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Research Article

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Determination of Methomyl and Imidacloprid in Water by Adsorption on Ni-Al Hydrotalcite Using HPLC

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Abstract: Column solid phase extraction (SPE) and batch procedures based on the use of synthetic hydrotalcite (HT) or layered double hydroxides (LDH) as solid phase for adsorption and extraction of Methomyl (MEL) and Imidacloprid (IMP) pesticides in water are investigated. The determination of the pesticides was carried out by high performance liquid chromatography (HPLC). The study was performed to determine the influence of various operating parameters, such as initial concentration, contact time, pH, and sorption capacity, on the procedure performance. The results indicated that calcinedhydrotalcite of the type Ni/Al-NO_3 is proved to be promising with sorption capacity (up to 43.02 mg g^{-1} at pH 4.5) for extracting pesticides from aqueous samples. Spiked water samples were tested by batch method and by passing the samples through the calcinated Ni-Al, HT column (500 mg) at a constant flow rate (4 mL min^{-1}). Adsorbed analytes were eluted with acetonitrile and analyzed by HPLC. Acceptable high recoveries with simple, reliable and sensitive HPLC procedure were obtained for the analysis of Methomyl and Imidacloprid in water samples.

Keywords: Hydrotalcite; Adsorption; Methomyl; Imidacloprid; HPLC.

1. INTRODUCTION

Pesticides are used worldwide to provide a necessary remediation measure for preventing or controlling insects that can adversely affect crops by diseases, fungi or even damage to the plants. They are classified according to the pest they control [1]. However, it has to be noted that only a fraction of the applied pesticides reaches its targets. The remaining part which is still toxicologically active accumulates and remains in the environment. These residues must be removed from the ecosystems to prevent contamination. With a special attention to water system in countries like Jordan that scarcity of water is of great concern and is mainly dependant on groundwater, it is of great importance to be able to predict the fate of pesticide residues and optimize their extraction. The toxic effect of pesticides on humans and animals varies on the basis of their chemical compositions. Smulders et al., [2] has reported that the carbamate pesticides inhibit the brain receptors and affect different subtypes of neuronal nicotinic receptors. The pesticides in this study were chosen due to their anionic nature as they mainly exist as

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anionic species in water and soil environment because of their polar character and mobilization ability. Methomyl (MEL) is a carbamate pesticide with a broad spectrum in controlling a wide range of insects, spider mites in fruits, vegetables and cotton. MEL is also used to control of flies in animal and poultry houses. Its toxicity to humans steam from its potential to leach to groundwater, as it moderately binds to soil and can be easily hydrolyzed, oxidized or degraded [3]. Imidacloprid (IMP) is a systemic pesticide with physical/chemical properties that allow residues to move into treated plants and then throughout the plant. It acts by disrupting nicotinic acetylcholine receptors in the insect central nervous system. IMP is used for controlling sucking insects, soil insects, termites, and some chewing insects. It is applied to seeds, soil, crops, and is used as a topical flea control treatment on domestic pets. Residues of the insecticide then enter the water bodies causing potential health effects [4]. According to European Community Drinking Water Directive, the standards for the individual pesticide and the sum of all pesticides are 0.1 and 0.5 ppb, respectively, which are both much stricter than health-based minimum level set by the World Health Organizations and the US Environmental Protection Agency (USEPA) [5]. In order to meet the pesticide standard of water bodies and protect human health, therefore, it is required that the treatment method is of high sensitivity and selectivity.

