commonly used for integrated pest management in vineyards. Cyazofamid is used not more than three times per year for the treatment of grapevine against *Plasmopora*, according to the guideline of the "Integrated production disciplines" (http://www.ermesagricoltura.it/Sportello-dell-agricoltore/Come-fare-per/Produrre-nel-rispetto-dell-ambiente/Fare-agricoltura-integrata-produzioni-vegetali/Disciplinari-di-produzione-integrata/Norme-generali-2009; http://www.ermesagricoltura.it/content/download/8991/119268/file/d09_vite.pdf). Penconazole was chosen as a fungicide used against powdery mildew (*Oidium*) and also in viniculture. In integrated pest management in Italy, the chemical class of penconazole, called sterol biosynthesis inhibitors, is authorized for use no more than three times per year. The commercial formulations of both pesticides are liquids, a suspension concentrate for cyazofamid and an emulsifiable concentrate for penconazole.

2.2 Chemicals

Analytical standards (99% purity) of cyazofamid and penconazole were purchased from Dr. Ehrenstorfer GmbH, Germany and LabServ Analytica, respectively. The two fungicides were used as the commercial formulations Mildicut (25 $\mathrm{g L^{-1}}$ cyazofamid, ISK Bioscience Europe S.A., Brussels, Belgium) and Topas (100 $\mathrm{g L^{-1}}$ penconazole, Syngenta Crop Protection S.p.A., Milan, Italy). Cyazofamid is a solid with a water solubility of 0.114 mg $\mathrm{L^{-1}}$ and log K_{ow} (where K_{ow} is the 1-octanol/water partition coefficient) of 3.2. Penconazole is a solid hydrophobic compound with a water solubility of 73 mg $\mathrm{L^{-1}}$ and log K_{ow} of 3.72.

The pesticide formulations were dissolved in deionised water at a concentration of 12 mg $\mathrm{L^{-1}}$ for cyazofamid and 25 mg $\mathrm{L^{-1}}$ for penconazole. The volume of pesticide formulation used was less than 1% of the final pesticide solution volume. Both commercial formulations contain agents to aid the mix of the active ingredient with the water, seeing their hydrophobicities. The penconazole solution (dissolved in an organic solvent) is mixed with an emulsifiable agent to allow a homogeneous water dilution. The cyazofamid formulation is a stable suspension of the solid fungicide in a fluid ready for dilution with water before use. Solid particles are suspended in the aqueous phase due to an anionic dispersant-wetting agent with a polymeric viscosity stabilizer. All the reagents used were of analytical grade.

2.3 Adsorbent characteristics

The adsorbent used was a commercial organoclay, Cloisite 20 A, obtained by the modification of natural montmorillonite with a micelle of quaternary ammonium salts. The modification process and the main properties of the adsorbent have been discussed in detail by Suciu and Capri (2009)

2.4 Laboratory studies

2.4.1 Pesticide adsorption

Pesticide adsorption on the substrate was conducted using a batch equilibrium technique. The adsorbent (20 mg) was treated with a pesticide solution (10 mL) at increasing concentrations. The concentrations of fungicides ranged from 16 to 24 mg L^{-1} for cyazofamid and from 5 to 25 mg L^{-1} for penconazole. Subsequently, the suspensions were shaken at 20±2°C for 3 h and centrifuged at 5,000×*g* for 15 min. Preliminary experiments revealed contact for 3 h to be long enough for equilibrium to be reached. After centrifugation, the suspensions were filtered using glass microfiber filters of 1.6-µm pore size, and an aliquot of solution (1 mL) was transferred to vials for analysis by high-performance liquid chromatography (HPLC). The chromatographic parameters of the method have been described by Suciu and Capri (2009). The wavelength used for the detection of cyazofamid was 290 nm and of penconazole was 220 nm. The retention time was 17.5 min for cyazofamid and 15.9 min for penconazole. The instrumental limit of detection for both analytes was 20 µg L^{-1}. The amounts of pesticide sorbed by Cloisite 20 A were determined from the difference in pesticide concentrations between the initial solution and the equilibrium solution.

Data were fitted to the Freundlich sorption isotherm: $q_e = K_F C_e^{\frac{1}{n}}$; where q_e is the amount of solute adsorbed per unit weight of adsorbent (milligrams per gram), C_e is the equilibrium concentration of solute in the bulk solution (milligrams per liter), K_F is the constant indicative of the relative adsorption capacity of the adsorbent (milligrams per gram), and $1/n$ is the constant indicative of the strength of the adsorption.

