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Efficient removal of imidacloprid pesticide by two eco-friendly activated carbons

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Abstract: In this study, the removal of imidacloprid (IMD) pesticide onto activated carbon produced from nut shells of hazelnut (HAC), and walnut (WAC) has been investigated. The prepared activated carbons were characterised by total carbon, nitrogen and hydrogen content, surface areas and pore volume. Fourier-transform infrared (FTIR), and scanning electron microscopy (SEM) were studied before and after adsorption experiments. Effects of adsorbent dose (0.02–0.2 g), contact time (10–120 min), initial imidacloprid concentration (10–100 mg·dm^{-3}), and pH (1–8), and temperatures (25–50°C) on the removal of IMD pesticide by HAC and WAC in the batch mode were studied. The removal percentage of imidacloprid pesticide by HAC and WAC was 93.79% and 94.72%, respectively. The study showed that the pseudo-second-order kinetics model fitted well for both activated carbons. Moreover, adsorption isotherm results were evaluated using Freundlich, Langmuir and Temkin isotherm models. The adsorption results correlated well with the Langmuir isotherm model (R^2 = 0.987 and 0.964) with maximum adsorption capacities of 76.923 and 83.333 mg·g^{-1} for HAC and WAC, respectively, and an equilibrium time within 120 min. The nature of the adsorption of imidacloprid pesticide onto HAC and WAC is exothermic, spontaneous and physical in nature.

The two prepared activated carbons (HAC, WAC) were successfully regenerated for three cycles and could be used as an effective and low-cost adsorbent for the removal of IMD pesticide from aqueous solutions. The production of the activated carbons of HAC and WAC will provide minimisation of these wastes in the environment.

Keywords: activated carbon, hazelnut, imidacloprid, pesticide, regeneration, removal, walnut

INTRODUCTION

Pesticides are one of the major classes of toxic organic compounds that are mainly released into the environment because of agricultural activities. About $2 \cdot 10^6$ Mg·y^{-1} is the global consumption of pesticides: 24% is consumed in the USA, 45% – in Europe, and 25% – in the rest of the world. Pesticides can cause acute and chronic toxicity to human health according to the time and amount of exposure (Gill and Garg, 2014). These compounds could be a considerable concern due to their persistence, high toxicity, and accumulation in the food chain (Thakur and Pathania, 2019).

More than 20% of neonicotinoids are present in the global market of insecticides (Calvo-Agudo *et al.*, 2019). The insecticide imidacloprid (IMD) belongs to the neonicotinoids class of pesticides. IMD is an extensively applied insecticide in the agriculture sector because of its high efficacy and low cross-resistance (Chen *et al.*, 2019; Wang *et al.*, 2022), and is used for controlling termites, turf insects, ectoparasites, and agricultural pests (Jeschke *et al.*, 2011; Starner and Goh, 2012; Singh *et al.*, 2021). But crops could only absorb less than 1% and the rest could possibly transfer to water directly or indirectly. Due to its resistance to self-degradation, and high photo stability and solubility, IMD could become a risk to ecological balance and human health. Therefore, it could be toxic to aquatic organisms and hepatotoxic or carcinogenic for mammals and humans (Li *et al.*, 2021; Wang *et al.*, 2022). Therefore, an efficient method is needed for its remediation.

Several techniques had been used to reduce or eliminate the releases of pesticides from water such as oxidation, ozonation, coagulation, adsorption, degradation, photocatalytic, electrochemical degradation, membrane filtration, and nano filtration. Adsorption is still favoured because of its high efficiency, simplicity, and relatively low cost (Gupta, Nayak and Agarwal, 2015; Maneerung *et al.*, 2016).

Among the adsorption materials, activated carbons (AC) are still used in the removal of organic and inorganic contaminants form wastewater due to their properties, such as high surface area, pore structure, low acid/base reactivity, thermo-stability and low cost (El-Refaey, 2016). Using agricultural wastes in the production of activated carbons offered an alternative source for producing low-cost AC with enhanced adsorption characteristics, especially with IMD pesticide contamination (Mandal and Singh, 2017; Mandal, Singh and Purakayastha, 2017).

Among agricultural wastes, hazelnut and walnut shells activated carbon had been used in the removal of heavy metals (lead, cadmium, zinc, chromium and copper), and organic (oil in wastewater) from wastewater (Kazemipour *et al.*, 2008; Devi *et al.*, 2017; Das, Banerjee and Bar, 2019; Albatrni, Qiblawey and Liang, 2022). Using activated carbon prepared from hazelnut and walnut shells in the removal of pesticides, especially imidacloprid, is a challenge.

The study aimed to produce a value-added product of activated carbons from waste materials of hazelnut (HAC) and walnut (WAC) for adsorption of imidacloprid (IMD) pesticide from aqueous solutions. The two production-activated carbons characterisations were compared. The Fourier-transform infrared (FTIR) and surface morphology were inspected before and after adsorption of the imidacloprid pesticide. Batch experiments were conducted for evaluating the impact of different conditions, such as adsorbent dose, initial IMD concentration, pH solution, and contact time on IMD removal. Kinetic studies were carried out using pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, while the equilibrium results were examined by Langmuir, Freundlich and Temkin isotherm models. Thermodynamic parameters and regeneration of the imidacloprid pesticide onto HAC and WAC were tested for three cycles of adsorption–desorption.

MATERIALS AND METHODS

REAGENTS

Acetonitrile and methanol high-performance liquid chromatography (HPLC) grade were purchased from Honeywell. Orthophosphoric acid H_3PO_4 (85 %) was purchased from Sigma-Aldrich and deionised water was obtained from Millipore Milli-Q Academic.

ADSORBATE

The pesticide used in this study is imidacloprid. Some characterisation of the imidacloprid and its chemical structure is presented in Table 1.

