Environmental Engineering and Management Journal *February 2020, Vol. 19, No. 2, 335-343*
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

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AGRI-WASTES AS A LOW-COST ADSORBENT FOR NICOSULFURON HERBICIDE

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Abstract

The contamination of aquatic and terrestrial environments by pesticides is highlighted by their possible toxic properties and poor biodegradability on the environment. The development of low cost by products from agricultural sectors as a suitable solution for contaminated areas remediation is of great environmental interest. Straw wastes can be considered as a promising alternative to remove different chemical compound that are environmentally toxic.
In this study, some materials derived from agricultural (agri)-wastes (wheat and corn straw) in mixture with soil, were investigates as potential adsorbents for nicosulfuron removal. After mineralization (850°C) and KOH activation to obtain the biochars, the samples were structurally characterized by scanning electron microscopy and Fourier transform infrared spectroscopy. Interaction studies between nicosulfuron - biochars and soil were performed at various concentrations and pH of 7. The adsorbent capacity was evaluated using batch sorption test and liquid chromatography coupled with mass spectrometry. The characterization results showed different functional groups present in the structure of these biochars while surface analysis showed an increase of surface roughness. The Langmuir isotherm and pseudo second order mechanism describes the kinetics of nicosulfuron herbicide. The results obtained highlight the importance of agri-waste as a natural adsorbent, being a solution for the removal of nicosulfuron from contaminated environments.

Key words: adsorption, agri-wastes, nicosulfuron, soil, straw

Received: January, 2019; Revised final: February, 2020; Accepted: February, 2020; Published in final edited form: February, 2020

1. Introduction

Nicosulfuron (2-[(4, 6-dimethoxypyrimidin-2-ylcarbamoyl) sulfamoyl]-N, N-dimethylnicotinamide) is a selective herbicide adopted by Integrated Pest Management to advocate growth of healthy crops and minimize pesticide use. This management practices have engendered the use of new-generation pesticides applied at lower doses (but often in mixture), in order to improve their efficiency in the range of weeds treated (Carles et al., 2018). Despite their low application rate (60 g a.i. ha^{-1}) on soil surface, this herbicide is persistent and do not degrade into less harmful components. Their metabolites present significant ecological and health risks in biotic and abiotic matrices (Petric et al., 2016; Hlihor et al., 2019). Therefore, the efficient removal and recycling of nicosulfuron from environment have become a significant issue from economical and health perspectives.

Different types of methods such as photocatalytic degradation, advanced oxidation

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processes, enzymatic biodegradation and adsorption are available to treat pesticides. Among these methods, adsorption is found to be promising technique due to its low operation cost, high attraction performance, and relatively low environmental impact (Ahmed and Hameed, 2018). Activated carbon (Suo et al., 2019), magnetic nanoparticles (Wang et al., 2017), silica nanomaterials (Kalhor et al., 2018) and graphene (Wanjeri et al., 2018) have been successfully utilized to treat various pesticide due to their high surface area and adsorption capacity. In terms of raw materials and preparation methods, these adsorbents are costly. For instance, the cost of activated carbon ranges between 1650 USD tons^{-1} to 9900 USD tons^{-1}, whereas that of carbon nanotubes is in the range of 20,000 - 80,000 USD tons^{-1} (Liu et al., 2018). Furthermore, the high cost of this approach has prompted the search for alternative that do not increases the operational price of treatment technique.

Recent findings have concentered on highly selective adsorbents of agriculture origin, as an efficient adsorbent in the field of land remediation, which can not only reduce the environmental charge but also achieve the effect of treating „waste by waste'' (Chesca et al., 2018; Huang, 2017; Periyaraman et al., 2019). Generally, the goal is to replace activated carbons - representing the state-of-the-art - by means of a byproduct coming from various activities such as agriculture and industry (De Gisi et al., 2016).

Straw biomass (wheat, corn, soybean, barley, rice, etc.) is a renewable energy source and very common all over the world. However, most straw biomass is incinerated and discarded, which has caused serious environmental pollution (Li et al., 2017). At present, modified biomass adsorption contaminants have been extensively studied, being reported to have potential for heavy metal and pesticides sorption (Bulgariu et al., 2018; Cara et al., 2015; Khambhaty et al., 2016; Tounsadi et al., 2019). Rojas et al., (2014) reported that atrazine, alachlor, endosulfan sulfate and trifluraline were efficiently removed by three adsorbents, sunflower seeds shells, rice husk and composted sewage sludge. Mandal et al. (2017) showed that rice straw biochar could effectively adsorb pesticides from water. Cara et al. (2017) investigated the potential of alkaline treated straw (wheat and corn) in mixture with soil, for the removal of sulfonylurea molecules from an aqueous solution. The results sustained that the alkaline treated straw have biosorption characteristics, being suitable adsorbent materials.

