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Removal of imidacloprid from polluted water using adsorption and membrane separation technologies

Mohannad Qurie[a], Mahmoud Alkhatib[b], Sabino Aurelio Bufo[c], Laura Scrano[d], Mustafa Khamis[e], Ibrahim Ayyad[f], Rafik Karaman[f,*]

[a]*Department of Earth and Environmental Sciences, Al-Quds University, Jerusalem, Palestinian Authority, Tel. +972598721021; email: mqurie@staff.alquds.edu*
[b]*Department of Chemistry and Chemical Technology, Al-Quds University, Jerusalem, Palestinian Authority, Tel. +972569920550; email: mkhatib@staff.alquds.edu*
[c]*Department of Science, University of Basilicata, Via dell'Ateneo Lucano 10, 85100 Potenza, Italy, Tel. +393293606251; email: sabino.bufo@unibas.it*
[d]*Department of European Cultures (DICEM), Via dell'Ateneo Lucano 10, 85100 Potenza, Italy, Tel. +393204371066; email: Laura.scrano@unibas.it*
[e]*Department of Biology, Chemistry and Environmental Sciences, American University of Sharjah, Sharjah, UAE, Tel. +971566379288; email: mukhamis@yahoo.com*
[f]*Faculty of Pharmacy, Department of Bioorganic Chemistry, Al-Quds University, Jerusalem, Palestinian Authority, Tel. +972597135199; emails: dr_karaman@yahoo.com (R. Karaman), ibrahimayyad86@yahoo.com (I. Ayyad)*

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ABSTRACT

In this work, the stability of imidacloprid in fresh water and sludge was studied. The results revealed that the pesticide is unstable in both media. In fresh water, it underwent hydrolysis whereas a degradation to several metabolites has been observed in sludge. The rate constants for the hydrolysis and degradation at 25°C were 0.0.0067 and 0.0.0099 d^{-1}, respectively. Monitoring the degradation of imidacloprid in sludge by high-pressure liquid chromatography-mass spectrometry (HPLC-MS) revealed that five metabolites have emerged during the study. These metabolites include imidacloprid urea, imidacloprid-guanidine, 6-hydroxynicotinic acid, an olefin, and 5-hydroxy, 1-(6-chloro-3-pyridylmethyl)-2-(nitroimino)-imidazolidin-5-ol. The efficiency of Al-Quds University Wastewater Treatment Plant towards the removal of imidacloprid indicates that the ultrafiltration-hollow fiber unit was insufficient, whereas the ultrafiltration-spiral wound, activated carbon, and reverse osmosis units were efficient for complete removal of the pesticide. Adsorption experiments of imidacloprid using either activated charcoal or micelle-clay complex were found to fit Langmuir isotherms better than Freundlich isotherm. The data demonstrate a higher Langmuir Q_{max} value for the activated charcoal (126.6 mg g^{-1}) when compared to the micelle-clay complex (11.76 mg g^{-1}). Filtration column experiments conducted with mixed micelle-clay complex and sand (using a ratio of 1/50 by mass) at a flow rate of 2 mL min^{-1} and influent concentration of 50 mg L^{-1} revealed that a sufficient removal of imidacloprid was achieved in the first fraction of 100 mL elution. These findings indicate that the adsorption technology using the micelle-clay complex provides efficient removal of imidacloprid in continuous flow mode.

Keywords: Charcoal; Imidacloprid; Pesticides; Langmuir isotherm; Freundlich isotherm; Micelle-clay complex

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* Corresponding author.

1. Introduction

The growth of population and intensive work in agriculture have drastically enhanced the use of pesticides in developing countries [1]. During the past few decades, new types of pesticides have emerged and consequently, a dramatic increase in pesticide consumption has been reported. The use of pesticides in agriculture and household results in the direct release of these entities to the environment [2]. This leads to contamination of the surface and groundwater through point and non-point sources [3]. The used pesticides follow several pathways: degradation, adsorption, and movement or transport with soil and water. Pesticides can undergo biotic (microorganism actions) and abiotic (chemical and photodegradation process) degradation [4].

Imidacloprid, 1-(6-chloronicotinyl)-2-nitroiminoimidazolidines, is the first commercial synthetic neonicotinoid [5]. Imidacloprid is a potent insecticidal that is effective against sucking pest and soil pests [6]. Imidacloprid acts as a Nicotinic Acetylcholine Receptor (nAChR) agonist. Imidacloprid's ingestion or exposure leads to the disrupting of the nervous system of an insect or pest [7]. Imidacloprid is a water-soluble compound with 514 mg L^{-1} solubility, low Koc (adsorption coefficient, which describes the tendency of a pesticide to bind to soil particles) of 132–310 mL/g [8], and is moderately adsorbed by soil. Due to these factors, imidacloprid may leach to groundwater and become immobile in silt loam soils [9].

Imidacloprid was found to be stable in acidic and neutral water, but more readily hydrolyzed in alkaline water, and it has been detected in Florida's surface water at concentrations in the range of 2.59 and 2.33 μg L^{-1} in surface and groundwater, respectively [10,11]. It should be worthy of note to indicate that imidacloprid is effective at low doses such as 0.3 mg L^{-1} [12].

Imidacloprid was found to affect human health at low concentrations. For example, it was documented that imidacloprid can cause drowsiness, dizziness, vomiting, disorientation, and fever upon humans' exposure [13]. Furthermore, exposure to high doses of imidacloprid can cause uncoordinated gait, tremors, and a reduction in the activity of animals [14]. Moreover, it documented that imidacloprid is absorbed by plants and is transferred to the plant system, thus causing poison to insects and humans who digest plants [15].