2.4.2 Mass balance in batch experiments

The Freundlich equation for mass balance was employed as in Suciu and Capri (2009):

$$\frac{M}{V} = \frac{(C_0 - C_e)}{q_1} = \frac{(C_0 - C_e)}{q_e} = \frac{(C_0 - C_e)}{K_F C_e^{\frac{1}{n}}} \tag{1}$$

where M (grams) is the amount of adsorbent and V (liters) is the pesticide solution volume. C_0 and C_e represent the initial and equilibrium pesticide concentrations, while K_F and $1/n$ are the experimentally determined Freundlich coefficients.

This equation was selected to predict the final pesticide concentration *(C_1)* of a volume V (liters) with an initial pesticide concentration *(C_0)* for a known amount of adsorbent M (grams). Under equilibrium conditions, the final pesticide concentration *(C_1)* became the concentration at equilibrium.

2.5 Pilot adsorption plant

2.5.1 Design and management

A pilot adsorption plant was developed, which included two parts—the first, where the adsorption takes place, and the second, where the adsorbent is separated from the suspension. The first part comprised a 120-L plastic tank, where the pesticide solution is added to the adsorbent. Subsequently, with an electric pump, the suspension is pumped in a closed-tube circuit that starts and finishes in the plastic tank. This operation allows the agitation and hence full contact of the pesticide solution with the adsorbent. At the end of the adsorption process, the suspension is pumped into the second part of the depuration system, a skimmer, where the clay particles are separated from the suspension in the form of foam. Foam fractionation has the capacity to remove dissolved organic compounds, proteins, and small-sized particles from waste water (Qu et al. 2009). The skimmer is a cyclonic countercurrent system, in which scum is trapped at the top and water is discharged from the bottom of a closed cylinder. The production of microbubbles is performed by the Venturi pump of the system, the "skimmer", similar to analogous systems used in aquaculture that allows also the control of output of the trapped scum. The water discharged at the bottom of the cylinder is recovered in the plastic tank and subsequently recirculated to the skimmer system until no foam formation is visible. During the entire process, the foam is recovered under gravity in a 10-L plastic receptacle installed near the bottom of the skimmer cylinder (Fig. 1).

For the adsorption process, the flow of suspension in the system was equal to the maximum outflow rate of the electric pump, whereas for the adsorbent separation process, the suspension flow to the skimmer was one third of maximum outflow rate of the electric pump.

Preliminary tests revealed the use of the adsorbent as a concentrate suspension in water instead of as a powder at the beginning of the experiment considerably increased adsorbent recovery in the skimmer after adsorption.

2.5.2 Adsorption tests

The pesticide concentrations used for the adsorption test in the pilot system were one third of the average fungicide concentrations measured in the field in a previous study (Fait et al. 2007), 34 mg L^{-1} for cyazofamid and 10 mg L^{-1} for penconazole. These concentrations could simulate the worst scenario occurring in vineyards: a residual fungicide volume in the spray tank after spraying one third of the total volume utilized that, subsequently, is diluted with the water used to wash the equipment. Generally, the volume of water used to wash the spray tank is around two thirds of the