In this work, an attempt was made to investigate two modified agri-wastes (wheat and corn straw) as a low - cost adsorbent for the removal of nicosulfuron herbicide from aqueous solution. Due to the fact that nicosulfuron is a sulfonylurea herbicide which has high solubility in water, high mobility and slow degradation, there are definite concerns about environmental risk. For this, the specific parameters associated with adsorptive capacity of agri-waste-soil mixture for nicosulfuron herbicide, as well as Langmuir and pseudo-second order models were used to identify the mechanisms involved in adsorption process.

2. Experimental

2.1. Materials

The soil and straw material (wheat and corn type) were collected from Ezăreni - the Experimental Farm of the Agricultural University Iasi Romania (47°07′ N latitude, 27°30′ E longitude). The agri-straws were washed several times with ultrapure water and cut into small pieces. The samples were dehydrated at 70°C for 24h, grinded, and sieved to obtained particle with a size of 500 -700 µm. Then they were subject to KOH activation in the ratio of 1:1 (w/w) at 100°C for 2 h. After that, the samples were transferred to furnace - 3 h at a heating rate of 10 C min^{-1}, 450 C + 2h at a heating rate of 10 C min^{-1}, 850°C. The samples were cooled at room temperature and washed with ultrapure water until a pH of ∼7 was reached (almost the same pH as the soil). Then, they were dried at 105 C for 24 h and stored in desiccators for further use. The agri-wastes samples acquired after KOH activation and 850°C mineralization were assigned as Cs-850°C and Ws-850°C.

To provide information on the physical and chemical nature of the soil, standard characterization methods were used. The soil of the study area is mainly characterized by clay-loamy texture (cambic chernozem - SRTS, 2012, haplic chernozem - WRB-SR, 2006) with 3.06% humus content and 21.22 me 100 g^{-1} soil cationic exchange capacity (Cara et al., 2017). The soil pH was measured in a 1/2.5(w/w) soil/ultrapure water mixture, using a direct-reading pH meter, while total organic carbon content (1.39% C org) was determined by dichromate oxidation.

Nicosulfuron with a purity of 95%, chemical formula of $C_{15}H_{18}N_6O_6S$ and molecular weight of 410.405 g mol^{-1} was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All other compounds were commercially available and of high-performance liquid chromatography grade.

2.2. Instrumentation

All adsorption measurements were performed at room temperature on a Thermo Scientific LC-MS coupled with an Orbitrap Q-Exactive analyser. The retention time of nicosulfuron was 5.38 min using methanol/water (60:40 v/v) as liquid phase, at a flow rate of 1 mL min^{-1}. A pH meter combined with glass electrode was employed to measure pH of all the solutions. Orbital shaker was used for shaking of solution during adsorption study. Scanning Electron microscopy (SEM) (FEI - Field Electron and Ion Company) was used to analyze surface morphology and structural images of each material. The functional groups and any chemical changes that may have occurred after activation and mineralization of the agri - wastes were obtained using KBr pellets (1:100

sample/KBr), and the spectra were acquired on a FT-IR spectrometer in the region of 400-4000 cm^{-1} in transmission mode with 4 cm^{-1} resolution and the average of 100 scans.

2.3. Adsorption performance

The performance of the agri-wastes for retaining nicosulfuron molecules was evaluated under initial nicosulfuron concentrations, contact time and solution pH of 7. 2 g of soil and 0.01 g of agri-waste was added to a set of 100 mL Erlenmeyer flasks containing 20 mL of solution with the required initial concentration. The content of the flasks was shacked on an orbital shaker at 350 rpm, at room temperature. The influence of initial concentration on agri-wastes performance was study at a pH=7, the pH value of the soil. The solution pH was adjusted using either 0.1 M NaOH or 0.1M HCl. The influence of contact time (0 -24 h) was explored at various initial concentrations (1 – 100 mg L^{-1}). The removal efficiency and the adsorbed amount q (mg g^{-1}) were evaluated by Eq. (1):

$$q = \frac{(C_0 - C)}{W} V \qquad (1)$$

where: C (mg L^{-1}) and C_o (mg L^{-1}) are the residual and initial concentration of nicosulfuron, respectively. The soil and agri-waste mass and the volume solution are W (g) and V (L), respectively.

