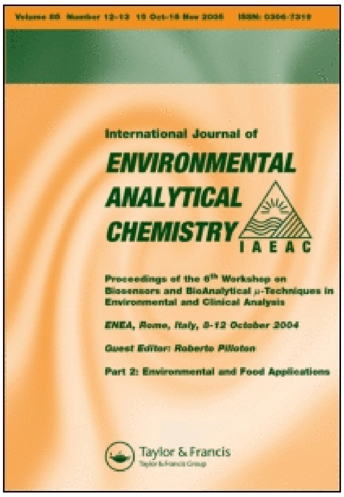

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Effect of vermicomposting process on pesticide sorption capability using agro-industrial wastes

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The aim of this work was to study the use of organic wastes from olive oil (*alperujo*), winery, and alcohol industries (vine shoots, spent grape marc, lees cake, and biosolids vinasse) as sorbents for pesticide control. The pesticide sorption capability of these organic wastes and the effect of vermicomposting process was also studied. The insecticide imidacloprid and different herbicides (diuron, metsulfuron-methyl, sulfuron-methyl, and flazasulfuron) were applied. The vermicomposting process was more effective for the agro-industrial wastes with a low lignin content. The sorption capacity of these wastes, natural or previously vermicomposted, was low for the anionic herbicides with respect to hydrophobic pesticides. Adsorption isotherms by the different wastes of confidor (imidacloprid 20% w/v) and diurokey (diuron 80% w/w) fit the Freundlich model ($R^2 > 0.933$). The larger K_f values ($231–138\,\mu g^{1/n-1} mL^{-1} g^{-1}$) correspond to the spent grape marc, untreated or vermicomposted, due to the high lignin content of this waste.

Keywords: Urea and sulphonylurea herbicides; Imidacloprid insecticide; Olive oil and winery wastes; Vermicomposting; Sorption capability

1. Introduction

The soil sorption capability of pesticides by soils is mainly governed by the organic-matter (OM) content [1]. In the Mediterranean countries, because of the low OM content, the addition of exogenous organic materials to soil can be necessary in order to increase the pesticide retention and prevent pollution of surface and ground waters [2]. Organic amendments can modify sorption and diffusion of pesticides in soil. These modifications can be related to the origin, nature, and evolution of organic wastes as well as soil and pesticide characteristics [3, 4].

On the other hand, olive oil, wine, and alcohol production are important industries in the Mediterranean countries. These industries generate a huge amount of waste, and its disposal is regarded as a serious environmental issue. The main waste from the extraction of olive oil in the 'continuous centrifugation two-phase process' is

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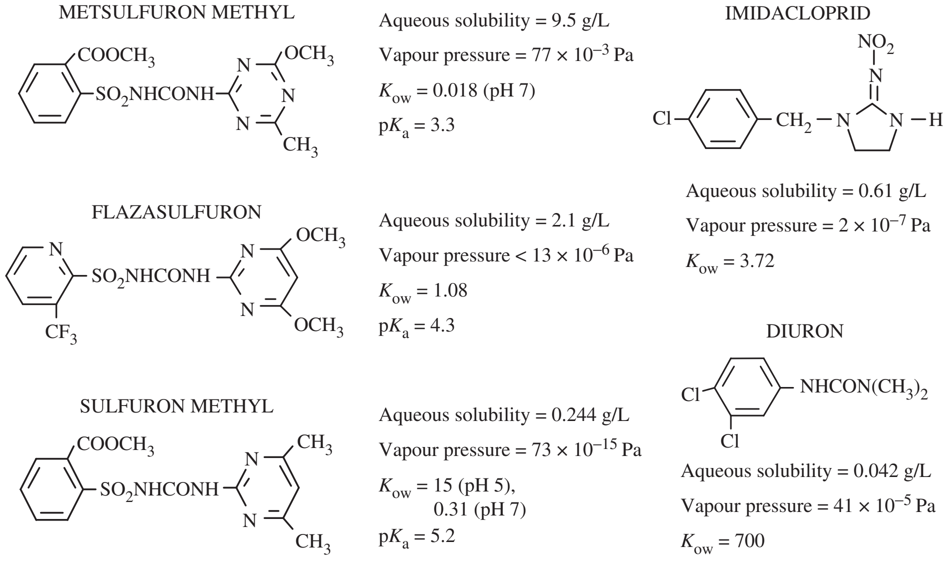
a two-phase olive-mill waste or alperujo (A). The main wastes from the winery and alcohol industries are vine shoots (VS), spent grape marc (GM), lees cake (L), and, after the depuration of vinasse, biosolids vinasse (BV). Recently, different solutions have been proposed for the efficient re-use of these wastes previously biostabilized and matured, via composting or vermicomposting, such as the addition to soils in remediation techniques or for agricultural purposes [5, 6].

