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Efficiency and kinetics of organics removal from landfill leachate by adsorption onto powdered and granular activated carbon

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ABSTRACT

This study compared the performance of powdered (PAC 200-1Wi and PAC 200-C303) and granular (GAC 10-GAC and GAC 10CO) activated carbons in organic removal from landfill leachate using the UV_{254} and UV_{280} indices, in addition to chemical oxygen demand (COD) and dissolved organic carbon. Process efficiency increased to the greatest extent when the range of carbon doses was 2–3 g/L (PAC 200-1Wi) and 2–10 g/L (both GACs). In these ranges, an increase in PAC dose of 1 g/L gave an increase in COD and UV_{254} removal efficiency of 19.1 and 15.4%, respectively, with GACs, the increase was 4.0–4.3% COD and 5.4–6.0% (UV_{254}). Higher doses proved less efficient because the high consumption of carbon yielded 8–10 times lower increase in process efficiency than lower doses. Organics adsorption followed pseudo-second-order kinetics. With PACs, equilibrium was reached in 30 min; whereas, with GACs, equilibrium was reached in 48 h. Q_e for PACs was 2–3 times higher than GACs.

Keywords: Landfill leachate; Organic compounds; Activated carbon; Adsorption; UV_{254}; UV_{280}

1. Introduction

Organic substances found in landfill leachate are directly related to the processes occurring inside the landfill. In favorable conditions, generally dictated by the presence of sufficient moisture to support microbial activity, landfills behave like large-scale anaerobic reactors. However, simultaneously with biochemical changes, physicochemical processes (i.e. dissolution, precipitation, adsorption, dilution, and volatization) influence leachate quality.

Leachates from young landfills are characterized by substantial amounts of volatile fatty acids, as a result of the acid phase of fermentation. Typically, old landfills produce leachate that is cataloged as stabilized and characterized by slightly basic pH, relatively low chemical oxygen demand (COD), and low biodegradability (low BOD_5/COD ratio) [1,2]. Moreover, landfill leachate contain refractory substances with high molecular weight (MW) compounds, i.e. humic substances. Wu et al. [3] showed that in leachate from stabilized municipal landfill (BOD_5/COD ca. 0.06) over 50% of organics were of high MW > 10 kDa), whereas organics with MW below 1 kDa made up

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only 20%. According to Kang et al. [4], leachate contains mainly humic substances with MWs ranging from 10 to 100 kDa. Substances above this MW comprise less than few percent, and organics with low MW (up to 1 kDa) make up only 15–19%. Ninety percent of fulvic acids have MWs below 50 kDa. Although the proportions of particular fractions of humic substances in leachate vary from landfill to landfill, they represent a significant share of organics. High concentrations of humic substances may increase the difficulty of treating landfill leachate, since humic substances cannot be easily biodegraded and oxidized. Thus, the possibility of separating these organics suggests that adsorption processes should be considered as treatment methods for leachate from old landfills.

Because adsorption is a surface phenomenon, the amount of organics adsorbed depends on the size of adsorbent surface area. As activated carbon (AC) has large surface area, microporous structure, and surface reactivity, adsorption onto AC may be one of the methods for removing recalcitrant compounds from landfill leachate. An additional benefit of using AC is that it efficiently removes not only organics, but also turbidity and color. High efficiency of COD and color removal using fruit seed derived granular AC were also confirmed by Foo et al. [2]. Furthermore, no harmful substances are formed after the treatment [5,6]. More importantly, the addition of AC can lower the environmental risk by decreasing the amount of hydrophobic natural organic matter and trihalomethane precursors [5]. Moreover, the newest works [7] showed that commercial AC can be used to remove different micropollutants present in landfill leachates such as phthalic acid, bisphenol A, diphenolic acid, 2,4-dichlorophenoxy-acetic acid, and 4-chloro-2-methylphenoxyacetic acid.

Organic matter in leachate is usually characterized in terms of BOD_5, COD, and total organic carbon (TOC). In addition, ultraviolet (UV) absorption, at wavelength 254 nm (UV_{254}) and 280 nm (UV_{280}), can be used as an index of humic substance concentration [8–10]. Currently, the literature provides only a little information concerning systematic comparison of the performance of different adsorbents for treatment of old landfill leachates using, in addition to COD and dissolved organic carbon (DOC), UV_{254} and UV_{280} as indices of the humic fraction.