2. 4. Adsorption studies

The adsorption isotherms and kinetics of the soil-agri-waste system were obtained under the same procedure as that for adsorption performance. Isotherm study was performed until an equilibrium state was reached, and the equilibrium uptake, q_e (mg g^{-1}) was determined by applying Eq. 1 at the equilibrium concentration, C_e (mg L^{-1}).

The adsorption studies were performed by adding 2 g of soil and 0.01 g of agri-waste to 20 mL of nicosulfuron solution at different concentrations (1-100 mg L^{-1}) at pH 7.0 for 120 min. the experimental data were analyzed by Langmuir and Freundlich models as follow:

$$\text{Langmuir isotherm: } q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \qquad (2)$$

$$\text{Freundlich isotherm: } q_e = K_F C_e^{1/n} \qquad (3)$$

where: q_{max} is the maximum adsorption capacity (mg g^{-1}); C_e is the concentration of nicosulfuron at equilibrium (mg L^{-1}); K_L (mg g^{-1}), K_F (L g^{-1}) and n are the Langmuir and Freundlich constants.

The kinetic study was conducted for the time range of 0 - 24 h; using the residual concentration at time t, C_t (mg L^{-1}), the adsorbed amount at time t, q_t (mg g^{-1}) was also evaluated from Eq. (1). Pseudo-first order (Langergren, 1898) and pseudo-second order (Ho and McKay, 1999) models were adopted for the analysis of kinetic data, as follows:

$$\text{Pseudo-first order: } q_t = q_e (1 - e^{-k_1 t}) \qquad (4)$$

$$\text{Pseudo-second order: } q_t = \frac{q_e^2 k_2}{1 + K2qet} \qquad (5)$$

where: q_e (mg g^{-1}) and q_t (mg g^{-1}) are the nicosulfuron adsorbed at equilibrium and time t, respectively; k_1 and k_2 (mg $g^{-1}min^{-1}$) are the rate parameters of both models.

3. Results and discussions

3.1. Characterization of the adsorbents

The basic and consequent analysis of the Cs, Ws, Cs-850°C and Ws-850°C are presented in Table 1. The results reveal that the H and O content of the obtained Ws and Cs-850°C, were 1.13-1.94% and 16.46 - 20.42%, and those of agri-waste (Cs and Ws) were 5.23 - 7.13% and 41.75 - 45.86%, respectively.

Analytical elements likewise the atomic H/C and O/C ratio are relevant indicators of biochar characteristics. Generally, the changes in oxygen and hydrogen content and the low (H and O) percentages denote an intense deoxygenation and dehydrogenation reaction through the mineralization process (Manya et al., 2014). Oxygen content and its close relationship with composition of functional groups substituted, plays an important role in surface chemistry of biochars. Therefore, the higher C content in Ws-850°C facilitated the formation of structures which can improve the adsorption of nicosulfuron and another aqueous contaminant (Yi et al., 2016). These results are in agreement with the results described by Peng et al., (2016) where they explored reed biochars, by pyrolysis temperatures ranging from 300°C to 600°C.

The molar ratios O/C and H/C of the Cs and Ws-850°C were lower than those of the raw agri-wastes. As well, the lower polarity index (O+N)/C suggest the same enhancement in hydrophobicity and reduction of surface polar functional groups. This finding confirmed the high mineralization of the wheat straw, which can provide favorable and hydrophobic adsorption sites for nicosulfuron (Sun et al., 2014). The high temperature involved in mineralization process, minimize the H/C and O/C ratios which reflects the loss of easily degradable carbon compounds (Manya et al., 2014). Similar results were found by Ahmed et al., (2018) who utilized barley straw as precursor to prepare biochar adsorbent through thermal pyrolysis. Important properties of adsorbents e.g. surface area, volatiles, ash and water holding capacity are susceptible functions of agri-wastes mineralization and process conditions (Chen et al., 2014; Varjani et al., 2019). Agri-wastes with high moisture content had the drawback of more energy input during water evaporation (Wang et al., 2017). Based on low moisture (2.56 - 4.58%) and ash percentages of Cs and Ws-950°C, and corroborated with high carbon content 76.48%, these results indicated that Ws and Cs are effective raw material for the preparation of adsorbents with highly reactive surfaces.