The importance of composting and vermicomposting processes to stabilize and mature organic wastes [7, 8] and the advantages of the final products to improve the quality of the agricultural soils has been well documented [6, 9]. Both processes also preclude several drawbacks such as the phytotoxicity and inhibition of the soil microbiota, often observed when the organic wastes are directly added to the soil [10].

The selected pesticides, imidacloprid (I), metsulfuron-methyl (M), sulfuron-methyl (S), diuron (D), and flazasulfuron (F), belong to different chemical classes (figure 1) and have different chemical properties. The sulfonylurea herbicides (M, S, and F) control a wide spectrum of broadleaf weeds and annual grass. Their sorption by soils is generally low, with a greater leaching potential in alkaline than in acid soils [11]. Diuron is a systemic herbicide used in many crops, and imidacloprid is a systemic insecticide used to control sucking insects and soil insects [12]. Diuron, is described as a ureic herbicide with a moderate persistence in soil, and as ‘transition’ pesticide [13], with a Gustafson index [14] of 2.6. Imidacloprid, in alkaline soils with a low content of organic carbon, is described as a ‘leacher’ pesticide [15, 16]. Leaching of this chloronicotinyl insecticide in soil columns was higher when treated with formulations than with analytical grade material [17]. Furthermore, these chemicals are being used for plant protection in agriculture intensive systems, so soil and water contamination by these compounds is highly probable.



Metsulfuron methyl:
Aqueous solubility = 9.5 g/L
Vapour pressure = 77×10^{-3} Pa
$K_{ow} = 0.018$ (pH 7)
$pK_a = 3.3$

Imidacloprid:
Aqueous solubility = 0.61 g/L
Vapour pressure = 2×10^{-7} Pa
$K_{ow} = 3.72$

Flazasulfuron:
Aqueous solubility = 2.1 g/L
Vapour pressure < 13×10^{-6} Pa
$K_{ow} = 1.08$
$pK_a = 4.3$

Diuron:
Aqueous solubility = 0.042 g/L
Vapour pressure = 41×10^{-5} Pa
$K_{ow} = 700$

Sulfuron methyl:
Aqueous solubility = 0.244 g/L
Vapour pressure = 73×10^{-15} Pa
$K_{ow} = 15$ (pH 5), 0.31 (pH 7)
$pK_a = 5.2$

Figure 1. Structures and main chemical properties of the pesticides.

Previous studies with alperujo have revealed significant changes in the behaviour of pesticides when the soils were amended with this organic waste [18, 19]. Nevertheless, there is a lack of information on the use of wastes from the winery or alcohol industries, for the same purposes. In addition, the potential use of natural and vermicomposted wastes from the olive oil, winery, and alcohol industries as materials for pesticide sorption before their addition to the soils has not been methodically studied. This investigation constitutes the main objective of this paper in order to select the appropriate soil organic amendment for pesticide retention.

2. Experimental

2.1 *Chemicals*

I, M, S, D, and F, all with a purity higher than 97.5%, were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Commercial formulations of 'I' (Confidor 20% w/v from Bayer), and 'D' (DiuroKey 80% w/w from Industrial Química Key, s.a.) were also tested. Analytical-grade 96% sulphuric acid from Panreac (Barcelona) and HPLC-grade acetonitrile from Scharlau Chemie (Barcelona) were used. Water was purified with a Milli-Q water purification system (Millipore, MA).