PREPARATION OF ACTIVATED CARBONS

The adsorbents used in this study were hazelnut and walnut activated carbons. The dried samples of hazelnut and walnut shells were collected from the local market. They were prepared with chemical activation of orthophosphoric acid (H_3PO_4, 85%) with a ratio of 1:1 for 24 h. Then the shells were dried at 100°C for 2 h and pyrolysed in the muffle furnace (Thermolyne, Thermo Scientific Inc.) at 500°C for 2 h in the absence of air. Finally, the produced activated carbon was dried, crushed and stored in plastic until used.

CHARACTERISATION OF ACTIVATED CARBONS

The contents of total carbon (C), nitrogen (N), hydrogen (H) and sulphur (S) in the HAC and WAC were determined by a CHNS analyser (Elementar, Vario EL).

The specific surface area of the activated carbons produced from HAC and WAC was determined by Brunauer–Emmett–Teller (BET) method from N_2 adsorption isotherms by a gas adsorption analyser (Beckman Coulter SA 3100). The Barrett–Joyner–Halenda (BJH) method from the N_2 desorption isotherms was conducted for calculating the total pore volume.

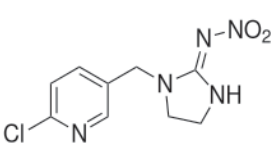
Fourier-transform infrared (FTIR) was conducted for helping in the detection of the responsible functional groups in the adsorption process. FTIR spectra were determined at the range 400–4,000 cm^{-1} by a Fourier-transform infrared spectrometer (Infra-Red Bruker Tensor 37) using the KBr disk technique. FTIR spectra were recorded before and after the adsorption of IMD pesticide by the two activated carbons (HAC and WAC).

The surface morphology of the used activated carbons (HAC and WAC) was examined by scanning electron microscope (Jeol IT-200). The samples were provided with a thin layer of gold in the sputter-coating unit (JFC-1100E), before the inspection. Scanning electron microscopy (SEM) images were obtained at different magnification scales before and after the adsorption process.

ADSORPTION EXPERIMENTS

Batch adsorption experiments were conducted for studying the removal of imidacloprid onto HAC and WAC. The experiments were conducted using a fixed materials dose of 0.1 $g\cdot(100\ cm^3)^{-1}$

Table 1. Some characteristics and chemical structure of imidacloprid

Characteristics	Description
Name	imidacloprid
Chemical structure	
Name in International Union of Pure and Applied Chemistry nomenclature	N-{1-[(6-chloro-3-pyridyl)methyl]-4,5-dihydroimidazol-2-yl}nitramide
Pesticide group	neonicotinoids
Molecular formula	$C_9H_{10}ClN_5O_2$
Molecular weight ($g\cdot mol^{-1}$)	255.66
Solubility in water ($g\cdot dm^{-3}$)	0.61
Purity (%)	97

Source: own elaboration based on MacBean (2012).

under different conditions. The different conditions included adsorbent dose (0.02–0.2 g), different initial concentrations of imidacloprid (10–100 mg·dm^{-3}); different initial pH (1–8); and contact time (10–120 min). For kinetic experiments, 0.10 g of materials was added to 100 cm^3 of 10 mg·dm^{-3} concentration of IMD pesticide solution in 250 cm^3 glass Erlenmeyer flasks and the samples were withdrawn at various intervals time.

CHROMATOGRAPHIC CONDITIONS

The determination of imidacloprid was conducted by High Performance Liquid Chromatography Agilent 1260 infinity (Agilent Technologies) equipped with a diode array detector (DAD) and column C18 (5 μm particles, 250 nm × 4.6 mm i.d). The conditions used for the analysis of imidacloprid are as follows: the mobile phase (65:35) acetonitrile to water at 270 nm and flow rate of 0.85 cm^3·min^{-1}. The adsorption amount (q_e), and the removal percentage of imidacloprid (R%) were determined by the following equations:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$R\% = \frac{C_0 - C_e}{C_0}100 \tag{2}$$

where: C_0 = initial imidacloprid concentration (mg·dm^{-3}), C_e = the equilibrium concentration, V = volume of solution, m = mass of adsorbent (g).

REGENERATION STUDIES

The regeneration studies of imidacloprid pesticide by HAC and WAC were carried out under the optimum conditions and tested for three adsorption-desorption cycles. During each adsorption cycle, the adsorbent was filtered, washed, and dried. Then, the adsorbent was dispersed into 100 cm^3 of 0.5 M HCl for 3 h to regenerate it.

RESULTS AND DISCUSSION

CHARACTERISATION OF ADSORBENTS

Characterisations of activated carbons from waste materials of hazelnut (HAC) and walnut (WAC) are presented in Table 2. For element contents, HAC was higher in total carbon and nitrogen content compared to WAC. Specific surface area, and pore volume are significant characteristics that participate in the purification. Results showed that the specific surface area of WAC was higher than HAC: 89.56 and 50.44 m^2·g^{-1}, respectively (Tab. 2). The total pore volume for HAC (0.302 cm^3·g^{-1}) was higher than for WAC (0.132 cm^3·g^{-1}).

Table 2. Some characteristics of hazelnut (HAC) and walnut activated carbon (WAC)

Adsorbent	C	H	N	S	Surface area (m^2·g^{-1})	Total pore volume (cm^3·g^{-1})
	%					
HAC	50.78	1.87	0.24	0	50.44	0.302
WAC	30.76	3.59	0.17	0	89.56	0.132

Source: own study.