Table 1. Basic and consequent analysis of Cs, Ws, Cs-850°C and Ws-850°C

Material	*Basic analysis (wt %)*		*Consequent analysis (wt %)*					*Atomic ratios (wt %)*	
	Ash	***Moisture***	***C***	***H***	***O***	***N***	***H/C***	***O/C***	***(O+N)/C***
Ws	8.72	2.56	48.29	7.13	41.75	2.83	0.147	0.864	0.923
Cs	5.23	2.87	47.62	5.23	45.86	1.29	0.109	0.963	0.990
Ws-850°C	6.77	4.32	76.48	1.94	16.46	5.12	0.025	0.215	0.282
Cs-850°C	3.28	4.58	71.76	1.13	20.42	6.7	0.015	0.284	0.377

Morphology analysis

Scanning electron microscopy (SEM) was used to examine the morphological features of agri-waste before and after mineralization. The SEM images of the Cs, Ws, Cs-850°C and Ws-850°C structures are presented in Fig. 1.

Were numerous well-ordered parallel textures on the surface of Ws and Cs previous to treatments (Fig. 1 a_1 and a_2). After mineralization and activated by KOH, the parallel structures were broken and with the release of the gases produced by high temperatures, the surface of the Ws and Cs presents different dimensions in the form of spherical agglomerates that are intersecting and interconnecting (Fig. 1 b_1 and b_2). Suo et al (2019) prepared activated carbon from starch by KOH activation and found that the porosity is created by KOH remaining intercalated in the lignocellulosic structure of the straw (Danish and Ahmad, 2018). Therefore, mineralization and KOH solution modified the morphology by destroying cell tissues and reduction the connection between the cells. The Cs-850°C and Ws-850°C were found to have rougher surfaces with increased specific area, which would strongly affect their adsorption properties.

FT-IR spectra of agri-waste (Cs and Ws) before and after mineralization (Cs-850°C and Ws 850°C) were used to characterize the adsorbents. The spectra consist of similar characteristics peaks, with a predominant analogous structure and bands typically assigned to cellulose and hemicellulose (Fig. 2).