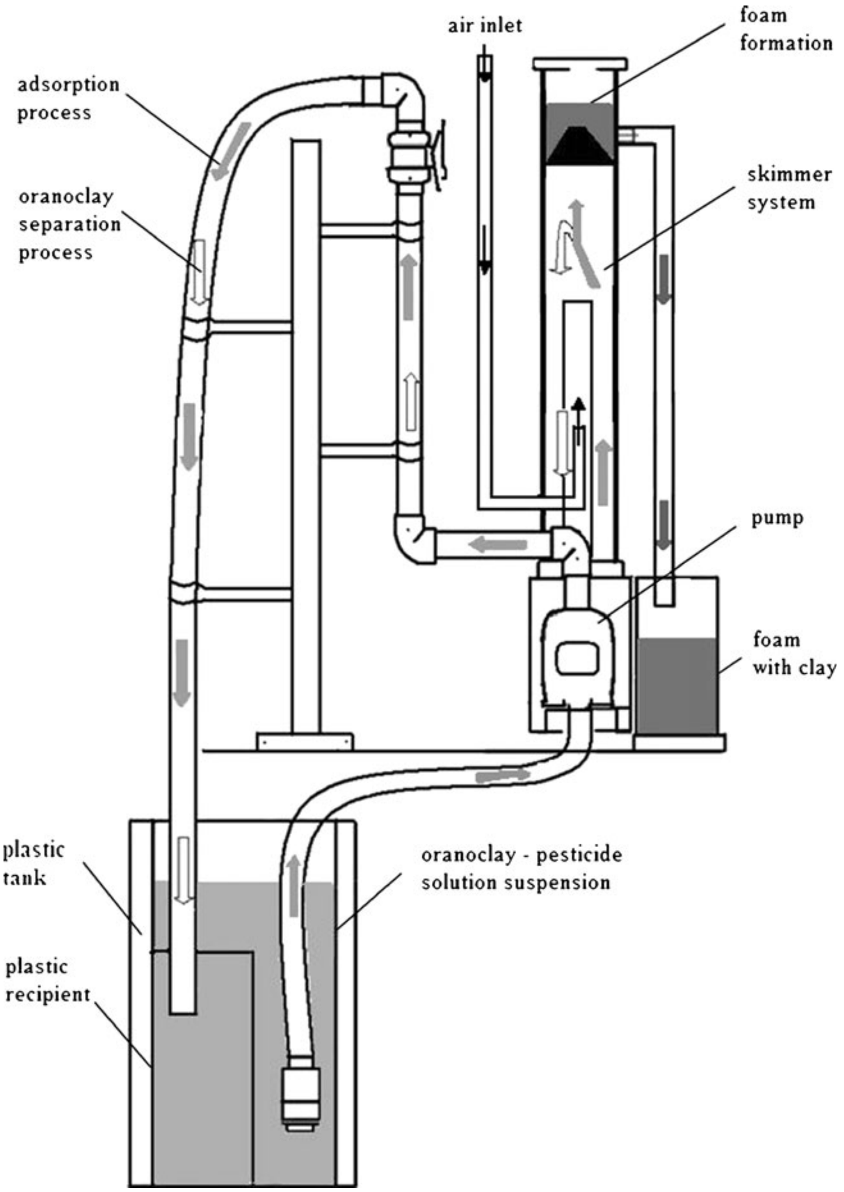

Fig. 1 Pilot system scheme

capacity of the tank. To obtain these concentrations, formulations of cyazofamid (136 mL) and penconazole (10 mL) were added to the water (98.5 L) in the tank. To obtain a complete homogenization, the pesticide-contaminated water was recirculated around the first part of the system for 5 min and then sampled (10 mL) for determination of the pesticide concentration. Subsequently, the adsorbent, as a suspension concentrate, was added to the contaminated water, and this final suspension recirculated in the system for 3 h. The concentrate adsorbent suspension was obtained by shaking for 15 min the powder adsorbent (100 g) with water (1.5 L) in a 2-L glass receptacle. At suitable time intervals, the suspension was sampled (10 mL), filtered, and the filtrate analyzed for the remaining pesticide concentration by high-performance liquid chromatography. The initial pesticide concentrations were finally calculated considering the total volume of the contaminated water (100 L). The environmental temperature was 26.8±1.8°C for the adsorption test with cyazofamid and 22.7±1.4°C for that with penconazole (http://www.arpa.emr.it/sim/?osservazioni_e_dati/dexter).

2.5.3 Organoclay separation and quantification

At the end of the adsorption process, the suspension was recirculated in the skimmer system until foam formation stopped. The foam collected in the plastic receptacle was left to liquefy for 2 h, and then, to quantify its organoclay content, the liquid concentrate suspension was mixed to obtain a homogeneous suspension, and 25% of the total volume was taken and filtered using a Bűchner funnel with weighed glass microfiber filters (1.6-µm pore size). Subsequently, the organoclay was heated for 12 h in an oven at 105°C, and the total quantity of organoclay in the system was then calculated.