FTIR ANALYSIS

The Fourier-transform infrared (FTIR) spectra of the HAC and WAC before and after the adsorption of imidacloprid are presented in Figure 1. There was a similarity in the broad bands' vibrations of the surface functional groups in both activated carbons that are involved in the imidacloprid (IMD) adsorption processes. The bands' vibrations in the range of 3000–3700 cm^{-1} can be attributed to the stretching of hydrogen bond and –OH groups in both materials (Gilca *et al.*, 2014; Halysh *et al.*, 2018). The 2805.8 and 1079.09 cm^{-1} in HAC, and 2928.07, 1074.49 cm^{-1} in WAC attributed to C–H stretching (Rangan *et al.*, 2017; Halysh *et al.*, 2018; Das, Banerjee and Bar, 2019). Aromatic groups (C=C and =C–O–C– stretching) observed at 2469.76, 1573.83, 1169.76 and 989.77 cm^{-1} for HAC, and 2386.99, 1585.28, 1155.05 and 991.47 cm^{-1} for WAC (Rangan *et al.*, 2017; Banerjee *et al*, 2018; Banerjee, Basu and Das, 2018; Das, Banerjee and Bar, 2019). The band at 1704.35 cm^{-1} in HAC could attribute to –C=O stretching (Bodîrlău and Teaca, 2007). The peaks at 495.12 cm^{-1} in HAC and 498.17 cm^{-1} in WAC could be attributed to PO_4^{3-} stretching vibrations as results of using orthophosphoric acid in preparation of active carbon (França *et al.*, 2014; Azzaoui *et al.*, 2015; Manalu, Soegijono and Indrani, 2015; Hernández-Hernández *et al.*, 2017; Saleh, El-Refaey and Eldamarawy, 2020). The comparison between FTIR spectra before and after the adsorption of IMD showed shifts in FTIR bands and some bands disappearing that could confirm the role of these function groups in the attachment of IMD on HAC and WAC surfaces.

SURFACE MORPHOLOGY OF HAC AND WAC

Scanning electron microscopy (SEM) images at different magnifications for the HAC and WAC that originated from treated shells before and after adsorption experiments are shown in Figure 2. The SEM images helped in identifying the surface morphology of the sorbents derived from agricultural wastes with knowledge of pore distribution and position (Loffredo, Scarcia and Parlavecchia, 2020). The SEM images before adsorption experiments represent the rough, channels and pores with irregular surface morphologies (Fig. 2). After adsorption, the surface morphology changed, as shown in Figure 2. The surface of the HAC became rougher and less porous and blocked the pores partially for both materials.

REMOVAL OF IMIDACLOPRID

Factors affecting the adsorption performance

In this study, the adsorbent dose, different concentrations of imidacloprid pesticide, pH and contact time were studied to achieve maximum adsorption efficiency.

Effect of adsorbent dose

In order to determine the optimum adsorbent dose, different adsorbent doses of HAC and WAC were studied (0.02–0.2 g), while the rest of the parameters were kept constant (Fig. 3a–3b).

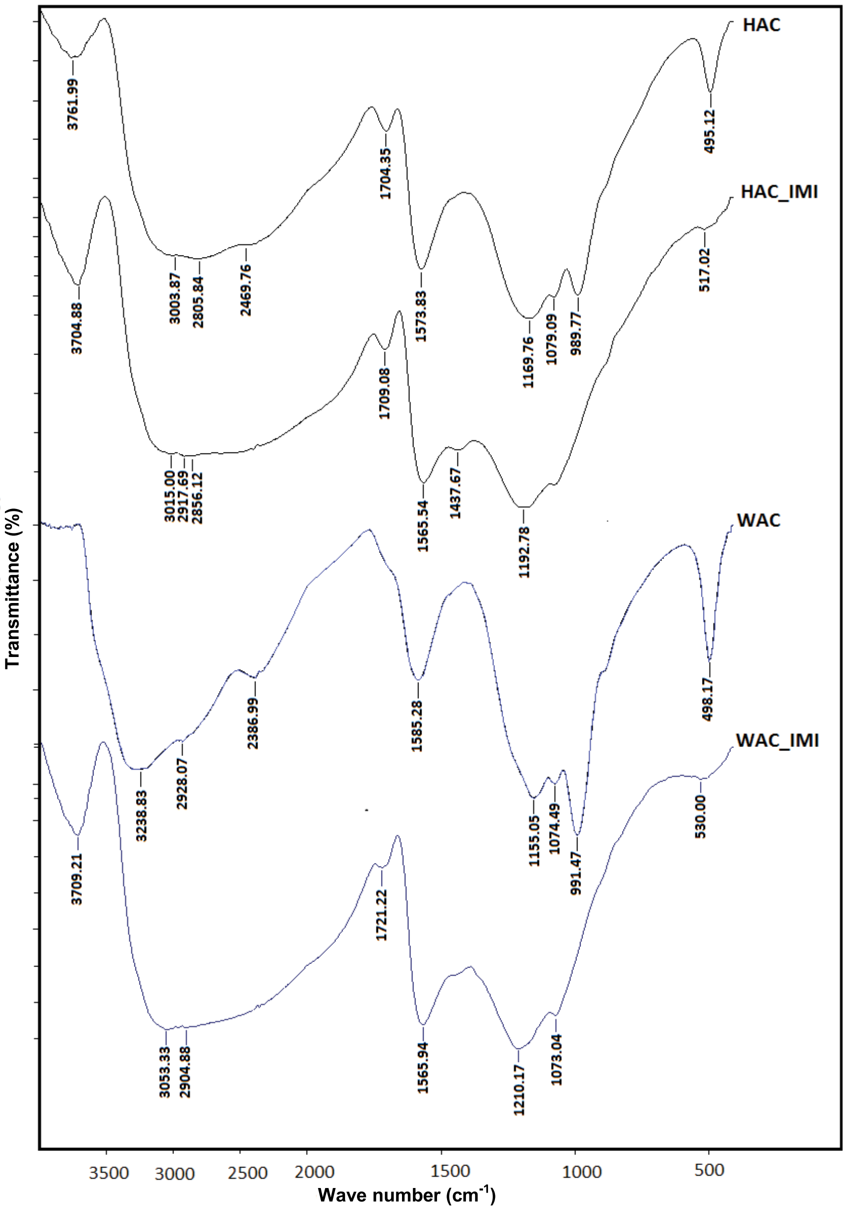


Fig. 1. The Fourier-transform infrared (FTIR) spectra of hazelnut (HAC) and walnut activated carbons (WAC) before and after imidacloprid pesticide removal reaction from aqueous solution; source: own study

As can be seen in this figure, the removal percentage of imidacloprid by two activated carbons increased from 44.1 to 93.79% and 48.41 to 94.72% for HAC and WAC, respectively, with increasing the adsorbent dose from 0.02 to 0.08 g due to increase in the amount of available binding active sites. On the other hand, the adsorption capacity (q) of imidacloprid by HAC and WAC decreased with increasing the adsorbent dose, from 22.005 to 11.27 mg·g^{-1} and from 24.205 to 11.43 mg·g^{-1} due to the rise in the number of free binding sites of the imidacloprid. As a result of these data, 0.1 g of HAC and WAC was the optimum adsorbent dose for the adsorption process.

