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Novel sorbent materials for environmental remediation via depolymerization of used tyres

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ABSTRACT

The present study describes the production of activated carbon (AC) from end of life tyres (ELT), by pyrolysis and physical activation, suitable for pesticide adsorption. ELT pyrolysis was conducted at 800°C in a fixed bed reactor. For the production of AC, the pyrolytic char was activated under a mixture of steam and CO_2 for 2.5 h in a bench scale reactor at 970°C. The produced AC was characterized by ultimate analysis and N_2 BET surface area. The surface area of the AC was found to increase up to 432 $m^2 g^{-1}$ at a burn-off level of 62.5 wt.%, while SEM analysis confirmed the presence of mesopores and macropores. The produced AC was used for Bromopropylate adsorption from aqueous solutions. Adsorption kinetics and equilibrium isotherms were investigated. The maximum removal reached almost 100% in 60 min. Experimental data of BP adsorption fitted best to the pseudo-second-order kinetic model and Langmuir isotherm. The produced AC from used tyres proved effective for water purification from pesticides.

Keywords: Tyres; Activated carbon; Bromopropylate; Adsorption; Kinetics; Pesticide removal; Water treatment

1. Introduction

As technology progresses, various methodologies of end of life tyres (ELT) management became more efficient. They are categorized into (i) product valorization, (ii) material valorization, and (iii) energy valorization methods [1–3]. Over the last 15 years, the percentage of both, material and energy recovery of ELT, increased from 31 to 78% of ELT in total, whilst landfilling as an option exhibited a rapid decrease resulting to 4% [1,4,5].

Regarding product valorization, retreading through tyre reconditioning aims to extend the useful life of a worn tyre by the addition of new material. Material valorization through rubber recovery of ELT is a common practice. The resulted products are consumed in civil engineering applications after either ambient or cryogenic grinding [6–8]. More specifically, they can be used as additives in road construction applications, or as key components in erosion and sound barriers. However, by implementing this type of valorization, concerns for toxic substances included in the final product are strong since polycyclic aromatic hydrocarbons

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(PAHs), vulcanization additives, antioxidants, and plasticizers were detected with the majority of them, at high or extremely high levels [9].

As far as energy valorization is concerned, ELT, due to their high calorific content, can provide sufficient amount of energy when combusted, compared to more conservative and non-renewable solid fuels (lignite coal/anthracite) [10]. Co-combustion with fossil fuels in existing industrial furnaces (cement kilns) as well as combustion in dedicated incinerators are the main routes for energy valorization. However, again, the strong concern about their combustion emissions limits the applicability of this route.

Pyrolysis is an alternative thermal valorization route for ELT, relying on the implication of their depolymerization. From ELT depolymerization, besides gas and liquid products, a solid product (char) is derived as well. Char contains the non-converted carbon and can be used either as adsorbent Activated Carbon (AC) and/or as additive in composites material production [11–13]. Based on published studies and market reviews, the majority of AC originates from coal or biomass although, recently, several studies have reported the production of AC from waste tyres as well [14–29]. In this domain, researchers' interest is strong due to the potential use of AC as adsorbents for various pollutants. Based on experimental findings, AC can become a commercial adsorbent for gas or wastewater stream purification processes, able to remove PAH or noxious compounds and dyes or even pesticides [30–35].

Regarding the latter, several methods were developed to purify aqueous streams, depending on the amount of contamination [36]. Dyes, organics and toxic contaminants (lead, mercury, and nickel) represent some of the undesired substances responsible for quality degradation of surface and subsurface waters [37,38]. For highly contaminated waters, the primary water treatment technologies established include screening, filtration, centrifugation, sedimentation, coagulation, gravity and flotation methods. Among them, the cost for filtration may differentiate strongly from the others. Through the secondary water treatment methods, soluble and insoluble pollutants are removed via biological routes, aerobic or anaerobic, by the use of microbes. Finally, tertiary wastewater treatment results to the elimination of contaminants. This can be achieved with the implementation of several techniques, including distillation, crystallization, evaporation, solvent extraction, advanced oxidation processes (Fenton and Photocatalytic oxidation at the surface of a semiconductor catalyst such as titanium dioxide), coagulation, precipitation and electrolysis [36,39–41]. The adaptation of one of the aforementioned technologies requires an additional cost that is bound to increase the overall cost of the process, thus excluding it as a sustainable choice. Thus, adsorption process, as a method for contaminants removal combining efficiency, simplicity and applicability even in large-scale operations, attracted the interest of the scientific community last years, although the manufacturing of adsorptive materials has to face in most cases, an increased production cost.