2.2 *Wastes used as pesticide sorbents*

The vermicomposting process with *Eisenia andrei* of the different wastes described above was carried out for 8 months on a pilot-scale as reported elsewhere [7]. Four vermicomposting beds, three with wastes from winery and alcohol industries, and the fourth with the two-phase olive-mill waste, were prepared: GM: spent grape marc alone; GML: spent grape marc mixed with lees cake in a 1 : 1 ratio to increase the nitrogen content of the substrate; BVS, biosolid vinasse mixed with vine shoots in a 2 : 1 ratio to improve the structure and C/N ratio; and AM, alperujo mixed 4 : 1 with manure. These initial substrates and their corresponding vermicomposts were assayed as pesticide sorbents.

pH, total organic carbon (TOC), total extractable carbon (TEC), humic acids (HA), fulvic acids (FA), total Kjeldahl nitrogen (TKN), total polyphenols, and total lignin were determined using validated methods [20–22] in the initial substrates and their vermicomposts. Analytical results are shown in table 1.

2.3 *Chromatographic analysis*

An Agilent (Germany) Series 1100 liquid chromatograph equipped with a diode-array detector was used. A Zorbax Rx-C8 150 × 2.1 mm i.d. analytical column packed with diisopropyl *n*-octyl (5 μm) and a guard cartridge Eclipse XDB-C8 (12.5 × 2.1 mm i.d.), packed with the same material were used. The operating conditions were: mobile phase, acetonitrile : sulphuric acid 0.005 M (pH 3) (45 : 55 v/v); flow rate 0.2 mL min^{-1}; column temperature 40°C; detection wavelengths, 270 nm for I, 237 nm for M, S, and F, and 254 nm for D; injection volume 10 μL. Stock solutions of I (431.64 μg mL^{-1}), M (398 μg mL^{-1}), S (47.76 μg mL^{-1}), D (417.3 μg mL^{-1}), and F (51.48 μg mL^{-1}) in acetonitrile were prepared. The retention times for I, M, S,

Table 1. Some characteristics of the organic sorbents.

Sorbents	pH	TOC ($g\,kg^{-1}$)	TEC ($g\,kg^{-1}$)	HA ($g\,kg^{-1}$)	FA ($g\,kg^{-1}$)	C/N	HR[a] (%)	Polyphenol ($g\,kg^{-1}$)	Lignin ($g\,kg^{-1}$)
GM	6.4	475	33	2.6	29.9	25	7	2.9	502
GML	6.3	492	61	15	45.5	25	12	6.7	447
BVS	6.3	482	64	16	48.5	17	13	17.7	168
AM	6.6	483	227	86	141	38	47	19.3	200
GM-V[b]	6.8	344	62	35	27.5	22	18	1.0	434
GML-V[b]	7.3	280	96	65	42.3	14	34	1.2	372
BVS-V[b]	7.3	295	247	146	101	11	84	1.2	255
AM-V[b]	8.6	292	201	75	126	15	69	1.3	200

[a] HR: humification rate = TEC/TOC × 100. [b] V: vermicomposted.

D, and F were 2.95, 4.35, 4.85, 5.92, and 7.13 min, respectively. The calibration graph, from triplicate injection of six calibration solutions in Milli-Q water at 5, 2.5, 1, 0.5, 0.25, and 0.1 $\mu g\,mL^{-1}$, obtained by the least-squares method, were linear over the concentration range tested ($R^2 > 0.999$). The peak symmetry was higher than 0.73, and the resolution calculated ($R_s > 2.07$) gives an indication of optimum separation. The relative standard deviation (RSD) obtained for seven injections on different days, for a standard solution containing all the pesticides at 0.25 $\mu g\,mL^{-1}$, were $0.27 \pm 2.35\%$, $0.27 \pm 0.67\%$, $0.26 \pm 0.80\%$, $0.26 \pm 0.50\%$, and $0.27 \pm 2.35\%$, respectively.

2.4 *Sorption experiment*

To determine the sorption capability of the initial substrates and the vermicomposts, 0.5 g of each one, air-dried and ground, was placed into 50 mL glass tubes and added to 20 mL of an aqueous standard solution containing 2 $mg\,L^{-1}$ of each pesticide. The tubes were agitated on a rotary shaker for 24 h at $15 \pm 1°C$ to achieve equilibrium, centrifuged at 3000 rpm for 20 min, and the supernatant filtered on 0.45 μm membranes for analysis by HPLC. The standard solution containing all the pesticides was run in parallel as a control. The amounts of pesticide adsorbed were calculated from the difference between the supernatant concentration in each sample and the control. This process was repeated twice. Blanks not containing pesticide were used for each waste. Under the same conditions, sorption isotherms at 0.6, 1.2, 2.5, and 5 $mg\,L^{-1}$ using two commercial formulations of the pesticides, which showed the highest sorption capacities, were carried out.