Hydrotalcites (HT) also known as layered double hydroxides (LDH), have been of interest, due to their potential application as adsorbents [6,7], anion exchangers [8] and catalysis [9]. In addition, the calcined or heat treated form of these adsorbents can be easily regenerated to a well ordered layered structure with no significant loss of the adsorption capacities [10]. Therefore, LDH had found its place in removing contaminates from the environment especially anionic species contaminated water [11,12]. In general, LDH consists of positively charged metal hydroxide sheets, that would increase the sorption ability of polar organic contaminates [13] with anions located in between the layers to compensate the positive layer charges. The composition of LDH is generally represented by the following formula [14,15]:

$$[M^{+2}_{1-x} M^{+3}_{x} (OH)_2]^{x+} A^{n-}_{x/n} \cdot mH_2O$$

Where, M^{2+} and M^{3+} are divalent and trivalent cations, respectively. Whereas, A^{n-} represent intercalated inorganic or organic anions (NO_3^-, Cl^-, SO_4^{2-}, ClO_4^-). These anions can be exchanged due to the layered structure and high anion exchange capacity. The interlayer water number m, and $x = M^{2+}/ (M^{2+} + M^{3+})$. The simplicity of synthesis is another advantage. Moreover, adsorption with LDH has advantage of low cost over other techniques employed to remove pesticides from effluents such as photocatalytic degradation [16], electrochemical degradation [17], oxidation [18, 19], membrane filtration [20], and nanofiltration [21, 22]. Over the past decade, many processes have been developed and successfully applied for separating the substance from its matrix with high adsorption capacity for the removal of organic pollutants, pesticides, and metal ions from aqueous solutions [23-25]. Activated carbons have also been extensively used for pesticide adsorption from water, but it involves high manufacturing cost [26-28]. With MEL and IMP being from the top most used carbamate pesticides, it is of importance to be able to predict the fate of such residue in the environment and optimize their extraction. Such determination is a key step towards this goal. In previous report by Ulibarri et al.,[29] an investigation was undertaken to evaluate the adsorption capacity of hydrotalcite of the type $[Mg_3Al(OH)_8]_2CO_3 . nH_2O$ and its calcined product as potential sorbets of anionic organic contaminants in water. The study demonstrated that hydrotalcite calcined at 500 ^oC was transferred to mix metal oxide that is capable of adsorbing anions from aqueous solutions through the reconstruction of its layered structure and in its ability to be recycled.

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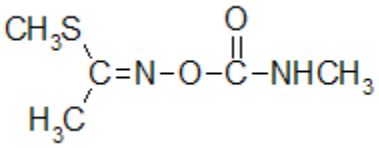
In continuation to our previous reports on layered double hydroxides and their ability to intercalate organic ligands, a study on the synthesis and application of this type of synthetic clays was carried out and the subsequent adsorption potential of metal ions from water samples were achieved [25]. In another recent report, the adsorption of Cr(III) from tannery wastewater was achieved using HT adsorbent [11].The aim of this work is to assess the adsorption potential of the calcined hydrotelecite of (Ni-Al) for the removal of MEL and IMP pesticides from its aqueous solution by batch and column methods using optimized HPLC technique to estimate the potential accuracy of the procedure at low level of pesticide residue in water.

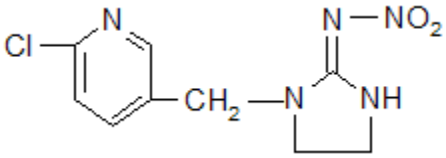
2. EXPERIMENTAL

2.1 Reagents and Chemicals

Nickel nitrate hexahydrate $Ni(NO_3)_2.6H_2O$, aluminum nitrate nonahydrate $Al(NO_3)_3.9H_2O$, sodium nitrate $NaNO_3$, sodium hydroxide NaOH analytical grade were from Merck, Germany. All chemical solutions were prepared fresh prior to use. The selected insecticides in this study are Methomyl and Imidaclopride purchased from local market, Jordan. Methomyl is the common name. The IUPAC name is: S-methyl N-(methylcarbamoyloxy) thioacetimidate. It is used to control a wide range of insects. The structure is shown in Scheme 1(a). Imidacloprid is a chloronicotinylnitroguanidine insecticides, the IUPAC name is 1-[(6-chloropyridin-3-yl) –n-nitro-4, 5-dihydroimidazol-2-amine. the structure is shown in Scheme 1(b).