Therefore, this study quantifies the relationship between the dose of powdered activated carbon (PAC) and granular activated carbon (GAC) and organics removal, measured with the above indices. In addition, the adsorption kinetics of organic removal were elucidated. The adsorption kinetics describe the rate of uptake of the adsorbate molecules onto adsorbent surfaces, which determines the contact time required for equilibrium needed for the design of batch adsorption systems.

2. Materials and methods

2.1. Leachate feed

Leachate used in this study was collected from a 14-year-old municipal landfill located in Poland where only municipal wastes are deposited, without fluid waste, fecal matter, hazardous substances or radioactive and toxic wastes. During the research period, there was an annual average of 5,000 m^3 of leachate. This was collected in a drain system and stored in a retention reservoir from which it was sprayed on the landfill or periodically taken to a municipal sewage treatment plant. Leachate samples for analysis were taken from the retention reservoir. The leachate was delivered to the laboratory twice a month and stored at 4°C. The landfill leachate composition is shown in Table 1.

2.2. Activated carbon characteristics

Commercially produced AC was used in this study. Two kinds of GAC, Organosorb 10 (GAC 10), and Organosorb 10 CO (GAC 10 CO), and two kinds of PAC, Organosorb 200-1Wi (PAC 200-1Wi), and Organosorb 200-C303 (PAC 200-C303), were tested. The main characteristics of these adsorbents are presented in Table 2.

Table 1
Composition of raw landfill leachate

Leachate characteristic	Unit	Value
pH	–	8.34
COD	mg/L	1,007
BOD_5	mg/L	98
BOD_5/COD	–	0.097
BOD_{20}	mg/L	369
DOC	mg/L	294
Total nitrogen	mg/L	1,015
Ammonia nitrogen	mg/L	833.7
Organic nitrogen	mg/L	35
Total phosphorus	mg/L	26
Total dissolved solids	mg/L	7,467
Volatile dissolved solids	mg/L	1,117
UV_{254}	cm^{-1}	11.04
UV_{280}	cm^{-1}	8.3

Table 2
Characteristics of activated carbon

Parameters	Values			
	GAC 10	GAC 10 CO	PAC 200-1Wi	PAC 200-C303
Origin	Bituminous	Coconut	Tree	Tree
Shape	Granular	Granular	Powdered	Powdered
Specific area (m^2/g)	1,000	1,000	900	1,200
Iodine number (mg/g)	1,000	1,000	900	1,100
Methylene number (mg/g)	190	–	300	300
Moisture content (%)	5	5	5	10
Ash (%)	12	5	5	6
Bulk density (g/L)	±470	±500	±280	±300
Size (mm)	0.6–2.36	0.6–2.36	70% < 0.0075	85% < 0.0075

2.3. Process configuration and system design

The experiment was conducted simultaneously with six samples in 2 L jar test beakers. The samples were stirred using magnetic stirrers. For each adsorbent, six doses of AC were tested (Table 3).

To determine the time required for adsorption equilibrium, 1.5 L of leachate and a fixed dose of AC (Table 3) were introduced to reaction vessels with a capacity of 2 L. Applied AC doses were used on the basis of literature view [2,6,8,11,12] and own preliminary studies. Then, in the case of PAC, after 0, 0.083, 0.167, 0.25, 0.33, 0.5, 1, 2, and 3 h samples were taken to determine the content of organics in the treated leachate. For GAC, sampling frequencies were: 0, 0.5, 1, 2, 5, 8, 12, 24, 28, 32, 36, 48, 60, and 72 h. A study of the kinetics adsorption of organics was performed using COD, the most commonly used indicator of the content of organics in leachate.