Several techniques have been proposed for the removal of pesticides. They include physical methods such as nanofiltration [16] and activated carbon adsorption [17], chemical methods such as ozonation [18], aqueous chlorine [19], Fenton and photocatalytic destruction [20,21,30], biological treatments [22], advanced oxidation processes [23], aerobic degradation [24], and adsorption [25–27]. Furthermore, the removal of three pesticides (imidacloprid, chlorpyrifos, and malathion) from simulated wastewater by electrocoagulation approach utilizing iron electrodes [28,29]. Otherwise, the removal of imidacloprid was reported by several methods such as advanced oxidation based on the photo-Fenton process [20,21,30], heat-treated kerolites [31] adsorption on powdered and magnetic-activated carbon [32].

The objectives of this work were to investigate the removal efficiency of imidacloprid by octadecyltrimethylammonium (ODTMA) micelle-clay complex and membrane separation technology. Furthermore, the stability and the kinetics of this pesticide in fresh water and sludge were studied as well.

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade. The clay used was Wyoming Na-Montmorillonite SWy-2 obtained from the Source Clays Registry (Clay Minerals Society, Colombia, MO). ODTMA bromide was obtained from Sigma-Aldrich (USA). Quartz sand (grain size 0.8–1.2 mm) was obtained from Negev Industrial Minerals (Israel). Imidacloprid from high purity was purchased from HPC Company (Germany). Activated charcoal (12–20 mesh) was obtained from Sigma (Sigma Chemical Company, USA). Deionized water was used to prepare all solutions. Methanol, acetonitrile, and water were high-pressure liquid chromatography (HPLC) grade and purchased from Sigma-Aldrich (USA). Magnesium sulfate was purchased from Sigma-Aldrich (USA).

2.2. Instrumentation

The high-pressure liquid chromatography-photodiode array (HPLC-PDA) system consists of an Alliance 2695 HPLC from (Waters Company: Milford, MA, USA), and a Waters Micromass® MassLynx™ Detector with photodiode array (Waters 2996: Milford, MA, USA). Data acquisition and control were carried out using Empower Software (Waters Company: Milford, MA, USA). Analytes were separated on a 4.6 mm × 150 mm C18 XBridge® column (5 μm particle size) used in conjunction with a 4.6 mm × 20 μm XBridge™ C18 column. Microfilter was used with 0.45 μm (Acrodisc® GHP, Waters Company, Milford, MA, USA). pH meter model HM-30G: TOA Electronics™ was used to measure the pH value for the samples. C18 (1 g) cartridges with 6 cc capacity and were purchased from Waters Company (Milford, MA, USA).

The identification of metabolites was performed using a liquid chromatography (LC) system coupled to a hybrid linear quadrupole ion trap – Fourier-transform ion cyclotron resonance-mass spectrometry (FTICR-MS) (Thermo Fisher Scientific, Bremen, Germany) in an extracted ion chromatogram (XIC) mode. The benefit of using very selective extracted ion chromatograms by FTICR MS generated with a tight mass-to-charge ratio window of ±0.0010 units around each selected protonated molecule (i.e., $[M+H]^+$ ±1.0 mDa), greatly reduced the signal complexity of the total ion current trace. The Wastewater Treatment Plant (WWTP) at Al-Quds University was described previously [33]. The WWTP at Al-Quds University collects a mixture of black, grey, and storm water. The treatment plant consists of primary treatment and secondary treatment (activated sludge with a hydraulic retention time of 16–20 h, coagulation, and chlorination). The secondary effluent is introduced into a sand filter before entering the ultrafiltration (UF) membrane (hollow fiber and spiral wound). After the UF process, the effluent is subjected to an activated carbon adsorbent followed by reverse osmosis (RO) (advanced treatment stage).

The UF process consists of two small-scale membrane treatment plants with a capacity of 12 m^3 d^{-1}. The first UF unit is equipped with two 2 × 4-inch pressure vessels with pressure resistance up to 150 psi. Each vessel holds two separation membranes (spiral wound with 20 kDa cut-off, equivalent to a 0.01 μ separation rate, Nirosoft, Israel). The designed permeate capacity of the system is 0.5–0.8 m^3 h^{-1}. This membrane can remove bacteria, suspended solids, turbidity agents, oil, and emulsions. The second unit is equipped with two pressure vessels made by Vendor (AST Technologies Model No. 8000 WW 1000-2M, Israel) that houses the hollow fiber (HF) membranes with 100 kDa cut-off (Vendor, AST Technologies, Model No. 8000-WWOUT-IN-8080, Israel). The two units are designed to deliver 1.5 m^3 h^{-1}. The RO system consists of a 1 × 4-inch pressure vessel constructed with composite material having a pressure resistance of up to 400 psi. The vessel holds two 4 inch special separation membranes (thin polyamide film with pH range 1–11, Model BW30-4040 by Dow FilmTec, USA). A membrane anti-scale (product NCS-106-FG) solution of phosphoric acid disodium salt is continuously dosed to the RO feed at a concentration of 4 mg L^{-1} to prevent deposition of divalent ions. The system is designed to remove major ions and heavy metals. The designed RO permeate capacity of the system is 0.45–0.50 m^3 h^{-1}.

2.3. Methods

2.3.1. Preparation of micelle-clay complex

The micelle-clay complex was prepared as described elsewhere [34]. Briefly, the micelle-clay complex was prepared by stirring 12 mM of ODTMA with 10 g L^{-1} clay for 72 h. Suspensions were centrifuged for 20 min at 15,000 rpm, supernatants were discarded, and the complex was lyophilized. The micelle-clay complex contains the cationic surfactant, ODTMA which contains an alkyl chain of 18 carbon atoms; its critical micelle concentration is 0.3 mM. The micelles, which include several tens to about several hundred molecules, are in the nanometer range, whereas the clay platelets have a thickness of the order of a nanometer and a typical area of the order of 1 μm^2. The complex exhibits excess positive charge and differs from complexes formed between clay and monomers as shown by X-ray and freeze-fracture electron microscopy [35].