(a)



(b)

Scheme 1. Chemical structure of: (a) Methomyl and (b) Imidacloprid

2.2 Instrumentation

Thermo-gravimetry and differential thermal analysis (TG and DTA) of the synthesized Ni-Al, HT was carried out in the Mettler Toledo thermo gravimetric analyzer (TGA/SDTA 851VR model) under N_2 atmosphere between 25 and 800^oC with a heating rate of 10^oC min^{-1}. The powder X-ray diffraction (PXRD) patterns of the Ni-Al, HT were recorded using Bruker AXS instrument equipped with Cu Ka (k51.5406 A˚) radiation operating at 40 kV and 40 mA between 2u ranging between 5 and 50^o with a scan speed of 0.05^{o}s^{-1}. pH measurements were recorded by Elico LI-IOT pH meter. A mechanical shaker was used for batch experiments. HPLC analyses were studied using Shimadzu LC-2010 AHT with RP C-18 column, 25 cm length x 4.6 mm.i.d. and5 µm particle size. Mobile phase consisted of acetonitrile (40) in

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water (60) at a flow rate of 1 mL min^{-1} and UV detector set at 235 nm for MEL and 250 nm for IMP, which showed a sharp peak at retention time of 4.598 min. for MEL standard and 2.909 min. for IMP standard under the set conditions. All other reagents and chemicals were either of analytical or HPLC grade.

2.3 Synthesis of Ni-Al-NO_3 Hydrotalcite

A co-precipitation route was employed for the preparation of Ni-Al, HT. First, an aqueous solution containing $Ni(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$ and $NaNO_3$ was prepared by taking the mole ratio of the nitrate salts as 2:1:2, respectively. To this prepared solution, 0.2 mol L^{-1}NaOHsolution was added drop wise with vigorous stirring until the pH reaches to 10. After which, the mixture was stirred at room temperature for 12 h. Finally, the obtained precipitate was filtered and washed thoroughly with distilled water until the pH of the filtrate was neutral. Subsequently the material was dried in a vacuum oven and ground with a mortar and pestle to get particles smaller than 160 mm. Then, the above Ni-Al, HT sample was calcined at 450^oC for 3 h in a muffle furnace (air atmosphere) with a heating rate of 2^oC min^{-1} to use in adsorption study.

2.4 Separation procedures

2.4.1 Batch method

A sample solution (100 mL) containing 50 µg mL^{-1} of MEL or IMP was transferred to 250 mL glass bottle. After adjusting the pH to the optimum value, 100 mg of the solid material was added. The mixture was shaken for 60 min, filtered, washed with double distilled water (DDW), and the analyte was eluted with 15 mL acetonitrile then determined by HPLC.

2.4.2 Column method

Calcined Ni-Al, HT (0.5 g) was kept for 6 h, packed in a glass column 25 cm length, treated with 20 mL of 0.1 mol L^{-1}HCl at the optimum flow rate and washed with DDW water to become acid free. 100 mL of 100 µg MEL or IMP at the optimum pH, were passed through the column at the optimum flow rate, the column was washed with 100 mL of DDW to remove any remaining analytes in the solid matrix bed. The stripping of MEL or IMP from the Ni-Al, HT solid phase was carried out by acetonitrile - water mixture. The eluted pesticides were collected in a 100 mL calibrated flask to be ready for the determination.

3. RESULTS AND DISSCUTION

3.1 Characterization of Ni-Al, HT adsorbent

Thermogravimetric analysis (TGA & DTA) of Ni-Al, HT is shown in Figure 1. Two regions of weight losses in the TG curve are observed for the heat treated Ni-Al, HT. The first region of weight loss in the temperature range lower than 230^oC is attributed to the removal of physically adsorbed and interlayer water molecules. The second region of weight loss in the temperature ranges between 230 and 500^oC is attributed to the release of the hydroxyl groups from brucite layers and NO_3^- anions from the interlayer [30]. The DTA curve also suggests that the decomposition of HT occurs at about 350^oC. There is no weight loss observed above 450^oC. It implies that there is no phase change after this temperature and hence the calcination temperature was fixed at 450^oC for the calcined Ni-Al, HT adsorbent.