2.4. Analytical methods

The following characteristics of the raw leachate were determined: pH (pH-meter HI 8818); COD, according to Standard Methods [13]; and BOD_5, according to DIN EN 1899-1/EN 1899-2 official EPA method using OxiTop WTW Wissenschaftlich-Technische Werkstätten GmbH, D-82326 Weilheim, Germany. In addition, Kjeldahl nitrogen, ammonia-N, and total phosphorus were determined by Standard Methods [13]. Total dissolved solids and volatile dissolved solids were measured according to Hermanowicz et al. [14]. Leachate samples were filtered through a 0.45 μm filter. DOC was determined using a Shimadzu Liquid TOC-V_{CSN} analyzer. Millipore membranes were used to remove suspended and particulate matter that could interfere with UV absorption measurements. Filtered samples were analyzed for UV optical density at $\lambda = 254$ nm (for aromatic and unsaturated organic compounds [10]) and at $\lambda = 280$ nm (for aromaticity [15]) with a Cary UV/Visible spectrophotometer in 1 cm path length quartz cuvettes. Distilled water was used as a blank. Measurements of leachate after adsorption included COD, DOC, UV_{254}, and UV_{280}.

Table 3
Assumptions of the experiment

AC	Carbon doses (g/L)
GAC 10 GAC 10 CO	2; 5; 10; 15; 20; 30
PAC 200-1Wi PAC 200-C303	2; 2.5; 3; 5; 8; 10

3. Results and discussion

3.1. Landfill leachate characteristics

Leachate originated from stabilized landfill, as shown by high pH 8.34 and low concentrations of organics determined by COD (1,007 mg/L), BOD_5 (98 mg/L), and DOC (294 mg/L) (Table 1). These results suggest that most of the organics in the leachate had been converted to methane, thus decreasing the biodegradability of the organics, which was also confirmed by BOD_5/COD ratio.

Compared to the leachate from other landfills, leachate used in this study contains a lower concentration of organic compounds expressed as BOD_5 and COD. According to Fan et al. [16] and Bila et al. [17], COD in leachate from a landfill that had been in operation for a similar amount of time ranged from 3,000 to 3,500 mg/L. Similarly, Calace et al. [18] showed that COD in leachate ranged from 2,400 to 9,100 mg/L.

The concentration of DOC was 294 mg/L. According to Leenheer and Croué [19] DOC is a heterogeneous mixture of humic substances, hydrophilic acids, proteins, lipids, carbohydrates, carboxylic acids, amino acids, and hydrocarbons.

UV_{254} indicates the presence of conjugated double bonds in aromatic and unsaturated organic compounds [8,10], UV_{280} indicates the aromaticity of a sample structure [15], both are used as indices of humic substance concentration. In the present study, in raw leachate UV_{254} and UV_{280} was 11.04 and 8.3, respectively. According to Rivas et al. [8], in leachate from a landfill in Italy, UV_{254} was 40 which is 4-times higher than in this study. Kang et al. [4] showed that UV_{280} values increase with landfill age, from 3.0 in leachate from landfill of <5 years to 12.6 in leachate from landfill of >10 years.

The leachate contained high concentrations of total nitrogen and ammonia nitrogen (1,015–834 mg/L). Total dissolved solids measured 7,467 mg/L.

3.2. The efficiency of organics removal using GAC and PAC

3.2.1. Efficiency of organics removal with PAC

The landfill leachate was adsorbed with two kinds of PAC (PAC 200-1Wi and PAC 200-C303) at doses from 2 to 10 g/L. Table 4 shows the concentrations of organic substances (expressed as COD, DOC, UV_{254}, and UV_{280}) after adsorption onto PAC.

With both PACs, organics concentration in the effluent decreased with increase in PAC dosage. Moreover, according to all indices, PAC 200-1Wi was more effective at all tested levels of dosage. As adsorption is a surface phenomenon, the adsorptive capacity of organic substances depends on the size of PAC surface area. In this study, however, lower organic concentrations (and higher process efficiency) were observed with PAC 200-1Wi, which has a lower specific area (900 m^2/g). The higher concentrations of organics after adsorption onto PAC 200-C303 (specific area 1,200 m^2/g) may be connected with the fact that large molecules in landfill leachate are unable to penetrate the smaller pores of this PAC [20]. According to other authors, AC preferentially removes organics with a MW of 100–10,000. Organic substances with a lower or higher MW are not efficiently retained, the first probably due to their high polarity (e.g. volatile fatty acids, hydroxylated acids, and sugars), the second due to the large dimensions of the molecules, which could clog the pores and decrease adsorption capacity for other molecules [21,22]. In this study, the second case was more likely because of the age of the leachate.