2.3.2. Batch adsorption experiments

Batch adsorption experiments were carried out for solutions of imidacloprid in the concentrations range of 100–700 mg L^{-1}. Experiments were performed in 100 mL Erlenmeyer flasks containing 0.125 g of either micelle-clay complex or activated charcoal. 25 mL of imidacloprid solutions having known initial concentration were then introduced to each flask. The flasks were shaken in an electric shaker for 3 h at 25°C, and then the content of each flask was centrifuged for 5 min and filtered using 0.45 μm cellulose nitrate filters. The equilibrium concentration of the pesticide was measured by the HPLC method as described in Section 2.8 – Sample, standards preparation and chromatographic conditions.

2.4. Adsorption isotherms

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. The two common adsorption models which are generally used are Langmuir and Freundlich adsorption isotherms. The first one is widely used for modeling equilibrium data and adsorption capacity determination. Eq. (1) illustrates its linear form:

$$\frac{C_e}{Q_e} = \frac{1}{\left(KQ_{\max}\right)} + \frac{C_e}{Q_{\max}} \tag{1}$$

where C_e: equilibrium concentration of adsorbent (mg L^{-1}); Q_e: equilibrium mass of adsorbent per gram of adsorbate (mg g^{-1}); K: Langmuir constant (L mg^{-1}); $Q_{\max}$: the maximum mass of adsorbent removed per gram of adsorbate (mg g^{-1}).

Freundlich isotherm describes equilibrium on the heterogeneous surface and its linear form is given by:

$$\log q_e = \log k + \frac{1}{n}\log C_e \tag{2}$$

where C_e: equilibrium concentration of solute (mg L^{-1}); q_e: the amount of solute adsorbed per unit mass of adsorbent (mg g^{-1}); k: Freundlich constant (mg g^{-1})/(mg L^{-1})$^{1/n}$; n: intensity of the adsorption.

2.5. Efficiency of advanced membranes of Al-Quds University's WWTP

To ascertain the removal efficiency of imidacloprid by the different units of the Al-Quds University WWTP (hollow fiber-ultrafiltration (HF-UF), spiral wound-ultrafiltration (SW-UF), activated carbon (AC), and reverse osmosis (RO)), a sample of 50 ppm of imidacloprid as initial concentration was added to the effluent of the activated sludge stage in the cleaned tank at the inlet heat of the HF-UF unit as described in Fig. 1. Five samples presented from No. 1–5 in Fig. 1 were collected using pre-cleaned 500 mL amber glass bottles, filtered using 0.45 μm cellulose nitrate, and finally analyzed by HPLC.

2.6. Filtration experiments

Column filter experiments were performed with a ratio of 50/1 (w/w) mixtures of quartz sand and micelle-clay complex (13 cm layer) in a column of 18 cm length and 4 cm diameter. The masse of both micelle-clay complex and sand were 3 and 147 g, respectively. The bottom of the column was covered by a 3 cm layer of quartz wool. Quartz sand was thoroughly washed with distilled water and dried at 105°C for 24 h. 50 mg L^{-1} of imidacloprid concentration was prepared by dilution of the stock solution with distilled water and was passed through the above column.

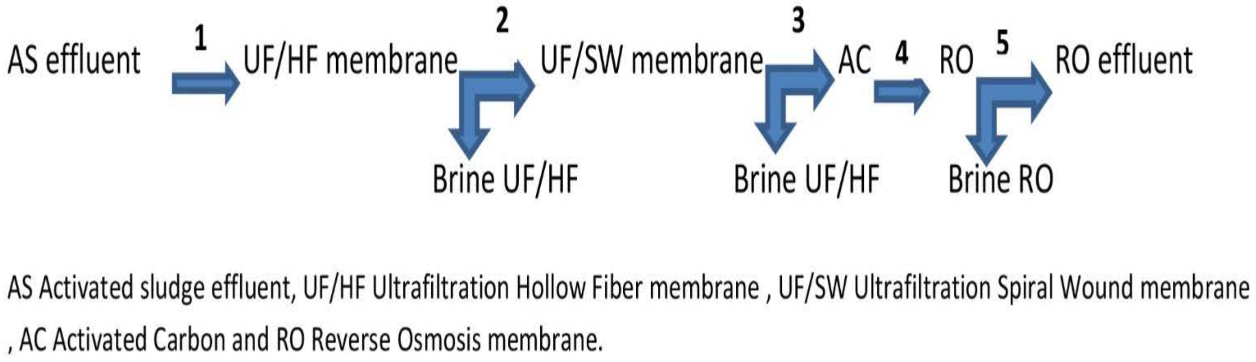

Fig. 1. A diagram illustrating the treatment processes ultrafiltration-hollow fiber, ultrafiltration-spiral wound, activated carbon and reverse osmosis filters. The numbering in the diagram indicates the sampling locations in the plant.

The flow rate was adjusted to 2.0 mL/min at 25°C and 10 fractions of 100 mL each were collected for assay.

2.7. Stability study in pure water and activated sludge

Stability studies of imidacloprid were performed at 25°C by preparing 100 mg L^{-1} of imidacloprid in pure water and activated sludge sampled from the Wastewater Treatment Plant at Al-Quds University. Samples were then collected at different times, filtrated using 0.45 µm cellulose nitrate filters, stored at 4°C, and analyzed by HPLC. The reaction progress in sludge was followed by LC-MS for metabolites identification.

2.8. Sample, standards preparation and chromatographic conditions

- *Stock solution*: Stock solution was prepared by dissolving the required mass of imidacloprid in distilled water to give a stock solution with a concentration of 500 mg L^{-1} the pH of the standard solution was 7.07 ± 0.10.
- *Calibration curves*: The following diluted solutions were prepared from the stock solution for all contaminants: 0.1, 1, 2, 5, 10, 20 and 40 mg L^{-1}.

The standards were analyzed by HPLC under optimal conditions that are listed in Table 1. The calibration curve was obtained by plotting peak height vs. concentration.