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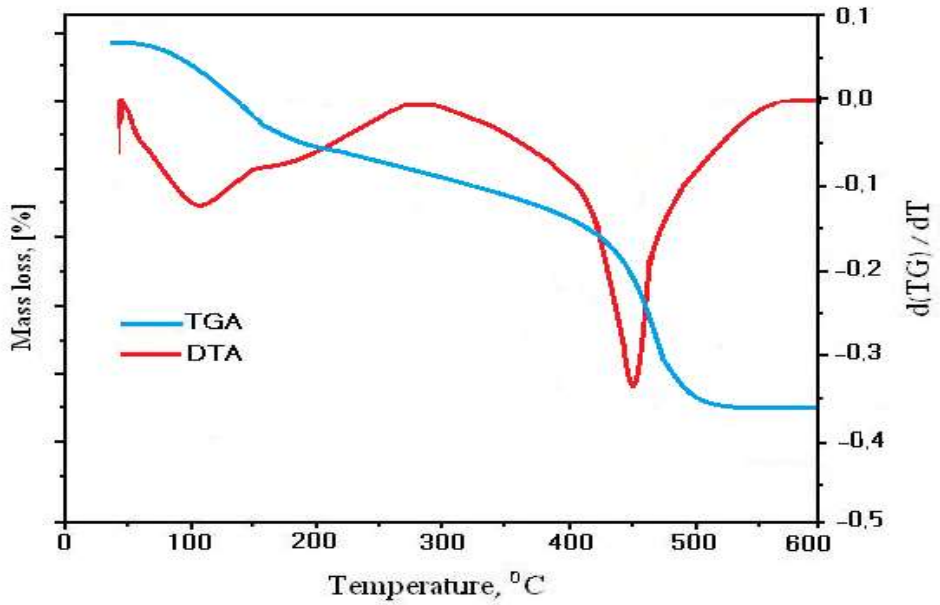

Figure 1. Thermogravimetry (TG) and differential thermal analysis (DTA) profile of the synthesized Ni-Al, HT adsorbent.

The PXRD pattern of Ni-Al, HT before and after calcination is shown in Figure 2. The prepared Ni-Al, HT displays a single phase corresponding to the layered double hydroxides with sharp asymmetric reflections at 003, 006, and 009 planes and broad asymmetric reflections at 015 and 018 planes. The position of the basal peak of Ni-Al, HT indicates the distance between two adjacent metal hydroxide sheets (d_{003}). The prepared Ni-Al, HT is readily converted to a crystalline layered phase after adsorption. The disappearance of the planes 003 and 006 confirms the complete degradation of HT and the formation of oxides of Ni and Al after the heat treatment above 450^{o}C.

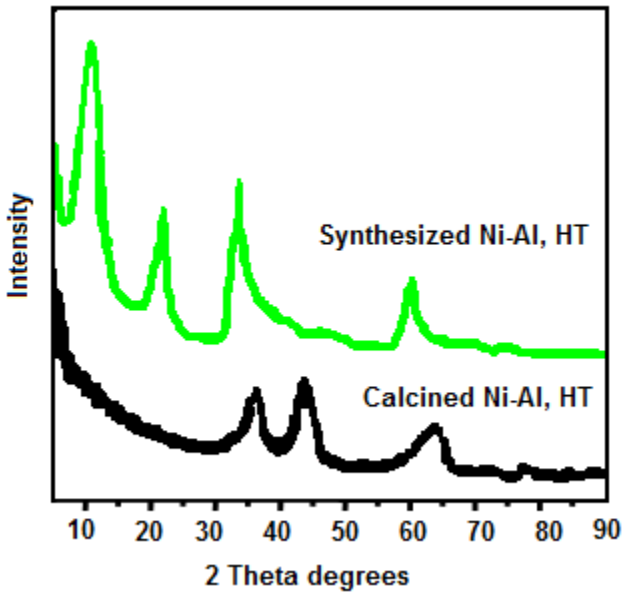

Figure 2. Powder XRD pattern of synthesized Ni-Al, HT and after calcination.