2.6 Degradation system

2.6.1 Design and management

The remaining suspension volume was then used to test for possible microbial degradation of adsorbed residues. The liquid concentrate suspension was mixed to obtain a homogeneous suspension, divided into two parts, and passed under gravity through commercial compost. This compost (2 kg) was held in a 3-L plastic receptacle containing a gravel layer of 2 cm at the bottom. Holes at the bottom of the plastic receptacle, and the presence of a funnel between the first and a second plastic receptacle (5 L) placed below, permitted the collection and recovery of effluent. The gravel layer prevents the migration of small pieces of the compost. Subsequently, the recovered effluent was recirculated through the compost. At the surface of the compost, the suspension was distributed with a watering can to give a homogeneous distribution. On the first 2 days, the operation was done three times per day to allow the full deposition of clay with pesticide on the compost. Subsequently, the effluent was recirculated twice daily for 7 days, daily until the 22nd day, once every 2 days until the 60th day, and once each 4 days until the 90th day. On the 7th, 15th, 22nd, and 60th days, a volume of tap water equal to the measured volume of effluent was added to the effluent. After the seventh day, a layer of plastic foam was placed on the surface of the compost to prevent the evaporation of water. For both fungicides, the experiments were carried out in duplicate. After 2 days, a sample of the matrix was taken from each receptacle to determine the initial pesticide concentration. After this, samples were taken after 7, 15, 22, 42, and 90 days and analyzed. At the same time, a sample of effluent was taken and analyzed in order to assess potential pesticide desorption. Any increase in pesticide concentration, for both penconazole and cyazofamid, could be detected in the effluent (data not shown). The minimum and maximum daily temperatures for the period of the study are presented in Fig. 2 (http://www.arpa.emr.it/sim/?osservazioni_e_dati/dexter; web site on line the 23/11/2009).

2.6.2 Biochemical parameters

Prior to the degradation study, the compost was placed in the receptacles (six in total) and maintained wet, and after 4 days, a sample was taken from each and used to determine the total aerobe population, the organic carbon content, and the total nitrogen content of the compost. The same analyses were made at the end of the degradation study. Two compost receptacles were used as control samples.

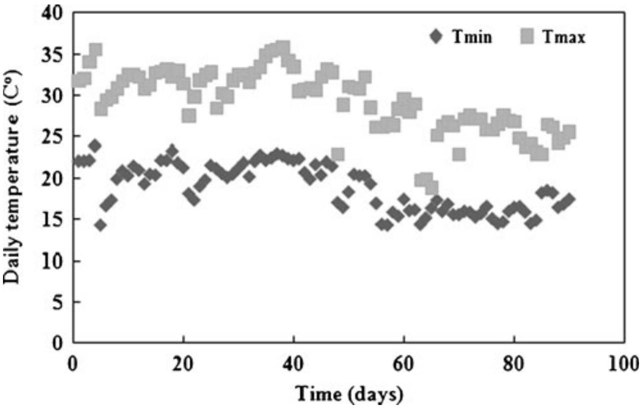

Fig. 2 Minimum and maximum daily temperatures of the degradation period

The concentration of organic C in each sample of compost was determined by the Walkley–Black procedure (Nelson and Sommers 1996); the total nitrogen (N_{tot}) was measured by the Kjeldahl method (Bremner and Mulvaney 1982). For the total aerobe population count, plating was done onto plate count agar and, after the incubation period of 72±3 h at 30±1°C, the colonies were counted (Lombardy Region 2002).

2.6.3 Pesticide extraction

Penconazole and cyazofamid were extracted from samples of the organic matrix (30±0.001 g), of which the dry matter content was determined gravimetrically after drying at 105°C for 12 h. Methanol (120 mL) was added to the organic matrix and shaken for 1 h at 180 rpm. The liquid phase was separated from the solid phase with a Bűchner filter and glass microfiber filters of 1.6-µm pore size. These steps were repeated three times; afterwhich, the liquid phases were collected and concentrated with a rotary evaporator. After filtration, the glass microfiber filters were added to the organic matrix to avoid any pesticide loss. Subsequently, methanol (up to 10 mL) was added to the concentrated phase and dried under nitrogen. The pesticides were redissolved in methanol 90:10 (*v*/*v*) methanol −0.1% H_3PO_4 water solution (5 mL) and injected in the HPLC (De Wilde et al. 2009).

2.7 Statistical analysis

For the degradation study, the linear regression model was used to evaluate the relationship between the variables of time (day) and active substance (a.s.) amount (percentage of a.s.), respectively. The amount found on the compost sampled after 2 days from application was considered to be the initial amount.

The first step was to calculate the regression curve:

$$y_1 = b_0 + b_1 x_1 \tag{2}$$

considering time as the x variable and the a.s. amount as the y variable. Using the Excel 2007 program, the b_0 and b_1 parameters were calculated:

$$b_1 = \frac{\sum xy - \frac{1}{n}\sum x \times \sum y}{\sum x^2 - \frac{1}{n}\left(\sum x\right)^2} \tag{3}$$

where n is the number of observations (in this case, n=6)

$$b_0 = \bar{y} - b_1 \bar{x} \tag{4}$$

where $\bar{y}$ and $\bar{x}$ are the averages of the variables time and a.s. amount, respectively.