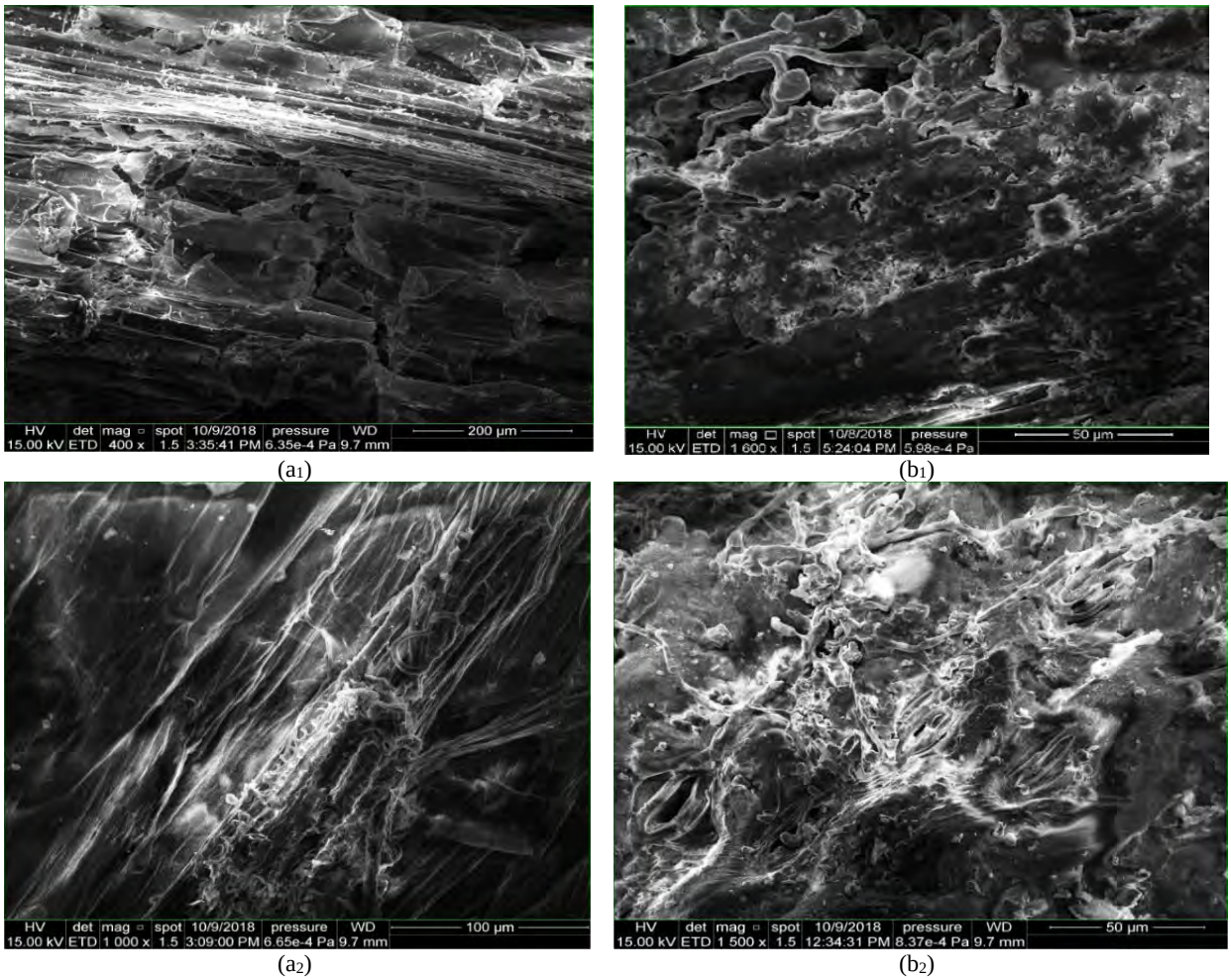
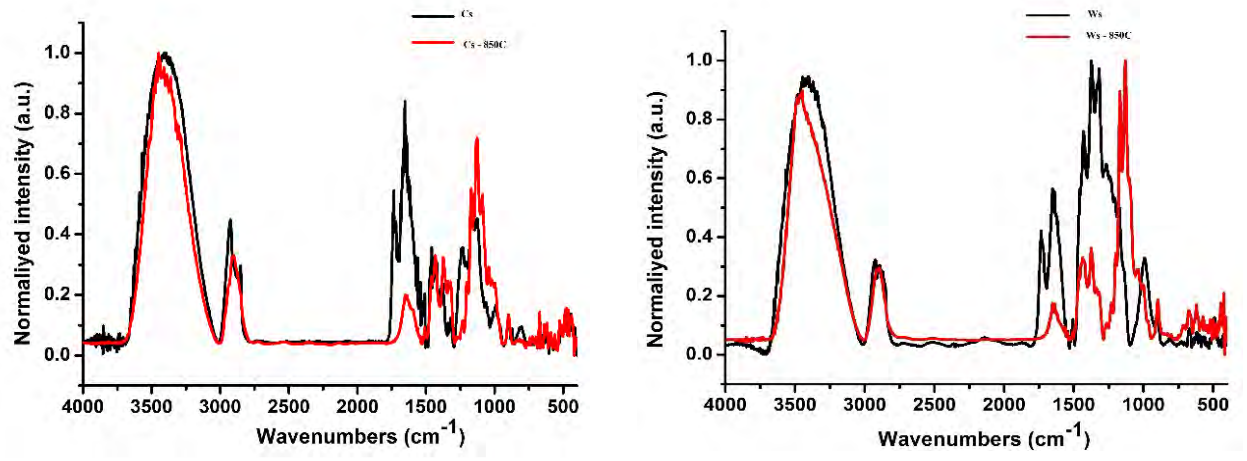


Fig. 1. SEM morphology for untreated wheat (a_1) and corn straw (a_2) and (b_1) treated wheat and corn straw (b_2)



(a) (b)

Fig. 2. FTIR analysis spectra of (a) corn straw and (b) wheat straw

A dominating band centered at 3398.1 cm^{-1} representing O-H and N-H stretching vibration, which is common in hydrophilic materials. The peak at 2990.63 cm^{-1}, represented C-H bonds in aliphatic radicals (Andrade-Mahecha et al., 2015; Martelli-Tosi et al., 2017). Moreover, the band at 1734.63 cm^{-1}, was attributed to the carbonyl groups present in carboxylic compounds (such as: uronic acids, hemicelluloses, etc). It may also be attributed to ester linkage of carboxylic groups of the ferulic and p-coumaric acids of lignin (Andrade-Mahecha et al., 2015). For example, this peak intensity significantly changed through the chemical treatment, due to lignin and hemicelluloses thermal degradation. The peak at 1458.39 cm^{-1} correspond to the aromatic skeleton of materials.

A minimization in its intensity and/or its shift to higher wavelengths was associated with modification of the aromatic radicals. The band at 1234.75 cm^{-1} was attributed to the C-N stretching vibration, while the band at 803.64 cm^{-1} is the fingerprint band. Based on these remarks, the hydroxyl, amine, carbonyl, carboxylic groups, etc. from the structure of agri-waste may interact with nicosulfuron molecules during the adsorption process.