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3.2 Batch technique

3.2.1 Effect of pH

To show the effect of pH (2.0–8.0) on the sorption of MEL or IMP by batch equilibrium experiments, a solution containing MEL or IMP was shaken with the solid Ni-Al, HT for sufficient equilibrium time. Figure 3 shows that, the maximum efficiency of Ni-Al, HT for sorption of pesticides was achieved at pH 3.0 – 7.0. For subsequent experiments, the working media were adjusted at pH 4.5. The influence of pH on the amount of pesticides adsorbed increased slightly with the decrease of the pH. Also, the stability of the HT at higher pH might be lowered. Therefore, the sorption of pesticides in alkaline solutions might be unsuitable. This behavior might be attributed to the hydrophilic (polar) interaction with the anionic hydroxide surface at higher pH > 8 which leads to a decrease in adsorption. In addition to that it was observed from the study of material stability that partial dissociation of the solid Ni-Al, HT in alkaline media occurred and hence reduced the available sites for adsorption.

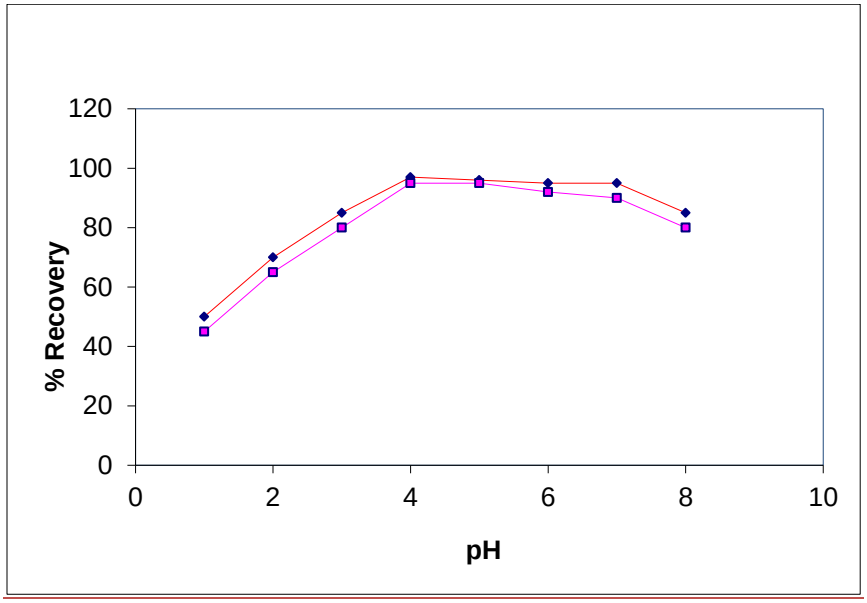

Figure 3. Effect of pH on MEL (◆) and IMP (■) recovery.

3.2.2 Sorption capacity

A stock solution with different concentrations of MEL or IMP pesticide was prepared and the experimental solutions of the desired concentration were obtained by successive dilutions of the stock solution. The amounts adsorbed were determined from the initial and the final concentration of the analyte solution. The solid/solution ratio chosen for all experiments was 0.5 g and 50 mL of solution of pesticides which was enough to be determined accurately. For adsorption experiments, 50 mL of pesticide solution of known initial concentrations was shaken with adsorbent (calcined Ni-Al, HT) at room temperature in a shaker at 100 rpm and at a neutral pH of the pesticide solution. The solution and solid phase were separated. The supernatant was decanted without disturbing the solution, filtered and the concentration of pesticides was then determined by HPLC. Figure 4 shows a fast and almost instantaneous adsorption and the equilibrium was reached in less than one hour for MEL, while for IMP it was a little slower, reached equilibrium in 1.5 h. This might be due to the bulky size structure of IMP in comparison to MET that caused a more steric hindrance which gave rise to a slow diffusion into the solid material. The maximum sorption capacity reached was 43.02 mg g^{-1}.