3. Results and discussion

3.1. Effect of time

Fig. 2 summarizes the percentage removal of imidacloprid as a function of time in a batch experiment using 100 mL solution of imidacloprid at a concentration of 100 mg L^{-1}, 0.50 g micelle-clay complex, and contact time of 3 h at 25°C. Inspection of Fig. 3 reveals that after 5 min, a constant % removal was obtained. This indicates that the kinetics of the removal of this pesticide by micelle-clay complex very fast with an optimal contact time of 5 min.

3.2. Adsorption isotherms

The adsorption isotherms of imidacloprid at different initial concentrations using a constant dosage of micelle-clay complex and activated charcoal were determined. The adsorption parameters were calculated by applying Eqs. (1) and (2) for Langmuir and Freundlich adsorption isotherms, respectively. Table 2 lists the calculated parameters for both adsorption isotherms. The parameters include $Q_{\max}$, K, Freundlich constants (k and n) and the correlation coefficient R^2.

Table 1
Optimal chromatographic conditions for the HPLC analysis of imidacloprid using C-18 as an analytical column

Parameter	Imidacloprid
Wavelength	270 nm
Flow rate	1 mL min^{-1}
% ACN in the mobile phase	80%
% Water in the mobile phase	20%
Injection volume	10 µL

Comparing the correlation coefficient values of imidacloprid obtained by both adsorption isotherms, revealed a better fit in Langmuir isotherms, 0.988 and 0.999, for both micelle-clay complex and activated charcoal, respectively. Also, the experimental parameters were found to fit Freundlich isotherm with correlation coefficient values of 0.972 and 0.948, respectively.

The calculated $Q_{\max}$ and K values for activated charcoal were higher than that for micelle-clay complex when fitting with Langmuir isotherm, whereas approximately the same $Q_{\max}$ values were obtained when fitting with Freundlich isotherms. Upon comparing the values of $Q_{\max}$ and K obtained in this work with those reported in the literature (Table 2) reveals that both activated charcoal and micelle-clay complex are suitable for imidacloprid removal from polluted water.

3.3. Efficiency of the WWTP at Al-Quds University for the removal of imidacloprid

Fig. 3 illustrates the removal efficiency of imidacloprid by HF-UF, SW-UF, AC, and RO units in the WWTP of Al-Quds University. The results revealed that HF-UF with 20–100 kDa cut-off was the least efficient as compared to the other units (66% removal). On the other hand, complete

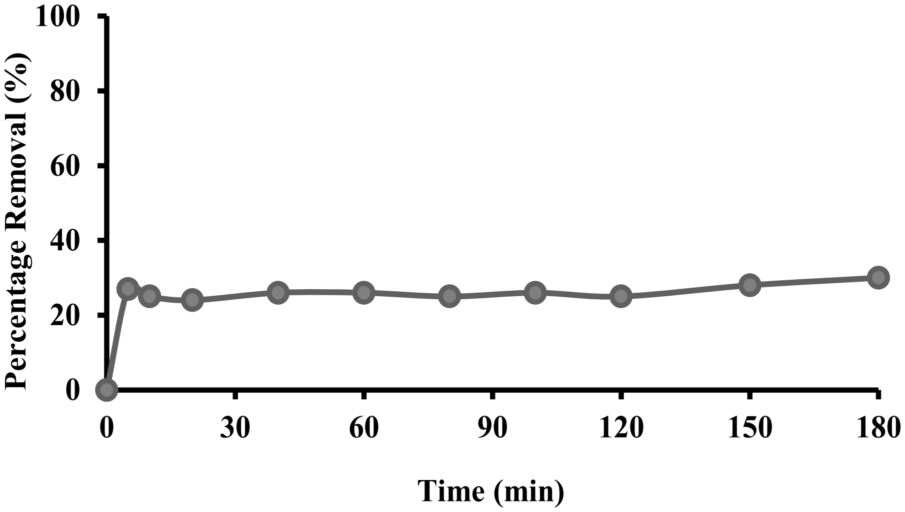

Fig. 2. The percentage removal (%) of imidacloprid using micelle-clay complex as a function of time. The initial concentration was 100 mg L^{-1}. Adsorbent dosage was 5 g L^{-1}, contact time of 3 h and T = 25°C.

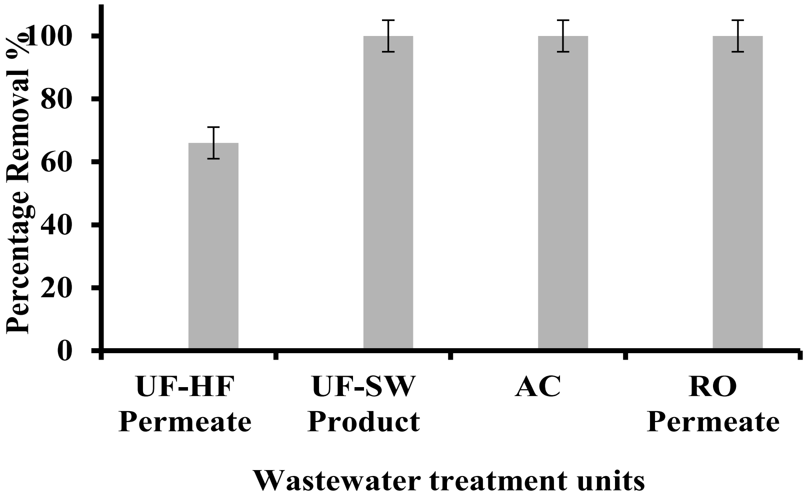

Fig. 3. The percentage removal of imidacloprid during the treatment process in Al-Quds University WWTP. The plant included ultrafiltration-hollow fiber, ultrafiltration-spiral wound, activated carbon, and reverse osmosis units.

removal was observed with the SW-UF, AC, and RO units. Furthermore, it is worth mentioning that complete removal of the pesticide by the SW-UF unit indicates that the remediation of this pesticide is achieved only by this unit, thus avoiding the use of AC and RO units.