Commercially available AC is still considered expensive because of the non-renewable and relatively expensive precursor materials. This has led a growing research interest regarding the production of AC from renewable and cheaper precursors, including agricultural residues, lignocellulosic biomass, algae, solid wastes, industrial wastes and ELT [14,15,25–28,42–52]. More specifically, algae were efficiently used [53,54] for hexavalent chromium or Ni(II) ions removal, whereas biomass waste materials, including wheat husk and de-oiled soya, also proved to be efficient as adsorbents [55–61]. Other waste materials, including hen feathers, successfully removed a hazardous dye, after treatment [62]. Besides biomass, industrial wastes, such as treated bottom ash, carbon slurry, blast furnace slag, dust and sludge, proved efficient as adsorptive materials for dyes or even toxic substances (Fluoride) removal [55–59,61,63–65]. ELT were also used as adsorbent for a hazardous dye [66].

Another environmental problem originates from pesticides. In general, they are used to control pests and diseases while increasing crop productivity. However, through their misuse, the contamination of underground waters as well as of aquifer systems, are bound to occur. As a result, pesticides were implicated on causing severe problems to public health and food chain [67]. Issues on environmental protection have raised over the years globally [30,68–78], thus requesting effective solutions. This study focuses on the production of AC for environmental remediation processes, and more specifically for pesticide removal. AC production from ELT is proposed to result from a hybrid pyrolysis and activation complex, where the produced pyrolytic gas and oil can be valorized towards electricity production, thus lessening the energy needs of the plant [11].

2. Experimental procedure

2.1. Material production via pyrolysis process

Pyrolysis of ELT relies on their thermal decomposition in the absence of air to prevent oxidation. It was studied thoroughly during the last decade and seems to be an interesting approach towards the production of liquid hydrocarbons [11]. However, the potential of upgrading the solid pyrolysis product into a high added value material is of great importance [12,13,24]. By the implementation of pyrolysis, product, energy and material valorization can be achieved (Fig. 1). In order to maximize the viability of an ELT depolymerization complex, the key objective is to upgrade the solid product's characteristics, by activation.

ELT samples were received from an Engineering Company of Ireland, Erneside Engineering steel-free. Their particle size ranges between 15 and 20 mm. Pyrolysis of ELT was conducted at 800˚C for 45 min in a fixed bed reactor, under nitrogen flow. The experimental apparatus is described elsewhere [13,79]. The produced ELT-based char was collected at the end of the batch process.

2.2. Solid material upgrading via activation

Numerous laboratory-scale experimental results show that used tyre-char activation produces AC with medium adsorption capacity (400–1,200 m^2 g^{-1} N_2 BET surface area). Based on literature findings, the most suitable operating conditions for the preparation of AC from used tyres' char include: physical activation under a mixture of steam and CO_2, operating temperature between 800 and 900˚C and residence time between 1.5 and 3 h.

For the production of AC, ELT pyrolysis char was activated under a mixture of steam and CO_2 at 970˚C for 2.5 h in the previously mentioned fixed bed reactor; nitrogen was substituted by the mixture of oxidizing agents. The activation of the ELT pyrolysis char was completed at a burn-off level of 62.5 wt.%.

2.3. Product characterization

Ultimate analysis of the produced AC was performed on a Thermofinnigan CHNS EA 1112 instrument of CE Instruments, resulting to the determination of C, H N, S and O (by subtraction) content. Porous characteristics of the AC were determined by N_2 (77 K) adsorption isotherm by an automated adsorption/desorption apparatus (Micromeritics, ASAP). Surface area was measured by Brunauer–Emmet–Teller equation (BET) method with the N_2 adsorption isotherm over a relative pressure (P/P_0) in the range of 0.05–0.15.

2.4. Adsorbate

The pesticide studied was Bromopropylate (BP). BP, although banned in several EU countries, can still be detected due to its illegal use [80]. Bromopropylate (isopropyl-4–4´-dibromobenzilate) is a bridged diphenyl acaricide (miticide) effective against all stages of mites, such as eriophyidae (eriphyid mites), tenuipalpidae (false spider mites) and tetranychidae (spider mites) [80,81]. It kills mites in all postembryonal stages [82]. The properties and uses are in many ways similar to those of chlorobezilate and chloropropylate. Its toxicity for humans is very high. The half-lives on plant surfaces for BP were found in literature to range from 4.5 d up to 8.8 d [83]. The applied solution of BP was of purity 99.2%, whereas its solubility in water was determined to 0.1 mg L^{-1}.

