Special Issue "Materiais 2015"

Adsorption of MCPA, 2,4-D and diuron onto activated carbons from wood composites

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Abstract

Activated carbon adsorbents were produced from particleboard and medium-density fiberboard, industry originated wastes, without value added applications. These materials were characterized, showing a well-developed microporous structure reaching 0.58 cm^3/g, and afterwards, their potential application for the removal of phenoxy acetic acids and substituted urea herbicide was evaluated. Studies in liquid phase were conducted in 2,4-dichlorophenoxy acetic acid (2,4-D), 4-chloro-2-methylphenoxy acetic acid (MCPA) and 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron), being the obtained data linearized using the Langmuir and Freundlich equations. Results indicated high removal capabilities for the adsorptives in study, reaching 0.97, 1.37 and 1.87 mmol/g for diuron, 2,4-D, and MCPA respectively, allowing the conclusion that these materials should be studied further, having in mind real life applications.

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Keywords: Activated carbon; adsorption; pesticides; monolith wood.

1. Introduction

Increasing use of pesticides, in agriculture and domestic activities for pest control is polluting our water resources, gradually forming a strong class of water pollutants, which is really a great concern, according to the World Health Organization and United States Environment Protection Agency [1,2].

Pesticides are also used in different purposes and they may be classified according to their function, chemical groups or even also to their nature, as organic or synthetic [3].

Several methods are described for pesticide removal such as ozonation, photocatalytic or aerobic degradation, combined photo-Fenton and biological oxidation, oxidation processes, filtration, coagulation, sedimentation and different adsorption systems.

Adsorption is considered an attractive method for removing pollutants and in particular pesticides from dilute solutions which involve the previous determination of the adsorptive behaviour on various adsorbents. Activated carbon (AC) materials have an important place among the adsorbents tested as they can be prepared from a wide variety of relatively low cost, natural or synthetic precursors, as largely described in the literature, and their improved properties allow them to adsorb various organic and inorganic compounds for a long time, being able to be regenerated and reused for several times [4-11].

The industries are still looking for environmentally friendly and cheaper AC retaining or increasing the adsorption capacities when compared with those often used for the same purpose. The use of agricultural or industrial by-products to produce high value AC can be the way to follow in order to increase the adsorbents efficiency and also reduce its final cost.

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The purpose of this work was to evaluate the adsorption potential of AC, prepared from the particleboard (PB) and medium-density fibreboard (MDF) monoliths, which are waste from the wood industries, for removal of selective herbicides, such 2,4-dichlorophenoxy acetic acid (2,4-D), 4-chloro-2-methylphenoxy acetic acid (MCPA), which are phenoxy acetic acids and 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron), which is a substituted urea herbicide, from the liquid phase. These pesticides were chosen since they present very different chemical and physical properties (Table 1) and could thereby be expected to give additional information on the adsorptive properties of the AC tested.

2. Experimental Procedure

2.1. Activated carbon preparation and characterization

A series of AC was produced, from MDF and PB monoliths, by physical activation with carbon dioxide. First, the monolith was submitted to a heating rate of 2 K/min, followed by a dwell time of 60 min, at 383 K; the second heating step was at 10 K/min until 1073 K, followed by a dwell time of 30 min, under a N_2 gas flow. The physical activation was carried out at 1073 K under a CO_2 flow and different dwell times were used in order to achieve a large range of burn-offs, ranging from 11 to 87 wt.%.

A complete characterization of the AC was achieved through different methods, normally used for this purpose, such as N_2 adsorption at 77 K, CHNS-O elemental analysis, point of zero charge and thermo-gravimetrical analysis of the precursors. The detailed description of the experimental procedure is given elsewhere [4,7,8].

2.2. Pesticides removal from liquid phase

Between the series of AC, those presenting a wider mean pore size and highest pore volume were selected, for MCPA, 2,4-D and diuron removal from the liquid phase. All pesticides used were obtained from Sigma-Aldrich, with purity ranging from 95.0 to 99.9%.

Previous studies on the influence of pH of the medium and contact time were performed in order to determine the ideal adsorption conditions for each pesticide [7]. The adsorption of different pesticides was carried out in a batch assays. A fixed quantity of AC was added to 25 mL of aqueous solutions of known concentrations of each pesticide, then the Erlenmeyer flasks were hermetically closed and placed in agitation for an equilibrium time, at 298 K.

The suspension was then filtered, and the residual pesticides were determined by UV/visible spectro-photometry, using a Thermo Nicolet Evolution 300 UV-VIS, at the appropriate wavelength. The amount of pesticides adsorbed on the AC was calculated by difference between the initial and the equilibrium concentrations.

Table 1. Pesticides physical properties.