3. Results and discussion

The vermicomposting process significantly altered the physical and chemical properties of different assayed substrates (table 1) due in part to the growth and reproduction of *E. andrei* in each substrate. The peak biomass in the growth curve of the earthworms followed the sequence: AM (116 $g\,kg^{-1}$ in the fourth month) > BVS (68 $g\,kg^{-1}$ in the third month) > GML (50 $g\,kg^{-1}$ in the second month), and finally GM (13 $g\,kg^{-1}$ in the second month). A low biomass was recorded after 8 months of vermicomposting in all organic substrates assayed. The lower efficacy observed in the substrates, GM and GML, would be attributed to the presence of high contents of recalcitrant compounds, as lignin, which makes the optimum development of the inoculated earthworms and the adequate biotransformation of these substrates difficult.

Vermicomposting causes an increase in pH values and a reduction in TOC content (table 1). The loss of TOC, due to OM mineralization in each waste, was as follows: GM-V (27%), GML-V (43%), BVS-V (38%), and AM-V (39%). The TEC and HA values increased after vermicomposting, except in the AM waste. As a consequence of these changes, the vermicomposted products showed a lower C/N ratio and higher humification rate (HR), which would imply a higher degree of stability, humification, and polimerization of the OM contained in these final products [7, 23]. The polyphenols were reduced in the vermicomposted products, showing the high effectiveness of this process to degrade these kinds of toxic compounds. The total lignin content decreased in GM-V and GML-V, whereas an increase in this compound was observed in BVS-V.

Figures 2(a) and 2(b) show the adsorbed pesticide percentages for the initial substrates and the vermicompost products. In the initial substrate, the higher percentages correspond to the non-ionic pesticides imidacloprid and diuron, with the lowest water solubility. In contrast, lower percentages were found in the anionic sulphonylurea herbicides (M, S, and F). According to the Henderson–Hasselbach concept, this behaviour can be attributed to the pK_a values of these pesticides (figure 1) with pH values of 6.3, equivalent to the values of the non-vermicomposted wastes (table 1); the S and F molecules remain around 10% and 1% undissociated; and metsulfuron-methyl is completely dissociated. At higher pH values, as in the final products (table 1), all these herbicide molecules are expected to be completely dissociated, with a subsequent decrease in percentage sorption (figure 2b). On the other hand, the competitive sorption of water molecules by the soil from the solution can

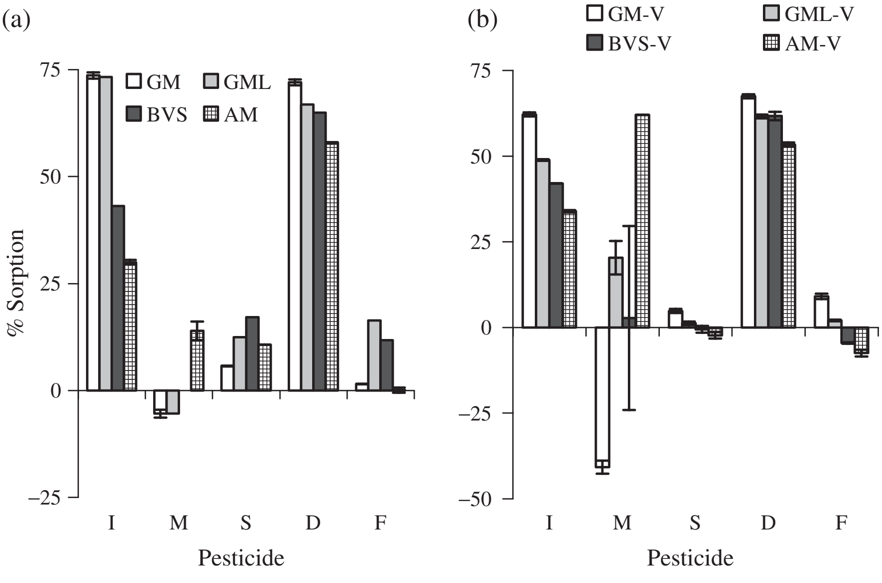


Figure 2. (a) Sorption percentages of imidacloprid (I), metsulfuron-methyl (M), sulfuron-methyl (S), diuron (D) and flazasulfuron (F) by the initial substrates and (b) their correspondent vermicomposts.

contribute to the negative sorption observed. The large standard deviation and the negative values in the sorption of metsulfuron-methyl (figure 2b) can also be explained by the appearance of an interference peak at 4.4 min in the chromatogram of the standard solution containing all the pesticides. This peak shows a similar UV spectrum to that obtained for the flazasulfuron molecule. Studies of the stability of the standards of I, M, S, D, and F in aqueous solution confirm the degradation of flazasulfuron with the presence of a metabolite at 4.4 min with the same UV spectrum of the interference peak.