By the years, several methods were developed providing a range of processes for pesticides removal, such as photocatalytic degradation, combined photo-Fenton and biological oxidation, advanced oxidation processes, aerobic degradation, nanofiltration

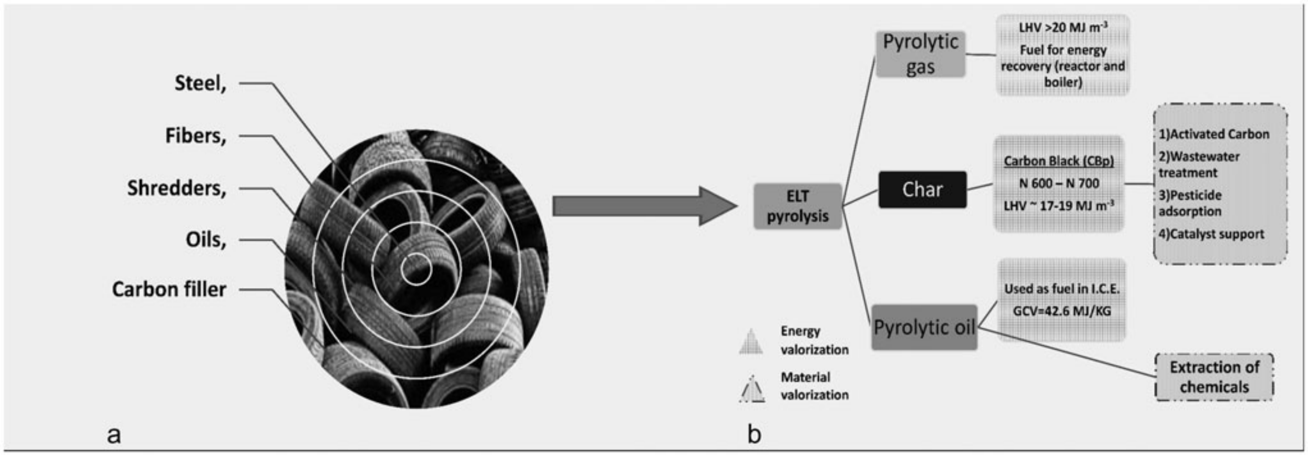

Fig. 1. Valorization of ELT by pyrolysis. (a) product valorization and (b) energy and material valorization.

membranes, ozonation and adsorption [30]. Adsorption on AC is nowadays a common technology that deals with purification of water contaminated by pesticides, dyes and phenols [34,67,84–90].

2.5. Kinetic studies

BP concentration in the prepared solutions was determined by a gas chromatographer (GC). The GC used for the analyses was a Shimadzu 14B, mounted with an ECD detector (63Ni electron capture) operating at 300℃; the column used was an ADB-1 (J&W Scientific, Folsom, CA, USA). For the needs of analysis bromophos-ethyl (purity 99.3%) was used as internal standard (IS) in the gas chromatograph. The applied temperature profile is described elsewhere [91]. Both compounds were supplied by the company Sigma Aldrich, Fluka (Germany).

The IS was added to the sample, and the response from the analyte peak is compared to that of IS. Through this process, instrument responses originated from the target compounds of the sample are compared to the responses of reference standards added to the sample. As a result, possible minor variations in the injection volume are corrected, thus improving the obtained data. The IS selection requires certain prerequisites, including similarities in analytical behaviour between the compound of interest and the selected IS, while assuring that the IS should not be expected to be found in the samples. BP appeared after 13.1 min, while IS (Bromophos-Ethyl) appeared about 2 min earlier (11.4 min).

The experimental set-up included the preparation of centrifuge tubes filled with 40 mL of aqueous solutions (0.5 ppm Bromopropylate) and 0.2 g of ELT-based AC, which were agitated for 165 min. Following, the samples were centrifuged at 4,200 rpm for 10 min and 5 mL of the supernatant solution were recovered with a pipette and centrifuged again in new centrifuge tubes for 10 min. The preparation is completed after a liquid–liquid extraction and a humidity elimination process (with the addition of a small amount of anhydrous Na_2SO_4). Finally, 50 μL of IS was added in each solution (1 ppm bromophos-ethyl) and then chromatographic analysis was performed. The percentage of BP sorbed by ELT-based AC was calculated using the following equation:

$$\text{Removal}\,(\%) = (C_0 - C_e)/C_0 \times 100 \tag{1}$$

where C_0 and C_e (mg mL^{-1}) are the initial and the equilibrium concentration; V (mL) is the volume of the solution; and m (mg) is the amount of AC. The adsorbed amount of the pesticide, Q_e, was calculated using the following equation:

$$Q_e = (C_0 - C_e) \times V/m \tag{2}$$

The kinetic study was performed for the produced AC in order to estimate the time required for adsorption to reach equilibrium. The experimental results were simulated by applying Lagergren's pseudo-first-order and pseudo-second-order kinetic models.