	Adsorptive		
	MCPA	2,4-D	Diuron
Molecular weight (g/mol)	200.62	221.04	233.09
Molecular form	$C_9H_9ClO_3$	$C_8H_6Cl_2O_3$	$C_9H_{10}Cl_2N_2O$
Water solubility T = 293 K (mg/L)	825	900	42

3. Results and Discussion

3.1. Textural and chemical characterization

In this work, the MDF and PB monoliths were used as precursor, resulting in AC samples that retain the initial shape, which is an important characteristic for industrial applications [10], especially in continuous flow systems for liquid phase adsorption. All AC from the series were textural characterized by N_2 adsorption at 77 K and the obtained isotherms were essentially of type I, agreeing to a microporous structure. The isotherms were analysed based on BET, DR and α_S methods and the textural parameters are presented in Table 2.

Table 2. Textural parameters of activated carbons.

Activated carbon	A_{BET} (m²/g)	A_S (m²/g)	V_S (cm³/g)	V_0 (cm³/g)	L_0 (nm)
MDF 5950	1195	19.7	0.48	0.47	1.02
MDF 5933	805	14.3	0.33	0.31	0.66
PB 5960	1211	15.7	0.58	0.49	1.15
PB 5936	926	11.8	0.38	0.37	0.80

A = surface area, V = pore volume, L= mean pore width. The BET, S and 0 subscripts correspond to BET, α_S and DR methods, respectively.

The sample PB 5960 and MDF 5950, and PB 5936 and MDF 5933 were prepared through the same activation time, 240 and 120 min respectively. It is evident that micropore volume and mean pore size increase with the activation time. Moreover, when using the same experimental conditions, the AC prepared from PB show a higher micropore volume, when comparing with MDF, reaching 0.58 cm³/g and

wider mean pore size, highlighting the effect of the macroscopic characteristics of the precursors.

In the series, the AC presented a high carbon content ranging from 66.7 to 72.6% and a nitrogen content varying from 2.5 to 3.8%. The AC prepared from MDF present the highest nitrogen content (> 3.5%) and a high oxygen content, ranging from 8.7 to 12.5%, inducing a basic character on the AC, noticeable on the point of the zero charge, as the four AC chooses exhibited a pzc > 10. Based on their textural and chemical characteristics, the PB 5960, PB 5936, MDF 5950 and MDF 5933 were selected for application on pesticides removal from the liquid phase.

3.2. Pesticides removal from liquid phase

The adsorption of MCPA, 2,4-D and diuron as a function of contact time was first evaluated and an example of these data is shown in Fig. 1.
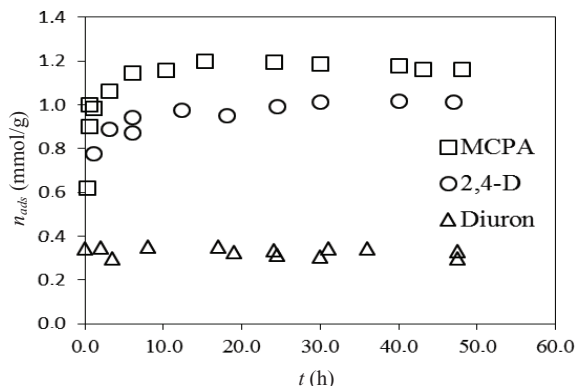

Fig. 1. Adsorption kinetics of MCPA, 2,4-D and diuron.

As it can be observed, the adsorption kinetics have similar trends and the pesticides adsorption can reach more than 80% in the initial 2.5h and apparent equilibrium is reached within 24h. The residual pesticides were evaluated at an adequate wavelength such: 228.6 or 279.0 nm for MCPA, 230 or 284 nm for 2,4-D and 212 or 250 nm for diuron. The pesticides adsorption isotherms were acquired at optimal conditions (pH=3.0 for MCPA and 2,4-D and pH=7.0 for diuron) and the data for the MCPA adsorption on the four AC are illustrated in Fig. 2.
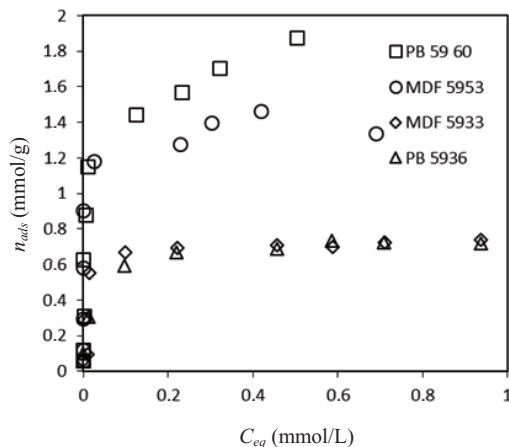

Fig. 2. Adsorption isotherms of MCPA from aqueous solutions, obtained at 298 K, on AC prepared from MDF and PB, by physical activation with CO_2.