Figures 3(a) and (b) show the sorption isotherms in the initial substrates and vermicomposted products used as sorbents of confidor (CF) and diukorey (DK), two formulations of I and D pesticides which showed the highest affinity for tested organic sorbents. Sorption isotherms fit well with the Freundlich model (equation (1)); the corresponding data are shown in table 2.

$$X = K_{\mathrm{f}} Ce^{1/n}. \qquad (1)$$

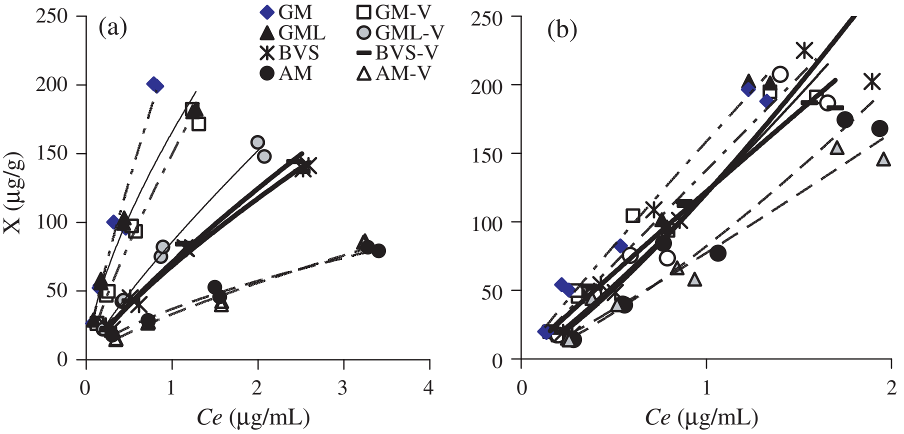


Figure 3. Amount sorbed (X) of (a) confidor and (b) diurokey at the corresponding equilibrium concentrations (*Ce*) by the initial substrates and their correspondent vermicomposts.

Table 2. Freundlich sorption coefficients (K_{f} and $1/n$), the determination coefficient and normalized K_{oc} values for the sorption of confidor and diurokey in the initial substrates and the vermicomposted products.

	Confidor (CF)				Diurokey (DK)			
Wastes	K_{f}[a] ± SE	$1/n$ ± SE[b]	R^2	K_{oc}	K_{f}[a] ± SE	$1/n$ ± SE[b]	R^2	K_{oc}
GM	231 ± 18.49	0.83 ± 0.05	0.980	486	158 ± 19.35	0.94 ± 0.09	0.956	333
GML	166 ± 8.92	0.67 ± 0.03	0.984	337	147 ± 7.91	1.28 ± 0.05	0.988	299
BVS	62 ± 3.14	0.78 ± 0.05	0.973	129	121 ± 12.18	1.24 ± 0.12	0.948	251
A + M	37 ± 0.85	0.63 ± 0.02	0.990	77	82 ± 5.79	1.29 ± 0.09	0.971	170
GM-V	149 ± 4.76	0.83 ± 0.02	0.995	433	138 ± 10.80	0.99 ± 0.07	0.972	401
GML-V	86 ± 1.27	0.83 ± 0.02	0.998	307	121 ± 8.87	1.15 ± 0.08	0.975	432
BVS-V	71 ± 1.63	0.82 ± 0.03	0.994	241	122 ± 7.47	0.96 ± 0.06	0.978	414
AM-V	33 ± 1.04	0.76 ± 0.04	0.985	113	77 ± 0.79	1.09 ± 0.12	0.933	264

[a] Units of $K_{\mathrm{f}} = (\mu g^{1/n-1}\,mL^{-1}\,g^{-1})$. [b] SE: standard error of the mean.