Using AC is an efficient method of landfill leachate treatment as adsorption of pollutants greatly reduces organics concentration. However, the main drawback is the high consumption of AC. Therefore, it is important to determine the range of doses at which the process efficiency increases to the greatest extent to limit the PAC/GAC consumption. For leachate polishing, another method may be used.

Data on the percent of organics removal with different AC doses were plotted to show the relationship between process efficiency and PAC dosage. The slope of the best-fit line gives the increase in organics removal efficiency (in %) with an increase in carbon dose of 1 g/L.

An example of the relationship between the PAC doses and COD removal efficiency (experimental results) is shown in Fig. 1.

At dosages ranging from 2 to 3 g/L, process efficiency increased 19.05% with a 1 g/L increase in PAC 200-1Wi, and 9.53% with the same increase in PAC

Table 4
Organics concentration in the effluent after adsorption onto PAC

	Concentration in the effluent							
	PAC 200-1Wi				PAC 200-C303			
Carbon dose (g/L)	COD (mg/L)	DOC (mg/L)	UV_{254} (cm^{-1})	UV_{280} (cm^{-1})	COD (mg/L)	DOC (mg/L)	UV_{254} (cm^{-1})	UV_{280} (cm^{-1})
2	504	172.3	3.88	3.04	640	192.2	5.36	4.32
2.5	423	138	3.01	2.45	585	178	4.92	3.95
3	312	107.8	2.34	1.86	544	169	4.67	3.62
5	250	83.1	1.95	1.58	464	154.2	3.71	3.03
8	185	62	1.49	1.23	416	127	3.2	2.65
10	136	42.1	1.20	1.20	376	92.6	2.85	2.40

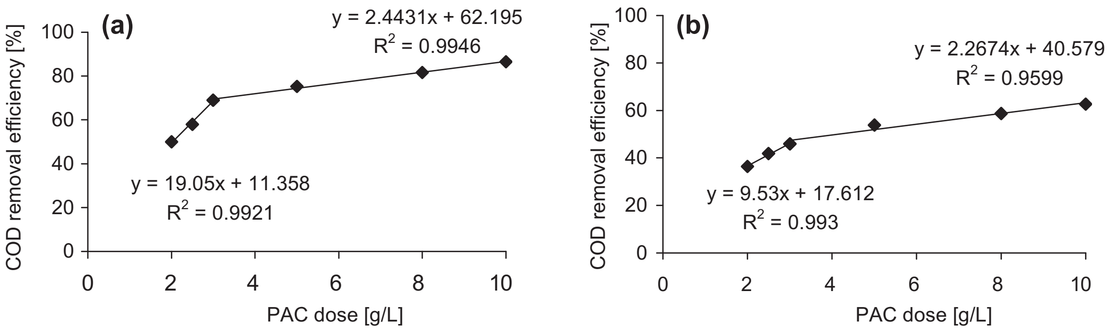

Fig. 1. Experimental data showing the relationship between the efficiency of COD removal and PAC dose, and the values of *a* coefficients. (a) PAC 200-1Wi and (b) PAC 200-C303.

200-C303. At higher doses (3–10 g/L), the increases in process efficiency were smaller (Fig. 1(a) and (b), Table 5).

The relationships between increases in PAC dosage and changes in DOC, UV_{254}, and UV_{280} were obtained in the same way. The results are presented in Table 5.

With both PACs, the most effective doses for organics removal are in the range of 2–3 g/L. Higher doses proved less efficient because the high consumption of carbon yields only a low increase in process efficiency.

3.2.2. *Efficiency of organics removal with GAC*

As with PAC, the landfill leachate was adsorbed with two kinds of GAC (GAC 10 and GAC 10 CO) at doses from 2 to 30 g/L. In Table 6, the concentrations of organic substances after adsorption with GAC are expressed in terms of COD, DOC, UV_{254}, and UV_{280}. As with PAC, organic substances concentration in the effluent decreased with increased GAC doses.