From the isotherms and the data show in Table 3, it is clear that the adsorbed quantities of MCPA, 2,4-D and diuron increase along the sample sequence MDF 5933 < PB 5936 < MDF 5950 and PB 5960.

Table 3. Adsorption isotherm parameters of MCPA, 2,4-D and diuron onto AC prepared from MDF and PB.

	System	n_{max} (mmol/g)	n_{mL} (mmol/g)	K_L (dm³/mmol)	K_F (mmol/g) (dm³/mmol)$^{1/n_F}$	n_F
MCPA	MDF 5950	1.46	1.44	188.6	1.54	13.90
	MDF 5933	0.73	0.72	185.6	0.74	23.20
	PB 5960	1.87	1.68	165.9	1.99	7.10
	PB 5936	0.78	0.73	161.2	0.74	20.50
2,4-D	MDF 5950	1.19	1.18	55.1	1.34	5.60
	MDF 5933	0.71	0.72	42.5	0.72	12.10
	PB 5960	1.37	1.40	65.2	1.48	10.90
	PB 5936	1.11	1.09	60.6	1.12	10.40
Diuron	MDF 5950	0.88	0.91	232.9	1.20	7.64
	PB 5960	0.97	1.03	158.7	4.53	1.93
	PB 5936	0.35	0.38	203.6	0.38	27.80

n_{max} - maximum adsorption from the isotherm; n_{mL} - monolayer capacity; K_L - Langmuir constant; K_F and n_F - constant and exponent of Freundlich

This sequence follows the same order as the surface area and the micropore volume of the adsorbent. The pesticides adsorbed follow the same order on each AC, it means diuron < 2,4-D < MCPA.

Taking into account the optimal pH of the adsorption medium and the basic nature of the adsorbents, it is understandable that MCPA and 2,4-D, presenting an acid nature, adsorbed more when compared with diuron. However, the lesser adsorption of diuron could also be attributed to its greatest molecular dimension and to its very low water solubility when compared with MCPA and 2,4-D. It means, in diluted solutions, the diuron molecules are too far from the AC surface and the external transport can be considered as the limiting step in the process.

The most widely used equations for modelling equilibrium data, from experimental liquid phase adsorption, are Langmuir and Freundlich equations.

The Langmuir equation presents some limitations, especially when the adsorption is not limited to a monolayer and the adsorbent surface is heterogeneous. On the other hand, the Freundlich equation provides a very acceptable description of non-linear adsorption isotherms and the applicability of this equation for systems involving heterogeneous surfaces are further recommended.

3.3. Langmuir adsorption isotherms

The Langmuir equation could be expressed as follow:

$$\frac{C_{eq}}{n_{ads}} = \frac{1}{n_{mL} K_L} + \frac{1}{n_{mL}} C_{eq} \qquad (1)$$

where n_{ads} is the measured adsorption at a solute equilibrium concentration C_{eq}, n_{mL} the monolayer capacity and K_L the Langmuir constant.

By plotting (C_{eq}/n_{ads}) versus C_{eq}, as illustrated in Fig. 3, the parameters n_{mL} and K_L could be obtained, as included in Table 3. With all combinations of pesticides/AC, the Langmuir equation fits very well with the experimental data and, in particular, a very good fit was found for system AC/MCPA.

For all systems, the values of n_{mL} agree well with the respectively maximum value adsorbed, obtained directly from the experimental data. Moreover, the K_L value, assessed for each pesticide, is relatively constant on the four AC tested.

3.4. Freundlich adsorption isotherms

The Freundlich equation can be described as follow:

$$\log n_{ads} = \log K_F + \frac{1}{n_F} \log C_{eq} \qquad (2)$$

K_F and n_F are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models.
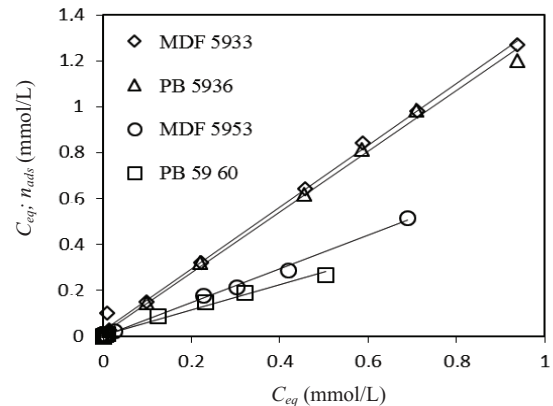

Fig. 3. Langmuir linearization for the adsorption isotherm of MCPA, from aqueous solutions, obtained at 298 K, on activated carbons prepared from MDF and PB.