Subsequently, the deviance decomposition theorem was applied:

$$\mathrm{SS_y} = \mathrm{SS_R} - \mathrm{SS_e} \tag{5}$$

The total deviance was calculated as:

$$\mathrm{SS_y} = \sum (y)^2 - \frac{\left(\sum y\right)^2}{n} \tag{6}$$

The deviance of the regression model was calculated as:

$$\mathrm{SS_R} = b_1^2 \times \left[\sum (x)^2 - \frac{\left(\sum x\right)^2}{n}\right] \tag{7}$$

and the error deviance was obtained with:

$$\mathrm{SS_e} = \mathrm{SS_y} - \mathrm{SS_R} \tag{8}$$

At this point, a significance test was applied. The first hypothesis to verify was $b_1 < 1$, with a level of significance of 99% (α=0.01). A one-tailed test was used as it was in our interest to verify that $b_1 < 0$ and not $b_1 \neq 0$.

Student's t test was applied, and a value of calculated t (t_c) higher than the value of t tabulated (t_{tab}) will indicate a value of b_1 significantly < 0. The formula used to calculate t_c was:

$$t_c = \frac{b_1 - o}{\sqrt{\frac{\frac{\mathrm{SS_e}}{n-2}}{\sum (x_i - \bar{x})^2}}} \tag{9}$$

3 Results and discussion

3.1 Pesticide adsorption in the laboratory tests

Over contact times in the range of 10–180 min, the removal efficiency of fungicide from solution (Fig. 3) increased with increasing agitation time and reached equilibrium at 60 min for penconazole and 180 min for cyazofamid. Therefore, shaking of the organoclay–water suspension for 3 h was chosen as the equilibration time.

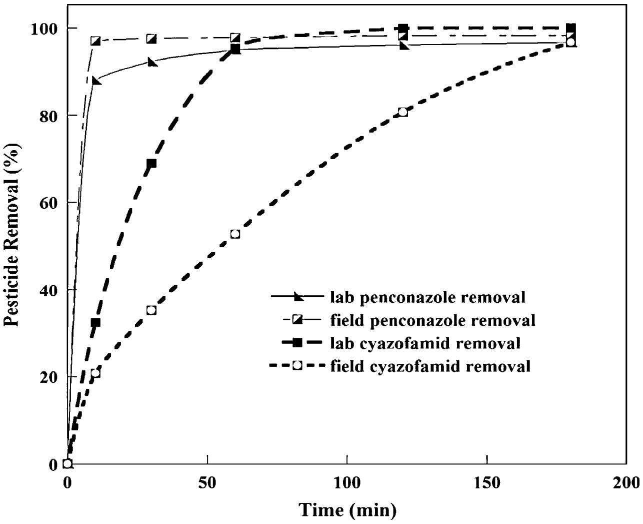

Fig. 3 Effect of contact time on fungicide sorption on Cloisite 20 A in laboratory and field tests; initial concentrations for laboratory tests were 14 mg L^{-1} for cyazofamid and 20 mg L^{-1} for penconazole

The Freundlich sorption model was fitted to the experimental sorption data (Table 1). The correlation coefficients (R^2) were 0.93 for cyazofamid and 0.99 for penconazole. Comparing the adsorption behavior of the two pesticides, the highest K_F value was obtained for cyazofamid (26.9 mg g^{-1}), though the Freundlich isotherm exponent $1/n$ was higher for penconazole. The strength of fungicide sorption on Cloisite 20 A can be explained by its aqueous solubility, as adsorption of organic compounds is generally inversely proportional to its aqueous solubilities (Giles et al. 1960). The aqueous solubility of penconazole is higher than that of cyazofamid hence making penconazole less adsorbed then cyazofamid. However, the higher $1/n$ value for penconazole indicates a higher strength of adsorption of this fungicide on Cloisite 20 A. This higher strength is in agreement with its shorter equilibrium time.

The slope ($1/n$) values of < 1 obtained for both fungicides (Table 1) indicate L-type isotherms, which are characterized by decreasing adsorption at higher concentrations; thus, sorption of both cyazofamid and penconazole on Cloisite 20 A was concentration dependent (Briggs 1981). This type of adsorption isotherm is observed when the molecules are adsorbed in a flat position, so not suffering strong competition from water molecules, which explains the high affinity to sorbent for solute at low concentrations. However, as the concentration increases, sorption sites become limiting, and therefore, sorption decreases.