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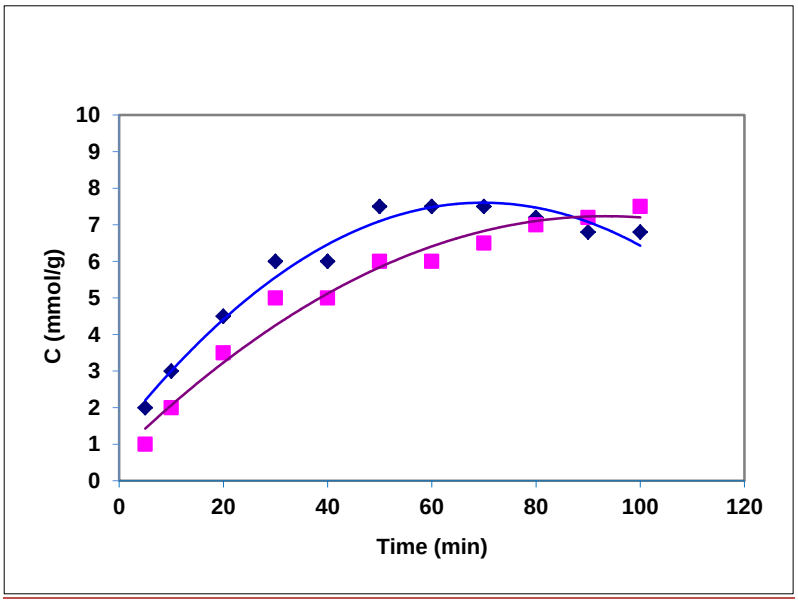

Figure 4. Effect of contact time on adsorption of MEL ( ) and IMP ( )

3.2.3 Ni-Al, HT stability and reusability

The calcined Ni-Al, HT (50 mg) was shaken with 100 mL of 0.1 mol L^{-1}HCl and organic solvents (ethanol or acetone) for 12 h, filtered and washed with DDW. After drying, the elemental constituents of the solid adsorbent were investigated. It was found that, no change in the composition suggesting a stable nature of the solid Ni-Al, HT. It was noticed that, the calcined Ni-Al, HT dissociate in alkaline solution (pH > 9) and the dissociation increased with increasing pH. The calcined Ni-Al, HT was subjected to several recyclability experiments by shaking 50 mg with 100 mL of 25 mg L^{-1} solution containing pesticides for 1 h at room temperature. The concentration of MEL and IMP pesticides was determined after elution with 15 mL of appropriate acetonitrile-water mixture. Sorption capacity was found to be constant indicating that the Ni-Al, HT is highly stable and may be used for several times.

3.3 Column technique

3.3.1 Effect of flow rate

The sorption of pesticides in this study was investigated at different flow rates (0.5-10 mL min^{-1}) under the optimum conditions. It can be seen from Figure 5 that the capacity of sorption was maximum at 4 mL min^{-1}. The faster sorption of pesticides with the calcined Ni-Al, HT was taken as an indication for its higher reactivity with the hydroxide surface of HT and the possible intercalation in between the HT layers. The flow rate was, therefore, set at 4 mL min^{-1} which allowed the maximum retention of both pesticides.

3.3.2 Column recycling

To test the long-term stability on the reuse of the column containing the calcined Ni-Al, HT, successive sorption and elution cycles were carried out by passing the pesticide solution through the column at the optimum flow rate, then elated. The procedure was carried out seven times and the stability of the column was assessed by monitoring the change in the recoveries of the sorbed pesticides. The results of

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sorption/desorption cycles on the regenerated adsorbent of calcined HT indicate good recovery, which reflect good stability and that it can be used again. Although, the efficiency show decreasing tendency with repetition of adsorption cycles. The recyclability profile for MEL and IMP is shown in Figures 6 and 7. Such behavior can be explained by the decrease in the available sites for adsorption both on the surface and in between the layers of the HT material.