Concerning the MCPA adsorption, and based on Fig. 4, the PB 5960 exhibits a lower n_F value, which is in agreement with the more rounded isotherm shape as showed in Fig. 2.
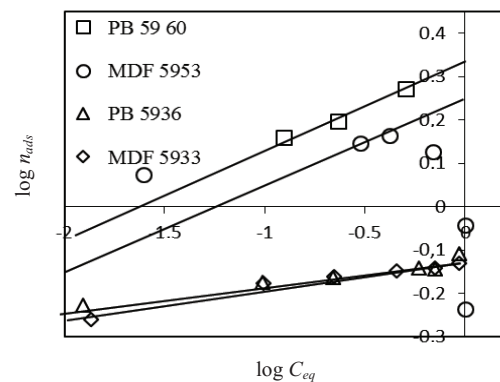

Fig. 4. Freundlich linearization for the adsorption of MCPA, from aqueous solutions, obtained at 298 K, on activated carbons prepared from MDF and PB.

The Langmuir linearization, for 2,4-D and diuron, not shown here, fits very well the experimental data and the n_{mL} obtained are really close to the maximum quantity adsorbed. With these pesticides, the Freundlich linearization was less applicable.

The AC prepared from MDF or PB by physical activation with CO_2, in particular the MDF 5960 and PB 5953, demonstrated high removal capacities for the three pesticides tested. For these systems, the amount adsorbed reaches almost the values found in

the literature when AC commercial was used. For example, the best results found, with the commercial AC Filtrasorb 400, were 1.94 and 1.86 mmol/g of MCPA and 2,4-D, respectively [12]. Also the commercial AC darco G-60 removed 1.29 mmol/g of diuron [12].

The AC prepared from PB and MDF and tested on the MCPA, 2,4-D and diuron presented adsorption capacities for these pesticides very close to those obtained with the commercial one, which allow us to state that PB and MDF AC could be a great substitute of those most commonly used for this purpose.

4. Conclusions

A series of activated carbon was produced from the particleboard and medium-density fibreboard monoliths by physical activation, with carbon dioxide, at 1073 K. A full characterization of the AC produced was achieved by nitrogen adsorption at 77 K, elemental analysis, and point of zero charge. The AC retains the initial shape, presenting a very well developed microporous structure, a high oxygen content and a basic character, these being determinant characteristics for possible applications in the removal of pesticides from the liquid phase. The AC adsorption potential, for phenoxy acetic acids removal, such 2,4-D, MCPA and diuron, from the liquid phase was evaluated. The PB 5960, having a larger specific area, higher micropore volume and a wider mean pore size showed a higher adsorption capacity for the three pesticides tested. With all AC, the extent of the adsorption was found as diuron < 2,4-D < MCPA and was attributed to the different chemical composition, molecular size and water solubility of the pesticides. However, the four AC revealed a good performance for pesticides removal, similar to that achieved with the commercial AC used for this purpose, indicating that these materials can be seen as an added value product with the capability to take its place along with the traditional adsorbents.

Acknowledgements

References

[1] Report of World Health Organization, Water Quality and Health Strategy 2013-2020, <http://www.who.int/water_sanitation_health/publications/2013/water_quality_strategy.pdf>, (accessed 12.04.2015).
[2] United States Environment Protection Agency, Technical support document for water quality based toxics control, Tech. Rep. EPA/ 440/485032, DC, USA, 1985.
[3] The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification, http://www.who.int/ipcs/publications/pesticides_hazard_2009.pdf>, 2009, (accessed 12.04.2015).
[4] I.P.P. Cansado, P.A.M. Mourão, A.I. Falcão, M.M.L. Ribeiro Carrott, P.J.M. Carrott, Fuel Process. Technol. 103 (2012) 64.
[5] M. Mahramanlioglu, I. Kizilcikli, I.O. Biçer. M. Tuncay, J. Environ. Sci. Health, Part B - Pesticides B38(6) (2003) 813.
[6] M.A. Fontecha-Camara, M.V. Lopez-Ramon, L.M. Pastrana-Martınez, C. Moreno-Castilla, J. Hazard. Mater. 156 (2008) 472.
[7] I.P.P. Cansado, P.A.M. Mourão, M.M.L. Ribeiro Carrott, P.J.M. Carrott, Adv. Mater. Res. 107 (2010) 1.
[8] I.P.P. Cansado, P.C. Galacho, A.S. Nunes, M.M.L.R. Carrott, P.J.M. Carrott, Adsorpt. Sci. Technol. 28 (2010) 807.
[9] J.M. Salman, B.H. Hameed, Desalination 256 (2010) 129.
[10] E. Ayranci, Nu. Hoda, J. Hazard. Mater. B112 (2004) 163.
[11] A.K. Kercher, D.C. Nagle, Carbon 41 (2003) 3.
[12] K.Y. Foo, B.H. Hameed, J. Hazard. Mater. 175 (2010) 1.