Table 1 Freundlich parameters for cyazofamid and penconazole adsorption on Cloisite 20 A

Pesticide	Freundlich coefficients		
	K_F (mg g^{-1})	1/*n*	R^2
Cyazofamid	26.9	0.25	0.93
Penconazole	25.5	0.84	0.99

3.2 Pilot depuration system

3.2.1 Pesticide adsorption tests

In the fungicide adsorption tests in the pilot depuration system (Table 2), the true initial fungicide concentrations experimentally determined were 31.2 mg L^{-1} cyazofamid and 9.08 mg L^{-1} penconazole. Starting from these concentrations, after 3 h of adsorption, the removal of both cyazofamid and penconazole from the solution was 96.6%. Comparing these results with those from the mass balance in batches, the percentage of removal of both fungicides from solution is similar to that predicted from the adsorption tests in the laboratory (Table 2).

The findings of the effect of contact time on fungicide removal from contaminated water in the pilot depuration system show that the time necessary to achieve 100% of the pesticide removal was comparable in both laboratory and field trials (Fig. 3). However, comparing the trend of pesticide removal, the adsorption in the pilot system for both compounds is slower than in the laboratory. This could be explained by the differences between the solid/liquid ratios used in the laboratory and the pilot system. The solid/liquid ratio used in laboratory was 1:500 and in the pilot depuration system was 1:1,000.

3.2.2 Organoclay separation after the adsorption phase

After the adsorption phase, the organoclay was separated from the suspension (Table 3). Around 65% and 45% of the organoclay utilized in the adsorption tests of penconazole and cyazofamid, respectively, was recovered in the foam. Approximately 5% of the total adsorbent amount utilized for adsorption of penconazole and 25% of that for cyazofamid remained in the skimmed water. This higher organoclay recovery in the foam for the adsorption test with penconazole can be explained by the presence of the emulsifier agent in its commercial formulation, which determinate the formation of the foam for a longer period in the skimmer system. Therefore, a higher amount of the clay could be trapped in the foam and subsequently recovered. However, the 5% that remained in the skimmed water is due to organoclay particles smaller than 5 μm and which can be separated subsequently by sedimentation.

Table 2 Removal of fungicides by adsorption on Cloisite 20A

Fungicide	C_{0R} (mg L^{-1})	R_T (%)	R_P (%)
Cyazofamid	31.2	95.3	96.6
Penconazole	9.08	96.9	96.6

C_{0R} initial fungicide concentrations—determined experimentally, R_T fungicide theoretical removal—determined from mass balance in the batch system, R_P fungicide practical removal—determined in the pilot depuration system

Table 3 Organoclay adsorbent separation after adsorption

Fungicide	Foam (%)	Skimmer system (%)	Water after skimmer (%)
Cyazofamid	45	30	25
Penconazole	65	30	5

After the adsorption tests, the skimmer system was cleaned, with the washing water being recovered and the organoclay content quantified. Around 30% of the total organoclay utilized for adsorption, in both cases, was found to remain in the skimmer system stuck to the cylinder walls. After the adsorption test, this amount could be immediately recovered by washing the skimmer system or could be recovered later in the next adsorption cycle.

The organoclay separation from suspension in the skimmer system after absorption was shown to be dependent on the presence of surfactants in the pesticide formulation. The adsorption test with cyazofamid, formulated as a suspension concentrate, gave an organoclay separation after an adsorption of 20% lower than that found for penconazole, which was formulated as an emulsifiable concentrate.

3.2.3 Removal of the pesticide residues

For both matrices considered, compost–clay with cyazofamid and compost–clay with penconazole, a study was made of their microbial development and of the amount of fungicide left in the clay over the experimental period. Bearing in mind the chemical structure of each pesticide, the chosen experiment time was 90 days, which represents the half-life (DT_{50}) of penconazole (the more persistent of the two fungicides) under field conditions (http://sitem.herts.ac.uk/aeru/footprint/it/Reports/509.htm). It is assumed that the experiments include both chemical and biological degradations. Pesticide dissipation in similar matrices generally depends on their availability, persistence, and affinity for organic matter. In this particular case, the fungicide dissipation depends also on their affinity for the modified clay, Cloisite 20A.