Effect of different concentrations of imidacloprid

The effect of different concentrations of imidacloprid adsorption onto HAC and WAC was studied at 10–100 mg·dm^{-3}, while other factors were kept constant. Figure 3c shows the percentage removal of imidacloprid by two activated carbons at different initial concentrations of imidacloprid. Otherwise, the percentage removal of imidacloprid decreases with increasing the concentration from 10 to 100 mg·dm^{-3} due to the saturation of binding sites. For WAC, the IMD pesticide removal percentage decreased from 96.29 to 73.62% (Fig. 3c), and from 95.22 to 66.13% for HAC with increasing the initial IMD concentration from 10 to 100 mg·dm^{-3} (Fig. 3c). Similar trends were observed by Doczekalska *et al.* (2018), they used activated carbon from pumpkin seed hulls for the removal of 2, 4 dichlorophenoxy acetic acid pesticide from aqueous solution.

Effect of pH

The effect of pH on imidacloprid removal affects the interaction between HAC and WAC and the pesticide. To study the effect of pH on the removal of imidacloprid by HAC and WAC, the pH of

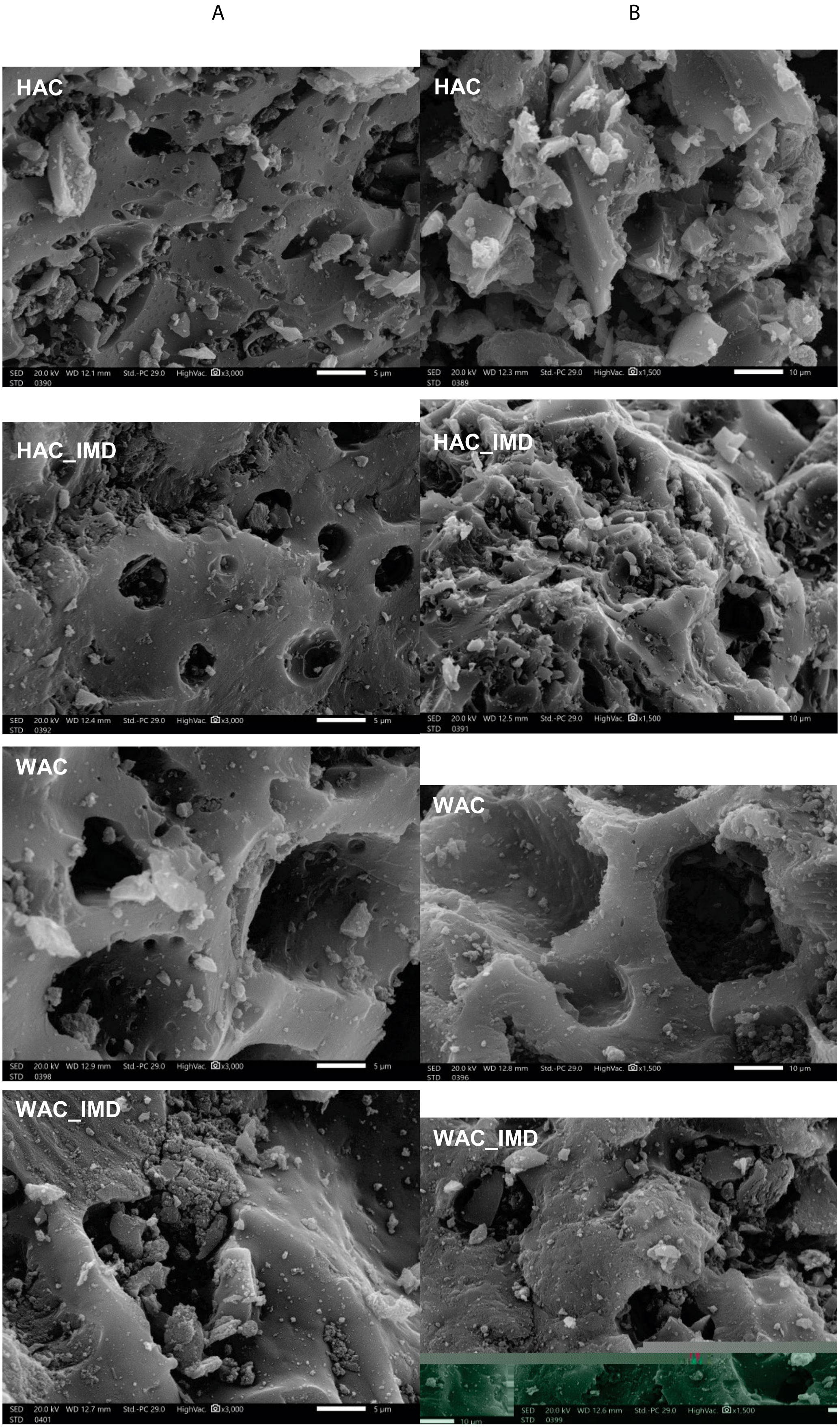


Fig. 2. Scanning electron microscopy (SEM) images of hazelnut (HAC) and walnut activated carbons (WAC) before and after imidacloprid (IMD) pesticide removal reactions from aqueous solutions at different magnification: column A ×3000, column B ×1500; source: own study