2.6. Adsorption studies

After the equilibrium time was determined, batch adsorption studies were carried out. Forty millilitres of BP solution and 0.2 g of AC and were filled in centrifuge tubes. The tubes were capped and shaken in a horizontal shaker at room temperature (20℃) for time equivalent to that of equilibrium. The experiments to determine BP maximum removal were repeated twice. For the adsorption study, two isotherms were applied: Langmuir and Freundlich.

3. Results and discussion

3.1. AC characterization

The produced ELT-based AC was subjected to N_2 BET surface area determination and ultimate analysis; the obtained results were compared to others from international literature and are presented in Table 1 [12,19,20,92–95]. Results from ultimate analyses of ELT-based AC indicated high amount of carbon, low oxygen content and a high C/H ratio; these represent factors that favour the creation of pores. Additionally, ELT chars as precursors exhibit high amount of ash and low initial porosity, representing factors that negatively affect pore creation. The surface area was found to increase up to 432 m^2 g^{-1} at a burn-off level of 62.5 wt.%. Through SEM analysis, the appearance of mesopores and macropores in the produced ELT-based AC was confirmed (Fig. 2). Their creation possibly stems from micropore widening, since steam was the primary activating agent [96]. Therefore, the produced AC is expected to be of medium capacity, suitable for liquid-phase applications.

3.2. Kinetic study of the BP removal

Initially, during the adsorption experiments with BP, the equilibrium time was determined. BP Removal based on experimental findings (Fig. 3) was calculated using Eq. (1). In 60 min, almost 100 wt.% of BP was

Table 1
Ultimate analysis and N_2 BET surface area determination of tyre-based AC

AC precursor	Activation conditions	Activation medium	Ash (wt.%)	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	BET (m^2 g^{-1})	References
Ground tyre granules	900˚C, 2 h	Physical	10.89	78.76	1.06	0.29	1.96	7.04	562	[92]
Demineralized tyres (HCl 1 M/ char ratio = 5)	950˚C, 6 h	Steam	27.90	67.40	0.3	0.10	0.30	32	962	[94]
Demineralized tyres (HCl 3 M/ char ratio = 30)	900˚C,6 h	Steam	10.60	90.30	0.50	0.60	0.80	8.90	788	
Shredded tyre rubber	950˚C, 16 h	CO_2	77.40	10.93	0.99	0.04	9.81	0.83	59	[99]
Demineralized shredded tyre rubber H_2SO_4 (1 M)	950˚C, 16 h	CO_2	19.42	78.05	1.21	0.20	2.48	0.84	1,118	
Scrap tyres	800˚C, 1 h	KOH	4.2	93.2	0.5	0.3	0.4	5.6	574	[95]
	800˚C, 1 h	CO_2	9.8	87.3	0.5	0.3	2.1	9.8	55	
Scrap tyres	850˚C, 3 h	Steam/ nitrogen (3/1)	–	77.29	1.1	0.06	0.57	–	500	[20]
Tyre rubber powder	925˚C, 9.3 h	Steam						22.5	1,022	[19]
	950˚C, 5.3 h	CO_2						15.5	632	
ELT	550˚C, 0.5 h	–	–	82.3	0.7	0.4	3.3	0	13.2	[93]
ELT	970˚C, 2.5 h	Steam/ CO_2	20.08	71	0.12	0.58	1.14	7.08	432	[This study]

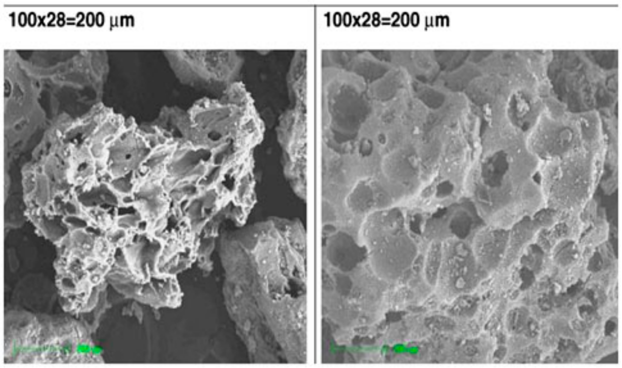

Fig. 2. SEM images of ELT-based AC.