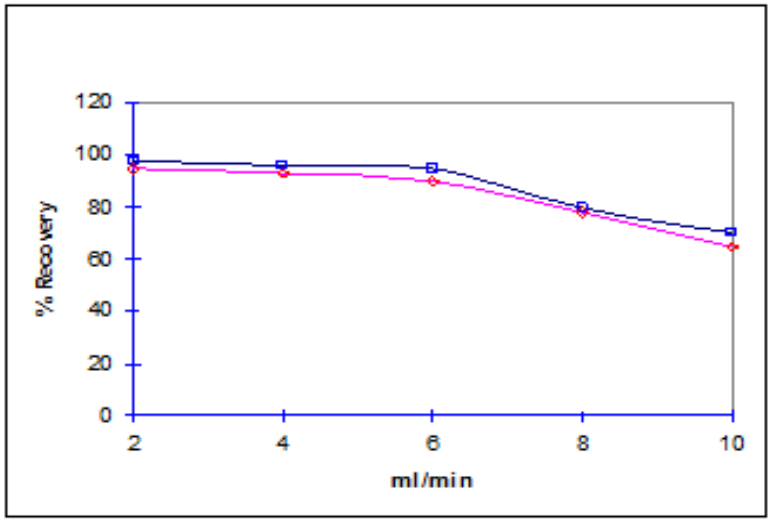

Figure 5. Effect of flow rate on recovery of MEL (□ and IMP (◆

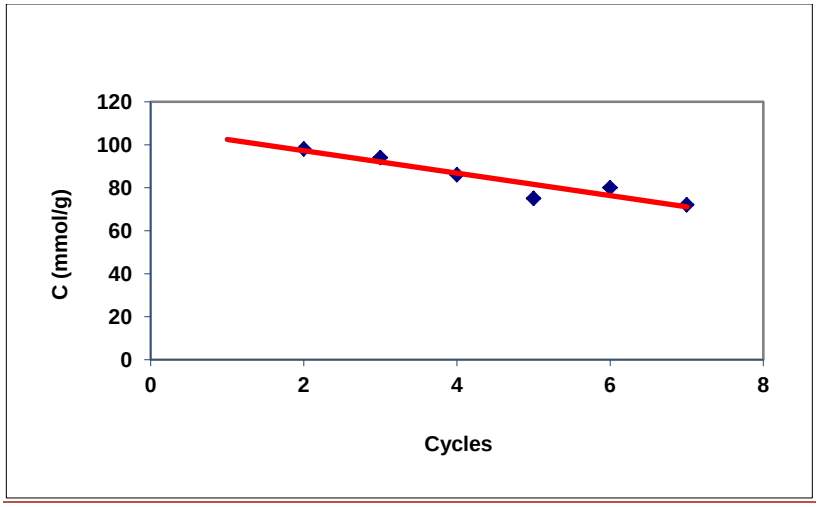

Figure 6. Recyclability of the adsorbent Ni-Al, HT with MEL.

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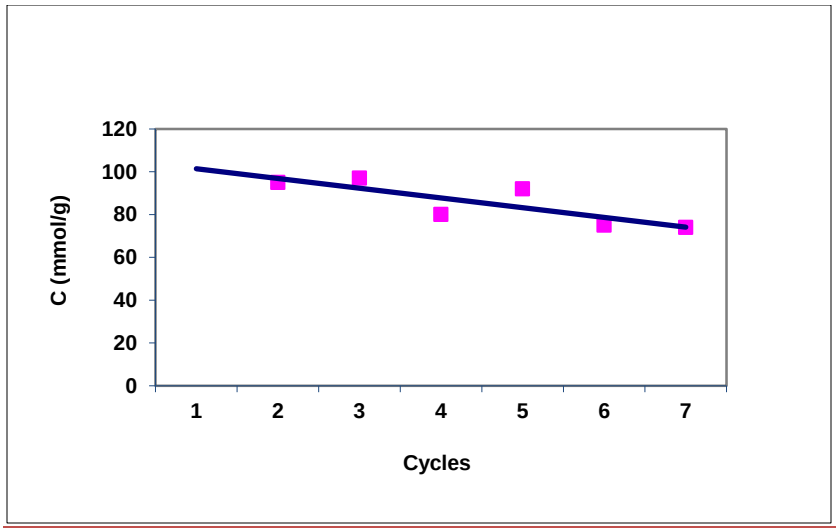