3.4. Filtration experiments

Fig. 4 displays the percentage removal of imidacloprid passed through a laboratory column consisting of 50/1 (w/w) sand and micelle-clay complex with 50 mg L^{-1} as initial concentration and flow rate of 2 mL min^{-1} at 25°C. The figure shows a satisfactory efficiency of the column in removing imidacloprid. Complete removal of imidacloprid was observed in the first fraction of 100 mL elution. The total retention of imidacloprid during elution of 1,000 mL of 50 mg L^{-1} was 23 mg. The total quantity of ODTMA used in this column was 0.9 g and was able to adsorb 23 mg of imidacloprid [33,41]) reported that the micelle-clay complex was efficient in removing non-steroidal anti-inflammatories (NSAID) drugs such as paracetamol, aspirin, diclofenac potassium, ibuprofen, and naproxen. They also concluded that the micelle-clay complex composite of montmorillonite and ODTMA is capable of binding negatively charged organic molecules in addition to bacteria [42]. It should be indicated that increasing the percentage weight of the micelle-clay complex or column length increases the contact time between adsorbate and adsorbent, thus enhancing the removal efficiency of the pesticide.

3.5. Stability of imidacloprid in sludge and fresh water

Stability studies of imidacloprid were performed at 25°C by dissolving 100 mg of imidacloprid either in 1 L of

Table 2
Imidacloprid adsorption isotherm parameters for Langmuir and Freundlich's isotherms upon using a micelle-clay complex and activated charcoal comparing with other adsorbents

Type of adsorbents	Langmuir equation			Freundlich equation			Reference
	R^2	$Q_{\max}$ (mg g^{-1})	K (L mg^{-1})	R^2	n	k	
Micelle-clay complex	0.988	11.76	0.010	0.972	3.08	4.60	This study
Activated charcoal	0.998	126.6	0.211	0.948	3.19	32.79	This study
Biochar		6.67–10.34					[36]
Five agricultural waste		4.5					[37]
a. Bentonite		9.1					[38]
b. Bentonite and clay		7.8					
c. Kaolin		7.7					
a. Orange peels activated carbon		151.7					[39]
b. Almond shells activated carbon		370.3					
Tangerine peels activated carbon		35.7					[40]

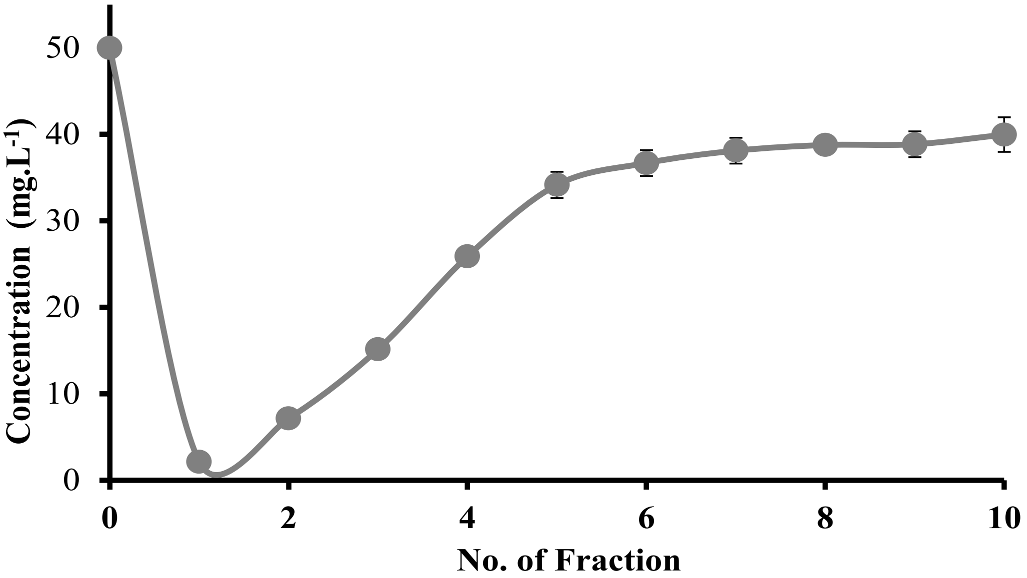

Fig. 4. A filtration of imidacloprid solution by a laboratory filter, which includes a micelle-clay complex mixed with excess sand at 1:50 (w/w). The flow rate was 2 mL min^{-1} and the initial concentration of imidacloprid was 50 mg L^{-1}.

pure water or in 1 L of activated sludge. Biodegradation analyses were performed in batch cultures using imidacloprid solutions (100 mg L^{-1}) to determine the degradation rate and identify the various metabolites in sludge. The biodegradation of imidacloprid was monitored by HPLC. Imidacloprid metabolites were detected by LC-MS.

3.6. Identifications of imidacloprid metabolites

Fig. 5 (left side) shows the progress of imidacloprid degradation in fresh water and sludge. Monitoring degradation revealed that imidacloprid underwent hydrolysis in both media during the experimental period. The degradation rate constants in both fresh water and sludge were 0.0.0067 and 0.0.0099 d^{-1}, respectively. Besides, the high degradation rate of imidacloprid in sludge demonstrates that the pesticide undergoes biodegradation in addition to the hydrolysis process. Fig. 5 (right side) depicts the chromatograms for the five major biodegradation products of imidacloprid in sludge after one month. The retention times for the metabolites are 3.35(3), 10.53(4), 3.44(5), 3.09(6), and 3.89(7) min. The metabolites were characterized based on the accurate m/z ratios as $[M+H]^+$ by liquid-chromatography-electron spray ionization-Fourier-transform ion cyclotron resonance-mass spectrometry (LC/ESI-FTICR-MS).

Zheng & Liu [10] and Wamhoff & Schneider [43] reported that the major breakdown products of Imidacloprid in water were 6-chloro-3-pyridyl-methylethylendiamine, 6-chloronicotinaldehyde, 6-chloro-N-methylnicotinacidamide, 1-[(6-chloro-3-pyridinyl)methyl]-2-imidazolidinone (i.e., imidacloprid urea), and 6-hydroxynicotinic acid whereas the minor breakdown product is imidacloprid-guanidine. On other hand, Liu et al. [44] found only one main metabolite which was 1-[(6-chloro-3-pyridinyl)methyl]-2-imidazolidinone.