The greatly distinctions through the new agri-waste (after KOH treatment), were in the region of 1641.95 cm^{-1} and 1127.12 cm^{-1} corresponding to the carbonyl C=O groups and C-O/O-C-O stretching vibrations respectively. The small bands at 1429.04 cm^{-1} and 1374.67 cm^{-1} proves the aromatic structure of materials. Due to the dominant C-C and C-H groups, a hydrophobic structure was established, with low oxygenated functional groups, which enhanced the adsorption process (Ahmed et al., 2018).

The mechanism revealed by FT-IR spectra, is proposed as follows (Bulgariu et al., 2011): neutralization of free carboxylic groups and/or alkaline hydrolysis of esters and others carboxylic acid derivates.

3.2. Adsorption performance

3.2.1. Influence of nicosulfuron concentration and time

Fig. 3 shows the time – dependent effectiveness of nicosulfuron – agri-waste – soil mixture, at different initial nicosulfuron concentration (10, 20 and 100 mg L^{-1}). A decrease in the amount of nicosulfuron adsorbed was noticed with time, until equilibrium was reached within 7 and 11 h for initial nicosulfuron concentration of 10 and 100 mg $L^{-1,}$ respectively. For all studied initial concentrations, the adsorption of nicosulfuron proved to be at an initial stage, fast and then slowed down gradually. Further increase of contact time showed negligible changes to the rate of adsorption, thereby confirming the equilibrium state. The preliminary high adsorption of nicosulfuron was due to the existence of available binding sites on the Ws and Cs - 850°C surface which accelerated the adsorption rate. The subsequent lower adsorption rate could be due to the cluster of nicosulfuron molecules onto the surface particles which delay the diffusion of nicosulfuron molecules towards the agri-wastes surfaces (Arshadi et al., 2017).

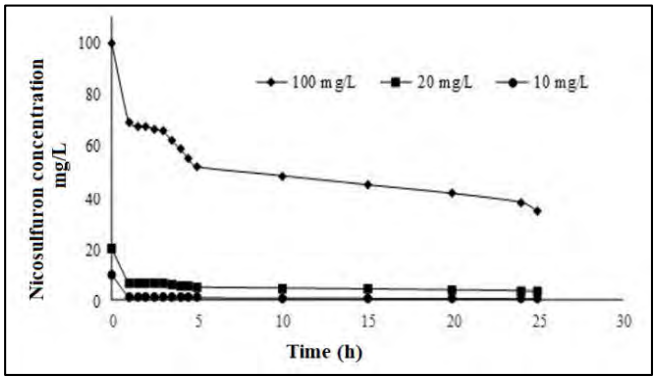


Fig. 3. Influence of initial nicosulfuron concentration on nicosulfuron adsorption by Ws - 850°C

After 24 h contact time, a decline around 89% and 84.37% in nicosulfuron concentration is related with low initial concentration of 10 and 20 mg L^{-1}, respectively. For concentrated nicosulfuron solution this reduction decreased to 69.87% due to the high percentage of nicosulfuron molecules compared to the available active sites from the surface of Ws and Wc – 850°C. Based on Mohammed et al., (2018) and Chen et al., (2016) the large amount of solute led to a competition between the molecules of solute towards the pores from the structure of the low-cost adsorbent and consequently reduces the adsorption extent. The obtained equilibrium time of 11 h, is in accordance with the results reported by Ogunah et al., (2016) where chlorsulfuron equilibrium was established in a period of 12h and no changes in concentration after 24h on different types of soil. Cara et al., (2017) studied the adsorption of chlorsulfuron on alkaline treated straw and found that equilibrium was reached after 12 h, while Otero et al., (2013) established a 4 h state of equilibrium for nicosulfuron on a calcinated Mg - Al hydrocalcite.

3.2.2. Adsorption isotherm

The study of adsorption equilibrium data by applying different isotherm models are used to express both the adsorption mechanism (surface properties) and the maximum adsorption extent. The analysis shows better fitting of data by the Langmuir model with R^2 values (0.968 - 0.997) relative to the R^2 values (0.8480 - 978) for the Freundlich model (Table 2). The analysis of experimental equilibrium data, reveals the monolayer coverage of nicosulfuron molecules may occur onto the homogeneous surface of Cs and Ws-850°C.