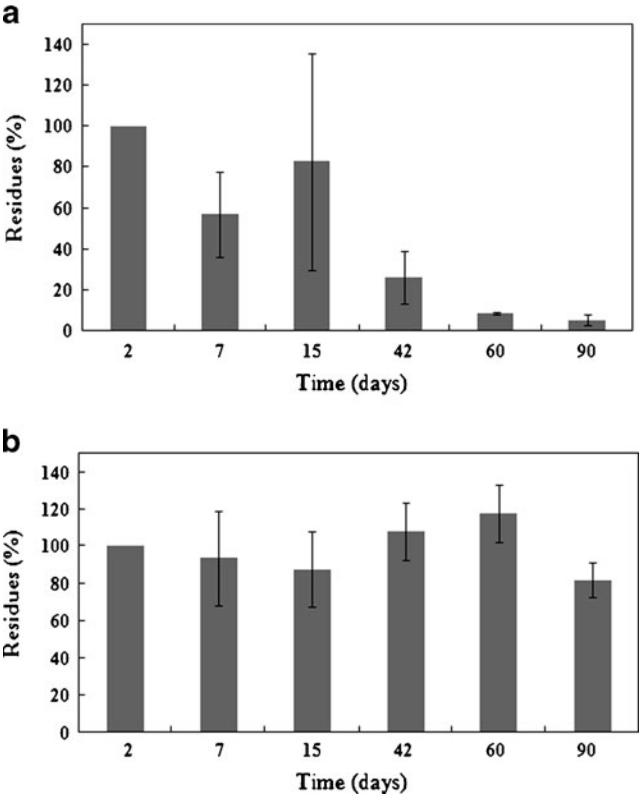

Fig. 4 Evaluation of fungicide residues in compost–clay matrices: **a** cyazofamid and **b** penconazole

Looking at the persistence of the fungicides over the 90 days (Fig. 4), the concentration of cyazofamid decreased in the matrix compost-modified clay (Fig. 4a), whereas penconazole (Fig. 4b) showed no breakdown. Such difference in their behavior could be expected as cyazofamid persistence is much lower (DT_{50} field=4.5 days) than that of penconazole; furthermore, the Freundlich adsorption coefficient $1/n$ is higher for penconazole on the modified clay, making it more strongly adsorbed and less available for degradation/dissipation.

Student's *t* test was used to verify the existence of a relationship between the level of fungicide residue on the matrices compost-modified clay and time. The Student's *t* coefficient calculated ($t_c = 4.08$) confirms the significance for the degradation of cyazofamid with a value higher than the *t* tabulated ($t_{0.05;4}=3.75; \alpha=0{,}01; n=4$), whereas for penconazole, the t_c was 0.01, confirming that no significant degradation/dissipation occurred.

Concerning the changes in compost properties during the degradation study (Table 4), a decrease in organic carbon was observed, which is the result of the mineralisation of the organic material with time. A slight increase in the total N content in the matrix containing cyazofamid and a

Table 4 Chemical characteristics of the compost matrix without clay with fungicides and with clay with fungicides

	OC (g kg^{-1})	N_{tot} (%)	C/N ratio
Initial[a]	238.9	24.1	9.9
Cyazofamid[b]	233	25.4	9.2
Penconazole[b]	216.9	21.8	9.9