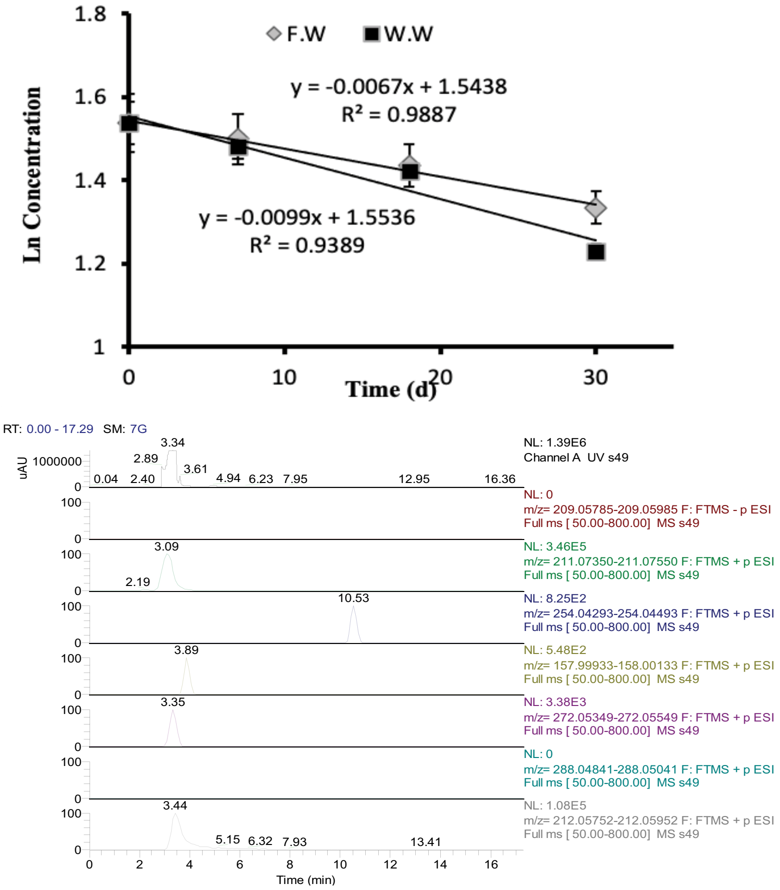

Fig. 5. Kinetics of imidacloprid degradation in sludge and fresh water at 25°C; initial concentration of 100 mg L^{-1} (Top) and extracted ion chromatograms (XICs) by LC/ESI-FTICR-MS acquired in positive ion mode of imidacloprid solutions after one month of biodegradation. The ions monitored are displayed in each trace and correspond to the most abundant protonated molecules, [M+H]$^+$, using a restricted window of ±0.0010 m/z unit centered around each selected ion (Bottom).

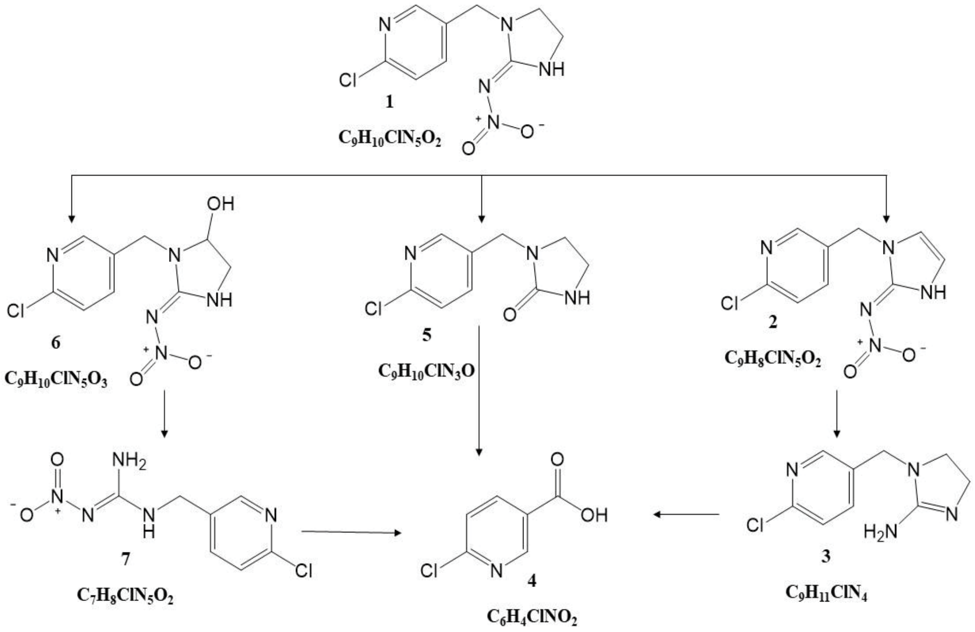

Fig. 6. Proposed transformation pathways for the biodegradation of imidacloprid.

Whereas Bacey [45] reported various compounds as a result of imidacloprid hydrolysis in water, 6-chloro-nicotinaldehyde, 6-N-methylnicotinacidamide, 6-chloro-3-pyridyl-methylendiamine, imidacloprid urea, and 6-hydroxynicotinic acid.

Researchers reported that the first product in the hydrolysis pathway of imidacloprid is imidacloprid-urea which may undergo oxidative cleavage to 6-chloronicotinic acid and imidazolidine [14]. Besides, Klein and Karl [46] suggested that imidacloprid may be metabolized by hydroxylation of the imidazolidine ring by a second major pathway. Metabolic products from the second pathway include 5-hydroxy and olefin derivatives. Fig. 6 summarizes the proposed imidacloprid degradation pathway.