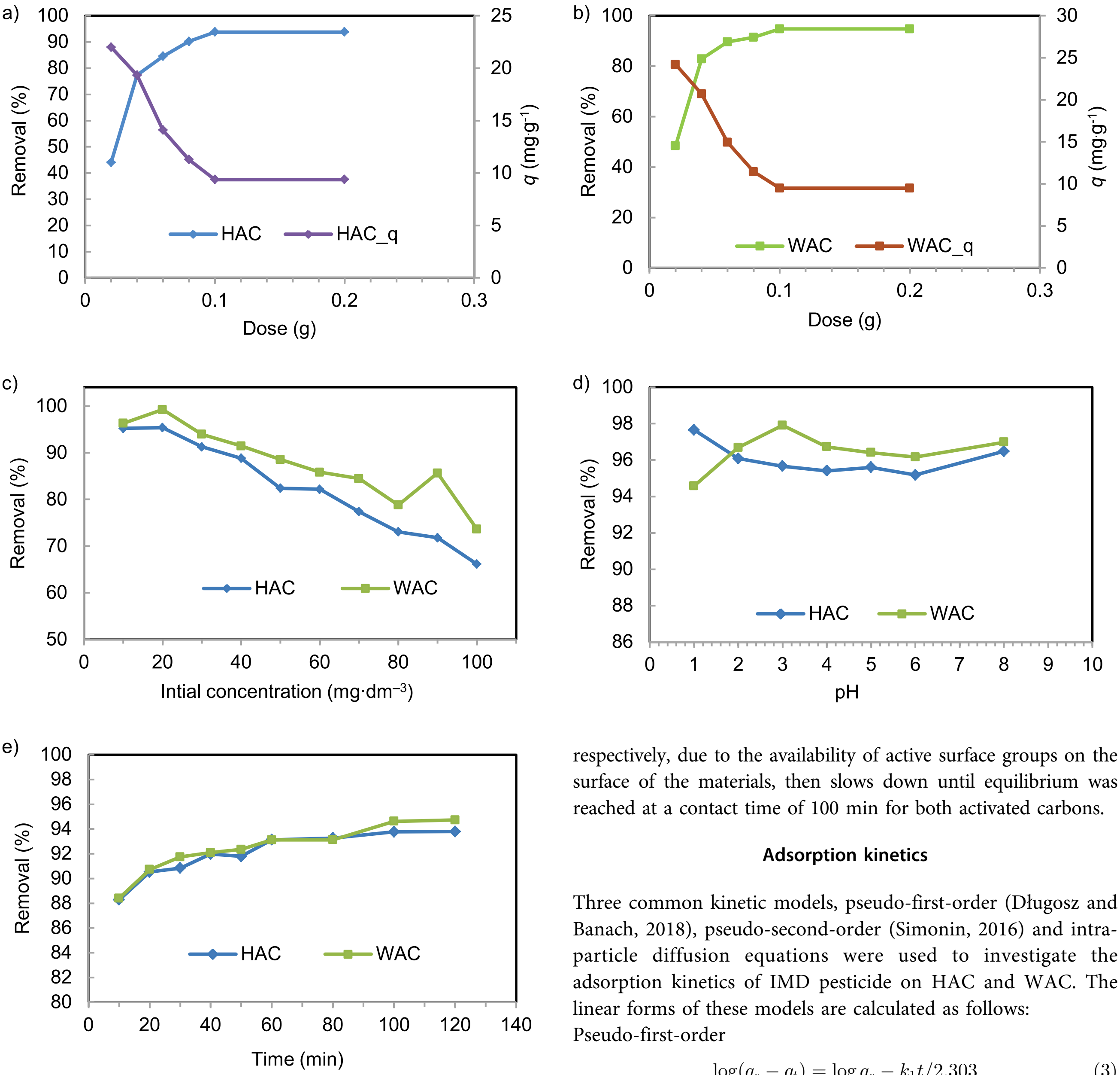


Fig. 3. Effect of the adsorption of imidacloprid pesticide (IMD) by hazelnut (HAC) and walnut activated carbon (WAC): a) HAC adsorbent doses, b) WAC adsorbent doses, c) initial concentration, d) pH, e) time; q = adsorption amount; source: own study

the solution was tested in the range of 1 to 8, initial concentration 10 mg·dm^{-3}, adsorbent dose – 0.1 g·(100 cm^3)$^{-1}$. As shown in Figure 3d, results reveal that the removal percentages of IMD pesticide by HAC and WAC had no significant differences as the pH value increased to 8.00 with similar trends observed for the adsorption of anthracene (Saad *et al.*, 2014) activated carbon derived from agriculture wastes.

Effect of contact time

In order to study the influence of contact time on the removal of imidacloprid by HAC and WAC, the tests were carried out at different time intervals (10–120 min), while the other parameters were constant. As shown in Figure 3e, the effect of contact time on the removal of imidacloprid by HAC and WAC increases rapidly in the first 10 min with percentage removal of 88.27 and 88.40%, respectively, due to the availability of active surface groups on the surface of the materials, then slows down until equilibrium was reached at a contact time of 100 min for both activated carbons.

Adsorption kinetics

Three common kinetic models, pseudo-first-order (Długosz and Banach, 2018), pseudo-second-order (Simonin, 2016) and intra-particle diffusion equations were used to investigate the adsorption kinetics of IMD pesticide on HAC and WAC. The linear forms of these models are calculated as follows:
Pseudo-first-order

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \tag{3}$$

Pseudo-second-order

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e} \tag{4}$$

Intra-particle diffusion

$$q_t = k_i t^{1/2} + C \tag{5}$$

where: q_e = IMD pesticide adsorbed by HAC at equilibrium and at a time t (mg·g^{-1}); q_t = IMD pesticide adsorbed by WAC at equilibrium and at a time t (mg·g^{-1}); k_1, k_2 = rate constants of pseudo-first (min^{-1}) and pseudo-second-order models (g·mg^{-1}·min^{-1}), respectively; k_i = intra-particle diffusion rate constant (g·mg^{-1}·min$^{-1/2}$); C = constant that gives indication of the boundary layer thickness (mg·g^{-1}).