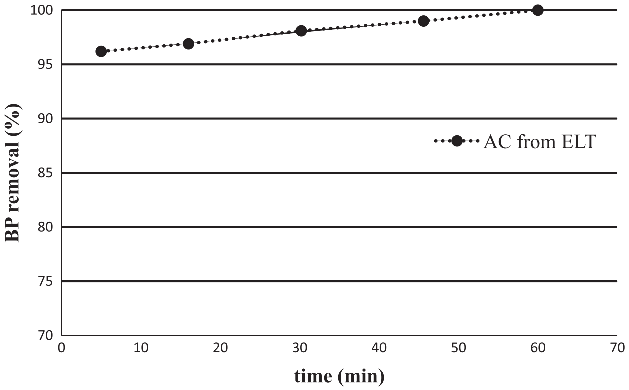

Fig. 3. BP Removal (%) vs. time.

removed. Through Lagergren's pseudo-first-order and pseudo-second-order models (Eqs. (3) and (4), respectively), the adsorption data were tested in order to investigate the kinetics of adsorption [97,98].

Lagergren's pseudo-first-order kinetic model can be applied to explain sorption kinetics based on the following equation:

$$\log(Q_e - Q) = \log Q_e - K_1 t/2.303 \quad (3)$$

while the pseudo-second-order kinetic model in its integrated and linearized form is:

$$t/q = 1/K_2 Q_e^2 + 1/Q_e t \quad (4)$$

where Q_e (mg g^{-1}) is the amount of pesticide adsorbed on the surface of the AC at equilibrium; Q (mg g^{-1}) is the amount of pesticide adsorbed at time t

(min); and K_1 (min^{-1}) and K_2 (g mg^{-1} min^{-1}) are the constants of pseudo-first- and pseudo-second-order, respectively.

Both kinetic models were described by their linear curves [log(Q_e–Q_t) via t], for the pseudo-first-order, and [t/Q_t via t] for the pseudo-second-order. K_1 and K_2 constants were estimated from the slope of the lines. The calculated kinetic parameters are reported in Table 2. Experimental data of BP adsorption fitted better to the pseudo-second-order kinetic model (Fig. 4); this is possibly attributed to chemisorption and more specifically to the formation of strong chemical bonds between AC and BP, assuming fast pore and film diffusion [98].

3.3. Adsorption isotherm models

For the needs of the adsorption study, linearized forms of Langmuir and Freundlich isotherms were applied (Eqs. (5) and (6), respectively).

$$1/q_e = (1/K_a q_m \times 1/C_e) + 1/q_m \tag{5}$$

$$\log q_e = \log K_f + 1/n \times \log C_e \tag{6}$$

Table 2
Kinetic parameters for the adsorption of BP onto ELT-based AC

Pseudo-first-order model			
Kinetic constant K_1 (min^{-1})	Q_e estimated (mg g^{-1})	Q_e calculated (mg g^{-1})	R^2
0.0034	0.1097	0.0896	0.9743
Pseudo-second-order model			
Kinetic constant K_2 (g mg^{-1} min^{-1})	Q_e estimated (mg g^{-1})	Q_e calculated (mg g^{-1})	R^2
10.6	0.0891	0.0896	0.9973

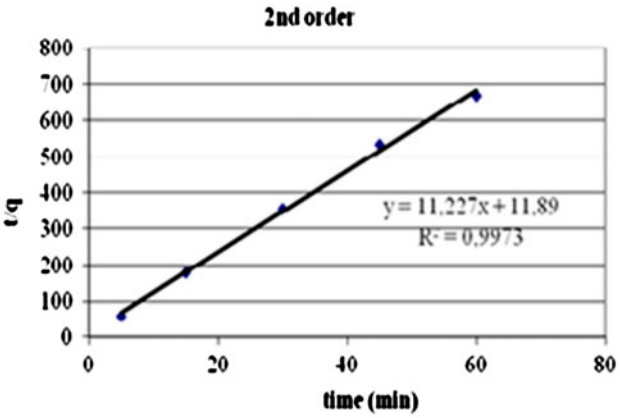

Fig. 4. Lagergren's pseudo-second-order adsorption kinetic study.