4. Conclusions

An advanced wastewater treatment plant composed of UF (HF and SW), AC and RO units demonstrated that conditioning with an ultrafiltration-hollow fiber unit is not enough in removing imidacloprid from spiked wastewater samples, whereas integration of ultrafiltration-spiral wound unit within the treatment plant was sufficient for complete removal of the pesticide.

adsorption studies on micelle (ODTMA)-clay complex and activated charcoal revealed that under steady-state conditions both adsorbents can be efficient in imidacloprid removal. Even though activated charcoal is more efficient as an adsorbent for the removal of imidacloprid, micelle (ODTMA)-clay complex has an advantage over activated charcoal because of two main reasons: the ease with which the clay complex is reactivated and the fact that it is cheaper than activated carbon.

Stability studies on imidacloprid revealed that the pesticide was unstable in both water and sludge. The kinetics results in sludge demonstrated that there was a degradation process in addition to the hydrolysis of the pesticide. In presence of sludge, imidacloprid underwent biodegradation in sludge to yield five metabolites which were characterized by LC-MS.

References

[1] D.J. Ecobichon, Our changing perspectives on benefits and risks of pesticides: a historical overview, Neurotoxicology, 21 (2000) 211–218.

[2] R.J. Gilliom, J.E. Barbash, C.G. Crawford, P.A. Hamilton, J.D. Martin, N. Nakagake, L.H. Nowell, J.C. Scott, P.E. Stackelberg, G.P. Thelin, D.M. Wolock, The Quality of Our Nation's Waters—Pesticides in the Nation's Streams and Ground Water, 1992–2001, Circular 1291, U.S. Geologcal Survey, 2006, p. 172.

[3] N. Stamatis, D. Hela, I. Konstantinou, Pesticide inputs from the sewage treatment plant of Agrinio to River Acheloos, western Greece: occurrence and removal, Water Sci. Technol., 62 (2010) 1098–1105.

[4] T. Osman, T. Cemile, The fate of pesticide in the environment, J. Boil Environ. Sci., 4 (2010) 29–38.

[5] A. Elbert, H. Overbeck, K. Iwaya, S. Tsuboi, Imidacloprid, A Novel Systemic Nitromethylene Analogue Insecticide for Crop Protection, Brighton Crop Protection Conference Pests and Diseases – 1990, Vol. 1, British Crop Protection Council Thornton Heath UK, 1990, pp. 21–28.

[6] P.N. Moza, K. Hustert, E. Feicht, A. Kettrup, Photolysis of imidacloprid in aqueous solution, Chemosphere, 36 (1998) 497–502.

[7] M.Y. Liu, J.E. Casida, High affinity binding of [^{3}H]imidacloprid in the insect acetylcholine receptor, Pestic. Biochem. Physiol., 46 (1993) 40–46.

[8] R.S. Oliveira Jr., W.C. Koskinen, N.R. Werdin, P.Y. Yen, Sorption of imidacloprid and its metabolites on tropical soils, J. Environ. Sci. Health., Part B, 35 (2000) 39–49.

[9] J. Rouchaud, F. Gustin, A. Wauters, Soil biodegradation and leaf transfer of insecticide imidacloprid applied in seed dressing in sugar beet crops, Bull. Environ. Contam. Toxicol., 53 (1994) 344–350.

[10] W. Zheng, W. Liu, Kinetics and mechanism of the hydrolysis of imidacloprid, Pestic. Sci., 55 (1999) 482–485.

[11] E.C. Bortoluzzi, D.S. Rheinheimer, C.S. Gonçalves, J.B.R. Pellegrini, A.M. Maroneze, M.H.S. Kurz, N.M. Bacar, R. Zanella, Investigation of the occurrence of pesticide residues in rural wells and surface water following application to tobacco, Quim. Nova, 30 (2007) 1872–1876.

[12] K. Moriya, K. Shibuya, Y. Hattori, S.-i. Tsuboi, K. Shiokawa, S. Kagabu, 1-(6-Chloronicotinyl)-2-nitroimino-imidazolidines and related compounds as potential new insecticides, Biosci. Biotechnol. Biochem., 56 (1992) 364–365.

[13] D. Deepu, I.A. George, J.V. Peter, Toxicology of the newer neonicotinoid insecticides: imidacloprid poisoning in a human, Clin. Toxicol. (Phila), 45 (2007) 485–486.

[14] J. Thyssen, L. Machemer, Chapter 9 – imidacloprid: Toxicology and Metabolism, I. Yamamoto, J.E. Casida, Eds., Nicotinoid Insecticides and the Nicotinic Acetylcholine Receptor, Springer-Verlag, Tokyo, 1999, pp. 213–222.

[15] I. Akça, C. Tuncer, A. Guler, I. Saruhan, Determination of lethal concentration of some insecticides to Honey Bee *Apis mellifera* (Apidae, Hymenoptera) with Laboratory Biossays, J. Anim. Vet. Adv., 8 (2009) 2380–2382.

[16] K. Košutić, L. Furač, L. Sipos, B. Kunst, Removal of arsenic and pesticides from drinking water by nanofiltration membranes, Sep. Purif. Technol., 42 (2005) 137–144.

[17] K.Y. Foo, B.H. Hameed, Detoxification of pesticide waste via activated carbon adsorption process, J. Hazard. Mater., 175 (2010) 1–11.

[18] P. Chelme-Ayala, M. Gamal El-Din, D.W. Smith, Kinetics and mechanism of the degradation of two pesticides in aqueous solutions by ozonation, Chemosphere, 78 (2010) 557–562.

[19] Q. Zhang, S.O. Pehkonen, Oxidation of diazinon by aqueous chlorine: kinetics, mechanisms, and product studies, J. Agric. Food Chem., 47 (1999) 1760–1766.

[20] Q. Wang, A.T. Lemley, Oxidation of diazinon by anodic Fenton treatment, Water Res., 36 (2002) 3237–3244.

[21] S. Malato, J. Blanco, A. Vidal, D. Alarcón, M.I. Maldonado, J. Cáceres, W. Gernjak, Applied studies in solar photocatalytic detoxification: an overview, J. Sol. Energy, 75 (2003) 329–336.