The kinetic parameters for the removal of IMD onto HAC and WAC are shown in Table 3. As shown from the obtained results for both activated carbons, data fitted well with the

Table 3. Kinetic parameters for imidacloprid (IMD) adsorption by hazelnut (HAC) and walnut activated carbon (WAC)

Adsorbent	**Pseudo-first-order**			**Pseudo-second-order**			**Intra-particle diffusion**		
	q_e	k_1	R^2	q_e	k_2	R^2	k_i	C	R^2
HAC	0.7542	−0.0299	0.963	9.091	0.110	1.000	0.068	8.711	0.902
WAC	0.887	−0.012	0.922	9.615	0.104	0.999	0.073	8.708	0.926

Explanations: R^2 = yielded regression coefficients values, q_e, k_1, k_2, k_i, C as on p. 225.
Source: own study.

pseudo-second-order kinetic model. The yielded regression coefficients values (R^2) for the two adsorbents regarding the pseudo-second-order model were more than 0.99 (Tab. 3). The excellent agreement of the obtained data to the pseudo-second-order kinetic model indicated the chemical nature of the adsorption process (Fig. 4).

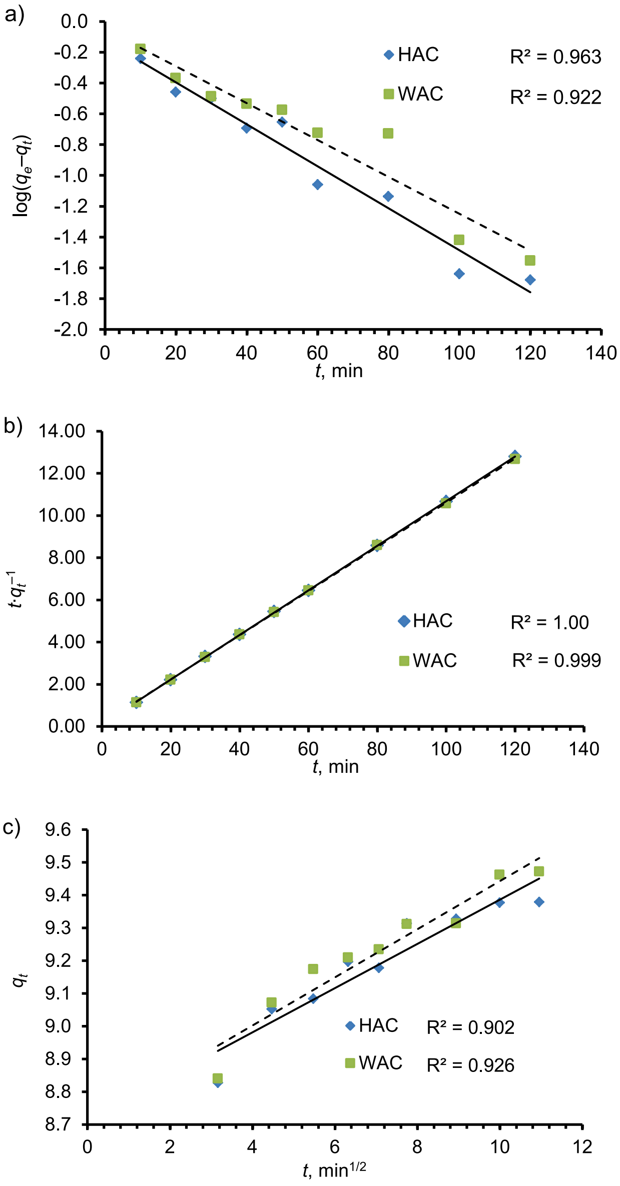


Fig. 4. Kinetic models for the removal of imidacloprid (IMD) pesticide by hazelnut (HAC) and walnut activated carbon (WAC): a) pseudo-first order, b) pseudo-second order, c) intra-particle diffusion; q_e, q_t, t, k_1, k_2, R^2, k_i, C as on p. 225; source: own study

According to Weber and Morris (1963), a plot of adsorption capacity versus $t^{0.5}$ should be a straight line having zero intercepts. The adsorption of imidacloprid onto HAC and WAC was not controlled by the intra-particle diffusion model.

Adsorption isotherm

The adsorption isotherms of imidacloprid pesticide onto HAC and WAC were analysed using different models. The most common isotherm models, Freundlich (Freundlich, 1906), Langmuir (Ghaedi *et al.*, 2013), and Temkin (Aharoni and Sparks, 1991), were applied to understand the nature of the adsorption process onto two prepared activated carbons. The Freundlich, Langmuir and Temkin models can be calculated by the following equations:
Freundlich

$$q_e = K_F {C_e}^{1/n} \tag{6}$$

Langmuir

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \tag{7}$$

Temkin

$$\theta = \frac{RT}{\Delta Q \ \ln K_0 C_e} \tag{8}$$

where: q_e = IMD pesticide adsorbed (mg·g^{-1}), C_e = equilibrium concentration of IMD pesticide (mg·dm^{-3}), K_F = constant related with the adsorption capacity (mg$^{1-(1/n)}$·dm$^{3/n}$·g^{-1}), n = constant to measure of the deviation for linearity of adsorption, $1/n$ = intensity of the adsorption process or the surface heterogeneity, $q_{\max}$ = maximum adsorption capacity (mg·g^{-1}), K_L = constant associated with the adsorption free energy (dm^3·mg^{-1}), θ = fractional coverage, R = universal gas constant (kJ·mol^{-1}·K^{-1}), T = temperature (K), $\Delta Q = (-\Delta H)$ adsorption energy difference (kJ·mol^{-1}), K_0 = Temkin coefficient (dm^3·mg^{-1}).

The isotherm parameters of IMD pesticide removal by HAC and WAC are presented in Table 4. Adsorption isotherm results were fitted well by the Langmuir equation according to regression coefficient values (R^2) (Tab. 4). The yielded R^2 for HAC and WAC were 0.987 and 0.964, respectively (Fig. 5b). The correlation coefficients for the Langmuir isotherm are higher than that obtained by the Freundlich, thus, indicating the exhibited of the monolayer adsorption with the homogeneous surface.