According to the parameters of the Langmuir model, the maximum uptake which is a measure of the adsorption capacity to form a monolayer, increases in the order Ws-850°C > Cs- 850°C under tested conditions. Moreover, the differences in adsorption capacity depends on the nature of the material (Fig. 4). Nicosulfuron adsorption on soil gave the lowest Langmuir sorption capacity (q_m). Thus, the sorption capacity and the q_m values increased with the addition of exogenous organic carbon. Adsorption being the main process, which reduces the mobility of pesticides in soil, the addition of exogenous organic carbon has been suggested as a method to reduce nicosulfuron leaching (Rojas et al., 2014). Fig. 5 presents the adsorption data and their correlation by Langmuir isotherm.

Similar results were found on various adsorbents derived from rice straw, corn straw and wheat straw (Tartakova et al., 2013; Zhao et al., 2013).

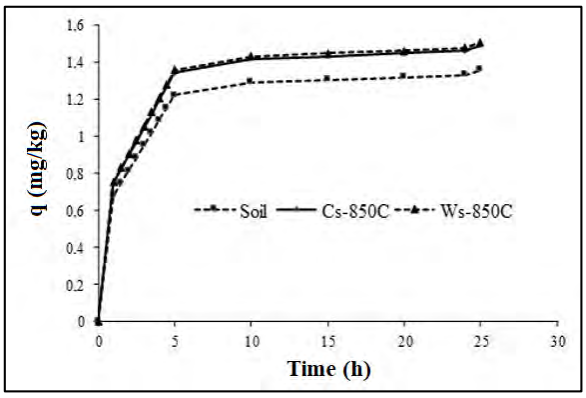


Fig. 4. Influence of the agri-waste and concentration on nicosulfuron adsorption

Additionally, the high values of adsorption equilibrium constant (K_L) confirmed strong chemical interaction between superficial groups of the Cs and Ws - 850°C and chlorsulfuron molecules, which enhance the adsorption process. The differences of the adsorption capacity among materials were caused by the raw material, H-bonding interaction between nicosulfuron and polar groups on the straw surface, π - π electron donor-acceptor interactions, and hydrophobic moieties from the straw surface (Liu et al., 2015). According to Ji et al., (2011) and Zhang et al., (2011), a larger surface area with more porous sites which favors the pore filling mechanism is due to the high temperature. These suggest the different mechanisms that might control the adsorption of nicosulfuron.

For nicosulfuron-agri-waste-soil mixture, the Freundlich isotherm is related to multilayer sorption and associated with heterogeneous systems (Freundlich, 1906). According to the parameters of Freundlich isotherm, the sorption is not linear due to the greater degree of heterogeneity on the surface of Ws and Cs-850°C which can influence the adsorption process (Rosa et al., 2018).

The fitted parameters of the isotherm models, suggested that the adsorption of nicosulfuron on Cs and Ws – 850°C was not govern by a strict monolayer adsorption process and heterogeneous surface adsorption and chemical adsorption might also be involved (Yi et al., 2016).

Table 2. Adsorption isotherm parameters for nicosulfuron on soil and treated straw

Isotherm	*Constants*	*Soil*	*Ws – 850°C*	*Cs – 850°C*
Langmuir	R^2	0.997	0.968	0.977
	q_L (mg g^{-1})	166.6	431.03	348.43
	K_L (L g^{-1})	0.50	0.53	0.174
	R_L	0.019	0.018	0.054
Freundlich	R^2	0.978	0.848	0.900
	n	0.7	0.6	0.67
	K_F (L g^{-1})	79.43	141.25	126.18