[a] Values obtained at the beginning of the experiment

[b] Values obtained at the end of the experiment

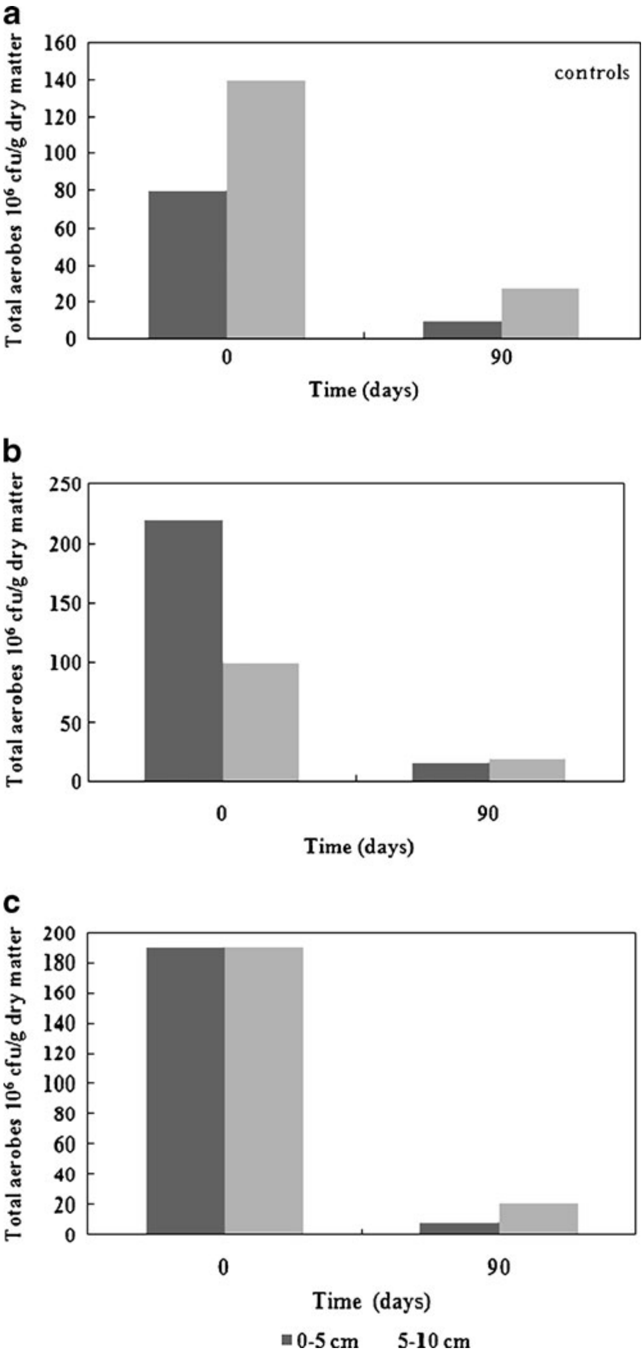

Fig. 5 Evaluation of the total aerobe population in compost matrices: **a** control (no clay with pesticide), **b** clay with cyazofamid, **c** clay with penconazole

significant decrease in the matrix containing penconazole were also observed. However, the C/N ratio of all matrices, with and without modified clay with fungicides, was low, which could be attributed to the fairly high total N content.

3.2.4 Development of the microbial population

One of the possible reasons of the low dissipation rate measured could be due to the toxic effect of the quaternary salts. With this in mind, we studied the development of the total aerobe population in the different matrices, at two depths. The first layer was between 0 and 5 cm, and the second layer was between 5 and 10 cm.

The general tendency in the microorganism populations in the controls (Fig. 5a) was a decrease in aerobes; after 90 days, the aerobes decreased approximately ninefold with respect to time 0 in the first layer and approximately fivefold in the second layer. The same tendency could be observed on the compost–clay with cyazofamid and compost–clay with penconazole matrices (Fig. 5b, c). After 90 days on the matrices containing cyazofamid, the aerobes decreased approximately 14 times with respect to time 0 in the first layer and five times in the second layer, while on the matrices containing penconazole, the decrease was even higher, 22 times in the first layer and nine times in the second layer.

The matrix used for control presents a decrease on aerobes population similar with the decrease observed on the matrix with modified clay with cyazofamid. Thus, the quaternary ammonium salt present on the modified clay does not have a toxic impact on the microbe population.

Finally, it is can be stated that mixing the modified clay after the adsorption with commercial compost and maintaining the obtained matrix under the described conditions did reduce the concentration of cyazofamid over the studied time frame; however, no removal occurred for the persistent fungicide penconazole. Thus, additional treatments still appear to be necessary in order to achieve lower concentrations that allow its disposal in the field as biomass. An improved composting process or a higher dilution in mass will allow agricultural use as required by the current legislations. If not, this organoclay will represent hazardous waste, and then, incineration rather than composting is preferable.

4 Conclusion

The depuration scheme developed showed to be efficient for decontaminating pesticide-containing water derived from vineyards. The adsorption tests in the pilot system show a removal of both pesticides similar to that predicted from the adsorption tests in the laboratory. The recovery of the modified clay after the adsorption was shown to be dependent on the presence of surfactants in the pesticide formulation. Concerning the waste disposal, for instance, the organoclay composted after the adsorption, and additional treatments appear to be necessary for persistent pesticides as penconazole. However, future decontamination research should be attempted for water contaminated with pesticides containing antifoaming agents in their formulations, in which case the present pilot system could not be applied.

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