The maximum adsorption capacity as predicted by the Langmuir model for IMD removal by WAC (83.333 mg·g^{-1}) was significantly higher than that of HAC (76.923 mg·g^{-1}) (Tab. 4).

Table 4. Adsorption isotherm parameters of imidacloprid (IMD) pesticide sorption by hazelnut (HAC) and walnut activated carbon (WAC).

Adsorbent	Freundlich			Langmuir			Temkin		
	K_F	$1/n$	R^2	$q_{\max}$	K_L	R^2	A	B	R^2
HAC	16.762	0.421	0.961	76.923	0.217	0.987	3.720	13.32	0.979
WAC	24.0874	0.356	0.840	83.333	0.316	0.964	10.626	12.33	0.844

Explanations: R^2 = correlation coefficient, A = Temkin isotherm equilibrium binding constant ($\text{dm}^3 \cdot \text{g}^{-1}$), B = constant related to heat of adsorption ($\text{J} \cdot \text{mol}^{-1}$), K_F, $1/n$, $q_{\max}$, K_L as on p. 226.
Source: own study.

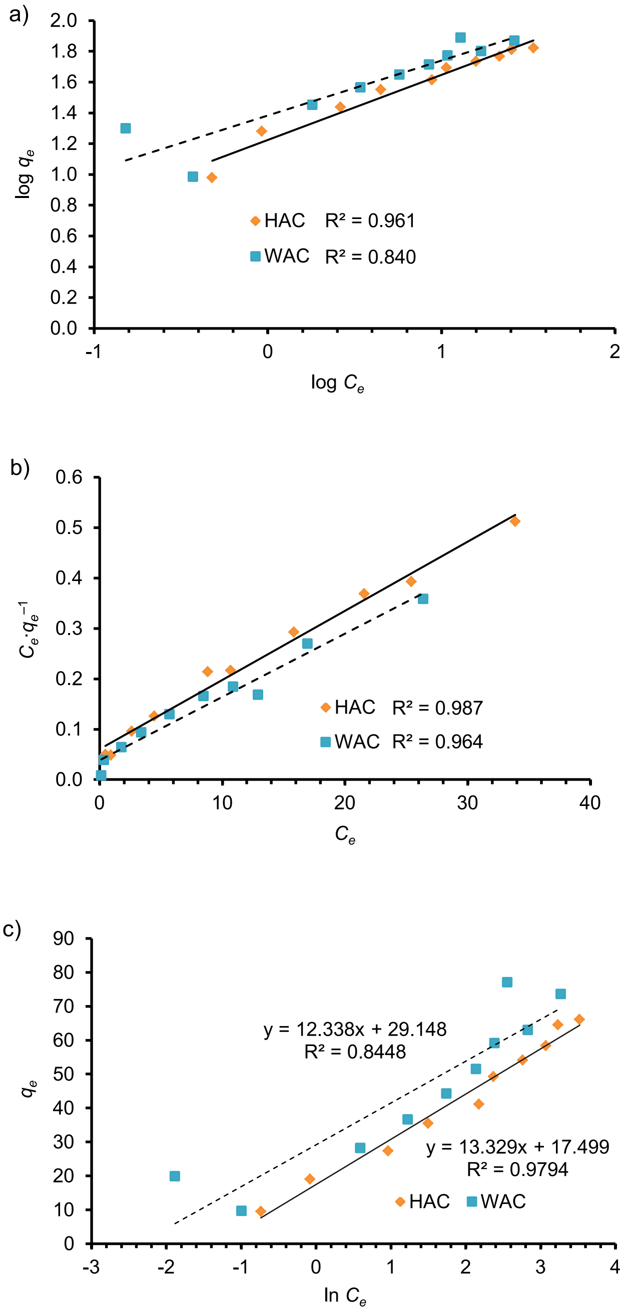


Fig. 5. Isotherm models for removal of imidacloprid (IMD) pesticide by hazelnut (HAC) and walnut activated carbon (WAC): a) Freundlich, b) Langmuir, c) Temkin; q_e, C_e as on p. 226; source: own study

One of the most important factors of the Langmuir isotherm is called dimensionless constant or separation factor (R_L) which can be calculated by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{9}$$

- unfavourable adsorption: $R_L > 1$;
- linear: $R_L = 1$;
- irreversible or favourable: $R_L = 0$, $0 < R_L < 1$;

where: C_0 = initial imidacloprid concentration ($\text{mg} \cdot \text{dm}^{-3}$).

The value of R_L in this study was found to be 0.32 and 0.24, respectively, indicating that the adsorption of imidacloprid onto HAC and WAC was favourable. The values of $1/n$ for the adsorption of imidacloprid onto HAC and WAC were 0.421 and 0.356, respectively, indicating the heterogeneous nature of the activated carbons. The values of $1/n$ were between 0 and 1, indicating that the adsorption of imidacloprid onto HAC and WAC is favourable.

COMPARISON OF IMIDACLOPRID ADSORPTION CAPACITY WITH OTHER ADSORBENTS

Thermodynamic studies

Table 5 represented the comparison of the adsorption capacities obtained in previous studies for the adsorption of imidacloprid pesticide in the present work. According to Table 5, the adsorption capacity of the imidacloprid pesticide onto HAC and WAC was higher than 70 $\text{mg} \cdot \text{g}^{-1}$ (Zhao *et al.*, 2018; Mohammad and El-Sayed, 2021), while lower than the other in comparison. The difference in adsorption capacity of different adsorbents is according to different parameters such as precursor used, and functional group. The activated carbon in this work can be successfully used as an adsorbent for the elimination of imidacloprid from contaminated water.