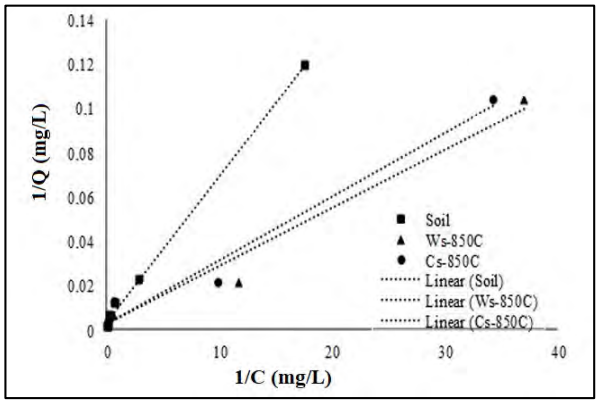


Fig. 5. Langmuir sorption isotherm of nicosulfuron

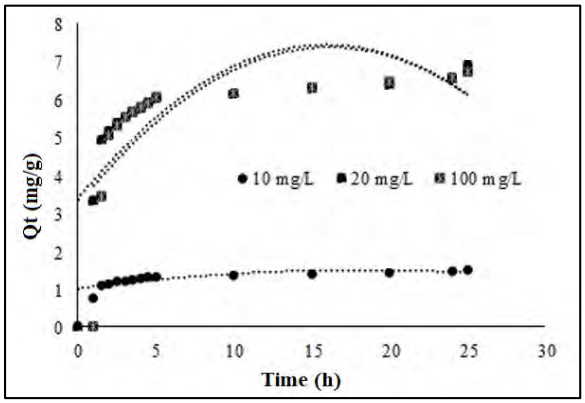


Fig. 6. Kinetic model of nicosulfuron

Compared with low cost adsorbents from other wastes, the data provides an intuitive adsorption performance towards nicosulfuron molecules that competes with other expensive adsorbents. For example, the capacity of the Ws and Cs – 850ºC was much higher than of the biochar from paper mill sludge (Devi and Saroha, 2015).

3.2.3. Adsorption kinetics

The experimentally kinetics data are widely applied to predict (identify) the mechanism and rate constant of the adsorption process. Fig. 6 presents the kinetics models based on the quantity of nicosulfuron adsorbed as a function of contact time. The pseudo-first-order kinetics model of Lagergren (1898) and the pseudo-second-order model of Ho and McKay (1999) were used to determine the rate of adsorption and to distinguish whether the adsorption was chemisorption or physisorption.

In terms of determination coefficient (R^2), the results showed that the pseudo-second-order type showed the successful fitting of the data, relative to the R^2 values of the pseudo-first-order kinetics model (Table 3). The results also showed good agreement between the experimental q_e values and calculated q_e values of the pseudo-second order model. The slight differences between the experimental q_e values and calculated q_e values may be due to the uncertainty inherent in obtaining the experimental q_e values (Kumar et al., 2012). The pseudo-second-order type suggests that the adsorption rate is controlled by the active sites, then the concentration of nicosulfuron, identifying adsorption under chemisorption type. Additionally, the second model, implies ion exchange or superficial complexation between the superficial groups of the Cs and Ws – 850ºC and nicosulfuron molecules from soil solution.

According to this model, the increase in nicosulfuron concentration from 10 mg L^{-1} to 100 mg L^{-1} enhance the calculated q_e values from 1.253 mg g^{-1} to 1.324 mg g^{-1} at room temperature. Moreover, the same increase in nicosulfuron concentration, decrease the values of the rate constant, k_2 from 1.52 mg g^{-1} min^{-1} to 0.87 mg g^{-1} min^{-1}. This finding might be (inter)connected with the presence of more nicosulfuron molecules with high competition towards active sites, leading a slow uptake (Reguyal et al., 2017). The best correlation of experimental kinetic data with pseudo-second-order model was also reported for nicosulfuron adsorption on Mg - Al hydrocalcite and other low cost adsorbents.

4. Conclusions

Corn and wheat straw were utilized as raw material to remove nicosulfuron herbicide from and agricultural soil. The analysis confirmed the efficient mineralization and activation of agri-waste with adsorbents generation towards highly reactive surfaces, as confirmed by SEM and FT-IR. Langmuir model and pseudo-second order model were successfully applied for the analysis of adsorption equilibrium and kinetics data. The adsorption process was found to be complex, depending on both time and concentration.

Additionally, the adsorption of nicosulfuron molecules onto the Ws and Cs - 850 ºC was not govern by a strict monolayer adsorption process; heterogeneous surface adsorption and chemical adsorption might also be involved. Thus, the agri-waste have great potential to be utilized as an effective low-cost adsorbent for the removal of contaminants such as nicosulfuron molecules from soil and aqueous solutions.

Table 3. Kinetic model parameters for nicosulfuron and soil-treated straw system

	Pseudo-first-order				***Pseudo-second-order***		
	$q_{e\ exp}$ (mg g^{-1})	**$q_{e\ est}$ (mg g^{-1})**	**K_1 (mg g^{-1} min^{-1})**	**R^2**	**$q_{e\ est}$ (mg g^{-1})**	**K_2 (mg g^{-1} min^{-1})**	**R^2**
Soil	1.3563	3.090	0.025	0.146	1.253	1.52	0.969
Ws – 850ºC	1.5065	5.584	0.0097	0.02	1.351	0.865	0.958
Cs – 850ºC	1.4905	5.714	0.009	0.02	1.324	0.87	0.963

Acknowledgements

This work was co-financed from Competitiveness Operational programme (COP) 2014 – 2020, under the project number 4/AXA1/1.2.3.G/05.06.2018, SMIS2014 +code 119611, with the title „Establishing and implementing knowledge transfer partnerships between the Institute of Research for Agriculture and Environment - Iasi and agricultural economic environment''.

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