[22] P. Saritha, C. Aparna, V. Himabindu, Y. Anjaneyulu, Comparison of various advanced oxidation processes for the degradation of 4-chloro-2 nitrophenol, J. Hazard. Mater., 149 (2007) 609–614.

[23] H.M. Rajashekara Murthy, H.K. Manonmani, Aerobic degradation of technical hexachlorocyclohexane by a defined microbial consortium, J. Hazard. Mater., 149 (2007) 18–25.

[24] A. Dąbrowski, Adsorption — from theory to practice, Adv. Colloid Interface Sci., 93 (2001) 135–224.

[25] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: a review, J. Hazard. Mater., 170 (2010) 70–80.

[26] I. Ali, V.K. Gupta, Advances in water treatment by adsorption technology, Nat. Protoc., 1 (2006) 2661–2667.

[27] S.A. Abdel-Gawad, A.M. Baraka, K.A. Omran, M.M. Mokhtar, Removal of some pesticides from the simulated waste water by electrocoagulation method using iron electrodes, Int. J. Electrochem. Sci., 7 (2012) 6654–6665.

[28] I. Ghanem, M. Orfi, M. Shamma, Biodegradation of chlorpyrifos by *Klebsiella* sp. isolated from an activated sludge sample of waste water treatment plant in Damascus, Folia Microbiol. (Praha), 52 (2007) 423–427.

[29] C. Segura, C. Zaror, H.D. Mansilla, M.A. Mondaca, Imidacloprid oxidation by photo-Fenton reaction, J. Hazard. Mater., 150 (2008) 679–686.

[30] C. Zarora, C. Segura, H. Mansilla, M.A. Mondaca, P. Gonzalez, Kinetic study of imidacloprid removal by advanced oxidation based on photo-Fenton process, Environ. Technol., 31 (2010) 1411–1416.

[31] M. Socías-Viciana, E. González-Pradas, M. Saifi, M.D. Ureña-Amate, F. Flores-Céspedes, M. Fernández-Pérez, The potential removal of imidacloprid from water by heat-treated kerolites, Pest. Manage. Sci., 59 (2003) 1162–1168.

[32] M. Zahoor, M. Mahramanlioglu, Adsorption of imidacloprid on powdered activated carbon and magnetic activated carbon, Chem. Biochem. Eng. Q, 25 (2011) 55–63.

[33] R. Karaman, M. Khamis, M. Quried, R. Halabieh, I. Makharzeh, A. Manassra, J. Abbadi, A. Qtait, S.A. Bufo, A. Nasser, S. Nir, Removal of diclofenac potassium from wastewater using clay-micelle complex, Environ. Technol., 33 (2012) 1279–1287.

[34] T. Polubesova, S. Nir, D. Zadaka, O. Rabinovitz, C. Serban, L. Groisman, B. Rubin, Water purification from organic pollutants by optimized micelle-clay systems, Environ. Sci. Technol., 39 (2005) 2343–2348.

[35] S. Nir, I. Brook, Y. Anavi, M. Ryskin, J. Ben-Ari, R. Shveky-Huterer, H. Etkin, D. Zadaka-Amir, U. Shuali, Water purification from perchlorate by a micelle–clay complex: laboratory and pilot experiments, Appl. Clay Sci., 114 (2015) 151–156.

[36] W.J. Zhang, Global pesticide use: profile, trend, cost/benefit and more, Proc. Int. Acad. Ecol. Environ. Sci., 8 (2018) 1–27.

[37] A. Mandal, N. Singh, T.J. Purakayastha, Characterization of pesticide sorption behaviour of slow pyrolysis biochars as low cost adsorbent for atrazine and imidacloprid removal, Sci. Total Environ., 577 (2017) 376–385.

[38] F.Z. Choumane, B. Benguella, Removal of acetamiprid from aqueous solutions with low-cost sorbents, Desal. Water Treat., 57 (2014) 419–430.

[39] S.G. Mohammad, S.M. Ahmed, Adsorptive removal of acetamiprid pesticide from aqueous solution using environmentally friendly natural and agricultural wastes, Desal. Water Treat., 145 (2019) 280–290.

[40] S.G. Mohammad, S.M. Ahmed, A. El-Galil E. Amr, A.H. Kamel, Porous activated carbon from lignocellulosic agricultural waste for the removal of acetampirid pesticide from aqueous solutions, Molecules, 25 (2020) 2339, doi: 10.3390/molecules25102339.

[41] M. Qurie, M. Khamis, L. Scrano, S.A. Bufo, G. Mecca, R. Karaman, Removal of two NSAIDs: naproxen and diclofenac and a heavy metal Cr(VI) by advanced membranes technology, Case Stud. J., 4 (2015) 51–63.

[42] D. Zadaka, Y.G. Mishael, T. Polubesova, C. Serban, S. Nir, Modified silicates and porous glass as adsorbents for removal of organic pollutants from water and comparison with activated carbons, Appl. Clay Sci., 36 (2007) 174–181.

[43] H. Wamhoff, V. Schneider, Photodegradation of imidacloprid, J. Agric. Food Chem., 47 (1999) 1730–1734.

[44] W. Liu, W. Zheng, J. Gan, Competitive sorption between imidacloprid and imidacloprid-urea on soil clay minerals and humic acids, J. Agric. Food Chem., 5 (2002) 6823–6827.

[45] J. Bacey, Environmental Fate of Imidacloprid, California Environmental Monitoring and Pest Management Branch, Department of Pesticide Regulation, Sacramento, CA, 2000.

[46] O. Klein, W. Karl, Methylene [14C] Imidacloprid: Metabolism Part of the General Metabolism Study in the Rat, Unpublished Report No. PF 3316, Submitted to WHO by Bayer AG, Mannheim, Germany, INCHEM Toxicological Evaluations: Imidacloprid, World Health Organization, International Programme on Chemical Safety, 1990.