Figure 7. Recyclability of the adsorbent Ni-Al, HT with IMP.

3.3.3 Effect of sample volume

In order to study the effect of larger sample volume, aqueous solutions of volume ranging from 0.1–1.5 L containing 25 mg of the desired pesticide were passed through the Ni-Al, HT bed, eluted with 25 mL of the appropriate acetonitrile-water mixture and determined. It was found that, pesticides may be removed quantitatively from volume up to 1.2 L, and then the recovery decreases remarkably.

3.3.4 Recovery, accuracy and linearity

Standard solutions and residues eluted from water samples of the two pesticides were analyzed using HPLC. For linearity test the standard peak area is equivalent to the average of three standard peak area injected in HPLC.

Table 1. % Recovery test results from different concentration levels of MEL and IMP

	Methomyl			Imidacloprid	
Level (%)	Conc. (µg mL^{-1})	Assay (%)	Level (%)	Conc. (µg mL^{-1})	Assay (%)
150	3.01	99.6	150	2.98	100.3
120	2.41	97.5	120	2.38	100.7
100	2.01	97.9	100	2.00	99.2
80	1.60	97.4	80	1.60	98.4
50	1.00	97.3	50	0.99	98.6
25	0.50	98.4	25	0.49	99.3
	Average	98.0		Average	99.4
	RSD	0.8927		RSD	0.9232

The results in Table 1 indicated that detection limit of both MEL and IMP were 0.073 and 0.013 µg L^{-1} respectively, and the linearity correlation coefficients were 0.9984-0.9990. The recovery of the two standard added to water samples were 97.3-100.7% with relative standard deviation (RSD) from 0.89-0.92% at different concentration levels from 25 to 150 % that is equivalent to (0.50- 3.0 µg mL^{-1}). Under

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the chromatographic conditions described, very good linearity and the correlation coefficient were achieved for MEL and IMP with three replicates and by plotting the concentration of pesticides against detector response (peak area). It was found to be linear over the concentration range from 0.05 to 4.0 µg L^{-1}. These data demonstrate an excellent sensitivity, selectivity and precision.

4. CONCLOSIONS

The adsorption potential of the calcined Ni-Al, HT adsorbent for MEL or IMP pesticides has been successfully investigated by batch and column adsorption experiments. The prepared Ni-Al, HT has been characterized with powder XRD and thermogravimetry (TG and DTA). These analyses reveal that the calcination of Ni-Al, HT forms the oxides of nickel and alumina at 450^{o}C. The maximum adsorption capacity of the Ni-Al, HT is found to be 43.02 mg g^{-1}. The adsorption of the selected pesticides of MEL and IMP on calcined Ni-Al, HT is strongly dependent on pH of the solution. Other parameters indicate that the adsorption is spontaneous and reaching equilibrium in a short time of less than one hour under the experimental conditions. The effectiveness of the calcined Ni-Al, HT as adsorbent was checked carefully by HPLC which allowed the detection of very small amount of 0.073 and 0.013 µg L^{-1} for both MEL and IMP, respectively. The recoveries were more than 97.3%. This investigation suggests that the calcined Ni-Al, HT coupled with a sensitive HPLC procedure could be used for the determination of pesticide residues in aqueous solution. Further work will be focused on the use of calcined Ni-Al, HT material in wastewater treatment and with different types of pesticides in non-aqueous media.

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The authors declare no conflict of interest

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