Data on percent of organics removal with different AC doses were plotted to show the relationship between process efficiency and GAC dosage (Fig. 2).

The relationships between changes in DOC, UV_{254}, and UV_{280} and increases in GAC doses are shown in Table 7.

With doses ranging from 2 to 10 g/L, each 1 g/L increase in GAC dose improved COD removal efficiency 4.3% for GAC 10, and 4.0% for GAC 10 CO. At higher doses (10–30 g/L), increases in process efficiency were much lower with both GACs (Table 7). A similar trend was observed in the case of all parameters. However, in this higher range of doses, a 1 g increase in the dose of AC gave an increase in process efficiency that was 2–3 times greater with GAC 10 CO than with GAC 10 (Fig. 1(a) and (b)). With both kinds of adsorbent, the efficiency of organic pollutants removal per gram of AC was higher with doses ranging from 2 to 10 g/L than with doses above 10 g/L.

As adsorption is an efficient method for removal of non-biodegradable organics from landfill leachate, many authors have analyzed the relationship between adsorbent dose and adsorption efficiency, mainly in terms of COD. Moreover, in many works, the authors have compared various types of adsorbents, such as carbon with resins or zeolites. Kargi, Pamugoklu [23] used AC and zeolite to remove organics from landfill leachate (4,300 mg COD/L).

Table 5
Increase in process efficiency with 1 g/L increase in PAC dose

	Increase in adsorption efficiency (%)			
	PAC 200-1Wi		PAC 200-C303	
Parameter	2–3 g/L	3–10 g/L	2–3 g/L	3–10 g/L
COD	19.05 (0.9921)	2.44 (0.9946)	9.53 (0.9930)	2.27 (0.9599)
DOC	21.8 (0.9999)	2.5 (0.9943)	8.7 (0.9989)	2.3 (0.9555)
UV_{254}	15.4 (0.9989)	1.6 (0.9957)	8.9 (0.9879)	2.2 (0.9567)
UV_{280}	14.9 (0.9998)	1.5 (0.9990)	8.8 (0.9899)	2.1 (0.9489)

Note: R^2 values are in brackets.

Table 6
Organics concentration in the effluent after adsorption onto GAC

	Concentration in the effluent							
	GAC 10				GAC 10 CO			
Carbon dose (g/L)	COD (mg/L)	DOC (mg/L)	UV$_{254}$ (cm^{-1})	UV$_{280}$ (cm^{-1})	COD (mg/L)	DOC (mg/L)	UV$_{254}$ (cm^{-1})	UV$_{280}$ (cm^{-1})
2	730	214.6	8.28	6.73	774	242.0	8.72	7.01
5	547	183.6	5.93	4.90	639	200.2	7.43	5.89
10	380	121.6	3.83	3.25	446	139.4	3.95	3.95
15	360	113.4	3.09	2.67	366	114.8	3.10	2.51
20	296	104.2	2.52	2.21	224	74.8	1.93	1.59
30	232	86.7	1.92	1.73	152	53.1	1.18	0.98

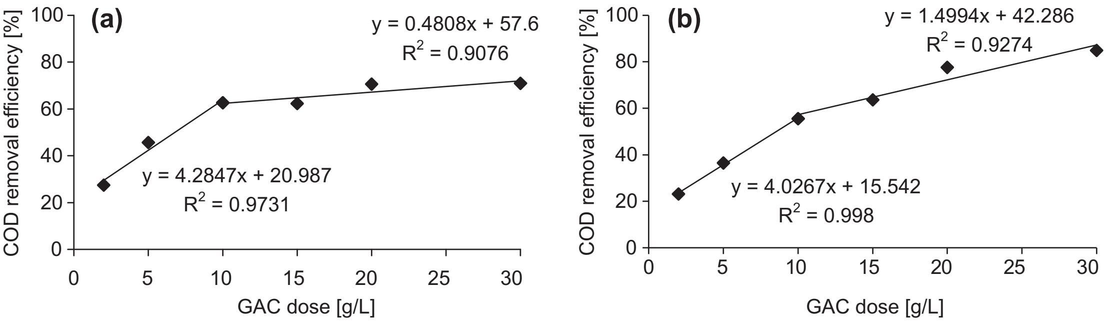

Fig. 2. Experimental data showing the relationship between the efficiency of COD removal and GAC dose, and the values of *a* coefficients. (a) GAC 10 and (b) GAC 10 CO.