In order to study the effect of temperature on the adsorption of imidacloprid onto HAC and WAC with the initial concentration of imidacloprid (10 $\text{mg} \cdot \text{dm}^{-3}$), adsorbent dose 0.1 g·(100 cm^3)$^{-1}$ at the temperature range of 25–50°C, the suspension was shaken for 2 h. The thermodynamic parameters including standard entropy change ($\Delta S°$, $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), standard enthalpy change ($\Delta H°$, $\text{kJ} \cdot \text{mol}^{-1}$), and Gibbs energy ($\Delta G°$, $\text{kJ} \cdot \text{mol}^{-1}$) were calculated from Van't Hoff equation:

$$\Delta G = -RT \ln K \tag{10}$$

Table 5. Comparison of the adsorption capacity of imidacloprid (IMD) pesticide onto different adsorbents

Adsorbent	Adsorption capacity (mg·g^{-1})	Reference
Ricinodendron heudelotii shells activated carbons	43.48	Urbain *et al.* (2017)
Peach stones activated carbon	39.37	Mohammad and El-Sayed (2021)
Peanut shells activated carbon	8.68	Zhao *et al.* (2018)
Sugarcane activated carbon	313.00	Ma *et al.* (2021)
Eucalyptus woodchip biochar	14.75	Srikhaow *et al.* (2022)
Sludge activated carbon	166.00	Sanz-Santos *et al.* (2021)
Hazelnut activated carbon	76.92	this study
Walnut activated carbon	83.33	this study

Source: own elaboration based on literature.

$$\Delta G = \Delta H - T\Delta S \tag{11}$$

where: R = universal gas coefficient (kJ·mol^{-1}·K^{-1}), T = temperature (K), K = the equilibrium constant.

The results of the thermodynamic adsorption of imidacloprid onto HAC and WAC are shown in Table 6. According to Table 6, the negative values of $\Delta H°$, indicate the adsorption of imidacloprid pesticide onto HAC and WAC exothermic and describe the decrease in the adsorption of imidacloprid with an increase in the temperatures. Furthermore, the negative values of $\Delta G°$ indicate that the adsorption of imidacloprid onto HAC and WAC is spontaneous. According to the value of $\Delta G°$, the adsorption process is classified as physical adsorption (from 0 to –20 kJ·mol^{-1}) and chemisorption (from –80 to –400 kJ·mol^{-1}) in nature.

Table 6. Thermodynamic parameters of imidacloprid removal by hazelnut (HAC) and walnut activated carbon (WAC) from aqueous solutions in the temperature range of 298–323 ±2 K

Adsorbent	$\Delta G°$			$\Delta S°$	$\Delta H°$
	298 K	308 K	323 K		
HAC	–5.559	–2.585	–2.083	–0.650	–1.936
WAC	–4.915	–2.747	–2.302	–0.500	–1.459

Explanations: $\Delta G°$ = Gibbs energy (kJ·mol^{-1}), $\Delta S°$ = standard entropy change (kJ·mol^{-1}·K^{-1}), $\Delta H°$ = standard enthalpy change (kJ·mol^{-1}).
Source: own study.

Regeneration of activated carbons

Regeneration or reusability is a very important determination of adsorbent in wastewater on the large scale. Three cycles of adsorption-desorption have been performed using 0.5 M HCl. The results are shown in Figure 6. The removal percentage of imidacloprid by HAC and WAC was the same during the three cycles, 93.98 and 95.25%, respectively. These results indicated that the two prepared activated carbons (HAC and WAC) have been reused and regenerated for three cycles.

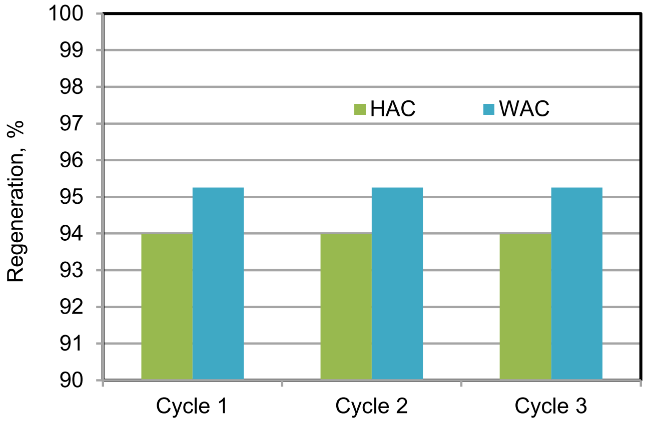


Fig. 6. Three cycles of regeneration (adsorption-desorption by HCl) of imidacloprid (IMD) pesticide by hazelnut (HAC) and walnut activated carbon (WAC); source: own study

CONCLUSIONS

The use of nuts like hazelnut and walnut shells as a low-cost precursor for the preparation of activated carbon for the removal of imidacloprid pesticide from contaminated water is a sustainable way to solve the problems in the environment. The characteristics of hazelnut (HAC) and walnut activated carbon (WAC) were studied by elements content, Brunauer–Emmett–Teller (BET) specific surface area, Fourier-transform infrared (FTIR), and scanning electron microscopy (SEM) examination. Different parameters have been studied for the removal of imidacloprid pesticide by HAC and WAC. The results indicated that the removal of IMD decreased as its initial concentration increased with the privilege to WAC than HAC. On the other hand, the removal of IMD pesticide onto HAC and WAC was not pH dependent in the examined pH range (1–8). Different kinetic models, pseudo-first-order, pseudo-second-order and intra-particle diffusion were applied to fit the experimental data. The data indicated that the pseudo-second-order model was the best for the description of the adsorption of IMD pesticide onto the two adsorbents with R^2 close to more than 0.99. Suggesting, that the imidacloprid (IMD) pesticide adsorption on two adsorbents is a chemical process, the Freundlich, Langmuir, and Temkin isotherm models were applied to describe the isotherms and the

Langmuir isotherm provided the best fit for the experimental results for both activated carbons. The maximum adsorption capacities for HAC and WAC were 75.923 mg·g^{-1} and 83.333 mg·g^{-1}, respectively. The two activated carbons (HAC and WAC) have been reused and regenerated for three adsorption–desorption cycles. These findings suggest that the prepared activated carbons of HAC and WAC are promising as adsorbents for the removal of imidacloprid pesticide from contaminated water.

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