Table 3
Isotherm results

Langmuir		Freundlich	
K_a (mL μg^{-1})	5.81	K_f (μg$^{1-1/n}$ g^{-1} mL$^{1/n}$)	1.62
q_m (μg g^{-1})	60.7 × 10^{-2}	n	1.05
R^2	0.9961	R^2	0.8316
F_{er}	4.4 × 10^{-3}	F_{er}	1.06 × 10^{-2}

where q_e (μg g^{-1}) is the adsorbed amount of solute; q_m (μg g^{-1}) is the maximum amount of solute adsorbed; C_e (μg mL^{-1}) is the concentration at equilibrium; and K_a (mL μg^{-1}) is the Langmuir constant; they can be determined from the linearized form represented by Eq. (5). In parallel, K_f (μg$^{1-1/n}$ g^{-1} mL$^{1/n}$) and n (dimensionless) represent Freundlich constants, related to sorption capacity and sorption intensity of the adsorbent, respectively. They can be determined from

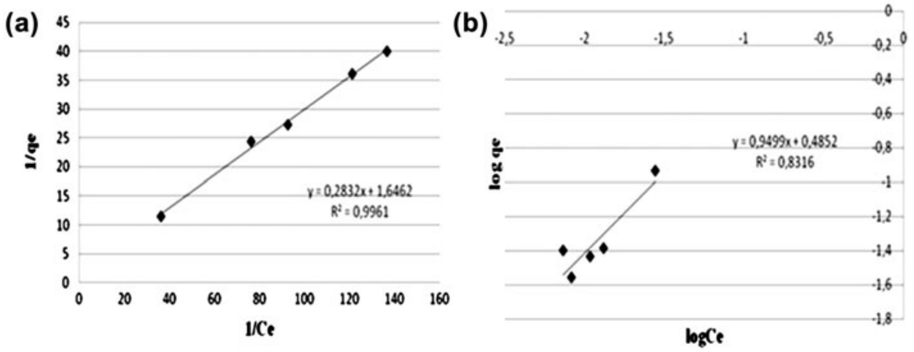

Fig. 5. Isotherms of (a) Langmuir and (b) Freundlich.

the intercept and slope of log C_e (x-axis) against log q_e (y-axis) plot, respectively.

Additionally, an error function was calculated for each case, using the following equation:

$$F_{er} = \sqrt{\frac{\sum_{I}^{P}\left[(q_{\text{ical}} - q_{\text{iexp}})/q_{\text{iexp}}\right]^2}{p}} \tag{7}$$

where q_{ical} is the amount of substance calculated (mg gr^{-1} AC); q_{iexp} is the amount of substance estimated experimentally (mg gr^{-1} AC); and p refers to the number of experiments.

Langmuir and Freundlich equation constants and isotherms are reported in Table 3 and depicted in Fig. 5, respectively. Langmuir isotherm fitted better the experimental results (higher regression coefficient) for the specific application. Comparing to the results of a previous study, the ELT-based AC marks the highest adsorptive capacity above commercial AC and residual biomass-based AC [80]. This is possibly attributed to the more mesoporous structure of the ELT-based AC.

4. Conclusions

ELT pyrolysis, followed by physical activation of the produced char resulted to the production of AC.

The produced AC was tested for BP adsorption from aqueous solution and the equilibrium constants were calculated. The maximum removal reached almost 100% in 60 min.

The kinetic study revealed that the pseudo-second-order kinetic model describes better the removal process of BP onto the AC. Also, the adsorption obeyed the Langmuir type of isotherm.

The prepared AC proved efficient as for BP removal from aqueous solutions, due to the increased mesoporosity of the sample compared to others prepared from conventional or renewable precursors, showing also a possible chemisorption mechanism.

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List of symbols

ELT — end of lfe tyres
AC — activated carbon
BP — Bromopropylate
PAH — polycyclic aromatic hydrocarbon
C_0 and C_e (mg mL^{-1}) — initial and the equilibrium concentration
V (mL) — volume of the solution
m (g) — amount of AC
Q_e (mg g^{-1}) — amount of pesticide adsorbed on the surface of the AC at equilibrium
Q (mg g^{-1}) — amount of pesticide adsorbed at time t (min)
K_1 and K_2 — constants of pseudo-first- and pseudo-second-order, respectively
q_e (μg g^{-1}) — adsorbed amount
q_m (μg g^{-1}) — maximum adsorptive capacity of AC
C_e (μg mL^{-1}) — concentration at equilibrium;
K_a and K_f — constant of Langmuir and Freundlich, respectively
n — exponential constant that expresses the curvature of the isotherm

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