Confidor gave sorption L-type isotherms ($1/n < 1$), while DK described C-type ($1/n \sim 1$) and S-type ($1/n > 1$) isotherms according to the Giles classification [24]. In general, the sorption capacity of both untreated and vermicomposted organic wastes, assessed from K_f values, follows the order: GM > GML > BVS > AM; confidor showed greater differences for K_f values.

Sorption of confidor by vermicomposts decreased 35%, 48% and 16% respective to the initial substrates GM, GML and AM, respectively. However, there was an increase of 14% in the case of BVS-V. These changes were lower for diurokey (table 2). The reductions in K_f values could be related to the decrease in TOC values (table 1) as described by other authors [3]. However, in the vermicompost BVS-V, the K_f values increased; thus, one must consider the increments obtained in the HA, FA and lignin contents. Since the TOC content of these wastes is similar, the dispersion of K_{oc} values, determined as $K_{oc} = K_f / \mathrm{TOC} \times 100$, ranged to the same extent as K_f [25].

Correlations between K_f values and chemical parameters of these wastes, untreated or vermicomposted (given in table 1), reveal a significant negative correlation with FA, and more significant for DK ($r = -0.88$, $p < 0.01$) than for CF ($r = -0.75$, $p < 0.05$). Nevertheless, there is no significant correlation with the HA fraction nor with the humification rate (HR). K_f values also correlate negatively with the TEC ($r = -0.74$ (CF), $r = -0.77$ (DK), $p < 0.05$) and indicate the inverse relationship between the pesticide sorption and the dissolved organic carbon content. The TOC content, polyphenols content, and C/N ratio were not correlated significantly. Significant positive correlations were obtained with lignin content for CF ($r = 0.93$, $p < 0.01$) and DK ($r = 0.83$, $p < 0.05$), which explain 86% and 68% of the variability in K_f, respectively.

The humification rate (table 1) indicated the formation of humic-like susbstances during vermicomposting. The sorption capacity of hydrophobic pesticides increases with the humification degree of soil OM or the evolution of exogenous OM added to the soils [3]. This increase in pesticide sorption with the humification degree was not observed, except for confidor in BVS-V (table 2). The extent of sorption is also related to the composition, structure, and functional properties of the humic-like substances in composts and vermicomposts [4].

On the other hand, the lignin content in all cases is higher than HA or FA. The surface area due to the degree of polycondensation of this material and the presence of a variety of functional group with different reactivity, like aromatic ring bearing polyphenols, hydroxyl constituents, carbonyl, etc. [26], could explain the significant relationship obtained in the confidor and diurokey sorption. In fact, pesticides can be incorporated into lignin and form unextractable residues that resist solubilization [26, 27]. This supports the greater sorption capacity of these pesticides by GM and GML that have lignin contents of $502\,\mathrm{g\,kg^{-1}}$ and $447\,\mathrm{g\,kg^{-1}}$, respectively. The lower K_f values in the vermicomposts GM-V and GML-V could be attributed to the loss during vermicomposting of lignin (14% and 17%, respectively) and total organic carbon (TOC) (27% and 43%, respectively).

The initial substrates BVS and AM show a lower lignin content (168–$200\,\mathrm{g\,kg^{-1}}$) and consequently lower K_f values. Nevertheless, after vermicomposting, there is an increase in K_f values for confidor in BVS-V, which was not observed for diurokey. In both cases, the loss of TOC (38–39%) cannot be the only explanation for this sorption behaviour. For confidor, the increment in BVS-V can be related to the increase in TEC, HA, FA, and lignin content. In the case of AM-V, the lignin content remains constant after vermicomposting, and the slight reduction observed in the K_f values for both pesticide formulations can be due to the lower TEC, HA, and FA recorded in this vermicompost.

The humification process of these wastes in soil could modify the sorption capacity of these pesticides. Thus, the evolution of these wastes in the amended soil, previous to the addition of the pesticides, will also be studied.

4. Conclusions

The vermicomposting process was more effective for agro-industrial wastes with a low lignin content. The sorption capacity of wastes from olive oil, winery, and alcohol industries, natural or previously vermicomposted, were low for the anionic herbicides with respect to hydrophobic pesticides. Non-ionic pesticides are retained mainly in the lignin fractions of these wastes.

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