Table 7
Increase in adsorption efficiency with 1 g/L increase in GAC dose

	Increase in adsorption efficiency (%)			
	GAC 10		GAC 10 CO	
Parametr	2–10 g/L	10–30 g/L	2–10 g/L	10–30 g/L
COD	4.30 (0.9731)	0.48 (0.9076)	4.00 (0.9980)	1.50 (0.9274)
DOC	4.0 (0.9978)	0.8 (0.9155)	4.3 (0.9986)	1.5 (0.9296)
UV$_{254}$	5.4 (0.9690)	0.7 (0.9489)	6.0 (0.9843)	1.4 (0.9406)
UV$_{280}$	4.9 (0.9842)	0.7 (0.9500)	6.1 (0.9915)	1.4 (0.9406)

Note: R^2 values are in brackets.

The authors found that with a dose of 2 g/L, the organics removal efficiency was 38% for AC and 17% for zeolite. Rodríguez et al. [22] studied the adsorption of non-biodegradable organic matter from landfill leachates that were previously recirculated through a simulated landfill pilot plant (1,300 mg COD/L). The adsorbents tested were AC (GAC-40) and three resins (Amberlite XAD-8, Amberlite XAD-4 and Amberlite IR-120) at doses of 30 g/L. After adsorption, COD in leachate was 180, 580, 700, and 900 mg/L, respectively. Castrillón et al. [24] obtained relatively high effectiveness of organics and color removal. The authors showed that Organosorb 10 MB reduced COD and color the most, followed by Filtracarb CC65/1240, although their adsorption capacities were low. COD and color removal efficiencies of 63 and 45%, respectively, were obtained with Organosorb 10 MB at a dosage of 20 g/L.

Although it is known that the removal efficiency of organic pollutants is largely dependent on the type of adsorbent and adsorbent dose, in the literature there is a lack of data about optimal dosage ranges above which the efficiency of the adsorption process is lessened. In this work, these ranges have been established: 2–3 g/L for PAC and 2–10 g/L for GAC.

3.3. The correlation between UV_{254} and organics concentration expressed as COD and DOC

For all kinds of AC used in this study, the correlation coefficient (R^2) for all plots of COD versus UV_{254} was over 0.98 (Fig. 3). Similarly, high correlations (0.91–0.99) were seen between UV_{254} and DOC (Fig. 4). Thus, UV_{254} was a reliable indicator of COD and DOC. Until now, a good correlation between COD and UV_{254} was observed with landfill leachate after electro-Fenton treatment [25]. However, Campagna et al. [26] found that absorbance at 320 nm was the best of indicator of COD in landfill leachate when studying landfill leachate treatment using a membrane bioreactor with a nanofiltration membrane.

3.4. Adsorption kinetics

In studies concerning organics adsorption, the time necessary to achieve equilibrium concentration of organics in the leachate must be established. So, in order to investigate the minimum contact time for removal of organics, adsorption kinetic experiments of leachate were performed using both PACs and GACs.

The relationship between the amount of adsorbed organics and adsorption time was also the basis for analysis of the kinetics of adsorption. Experimental data based on measurements of COD were fitted to different models previously reported in the literature (pseudo-first-order, pseudo-second-order kinetics). On the basis of R^2 values for linear forms of pseudo-first-order ($R^2 < 0.84$) and pseudo-second-order kinetics (R^2 in the range 0.9943–0.9999), it was assumed that pseudo-second-order kinetics would provide a better description of the adsorption process.

In all cases, organics adsorption followed pseudo-second-order kinetics:

$$\frac{\mathrm{d}Q_t}{\mathrm{d}t} = k_S \cdot (Q_e - Q_t)^2 \tag{1}$$

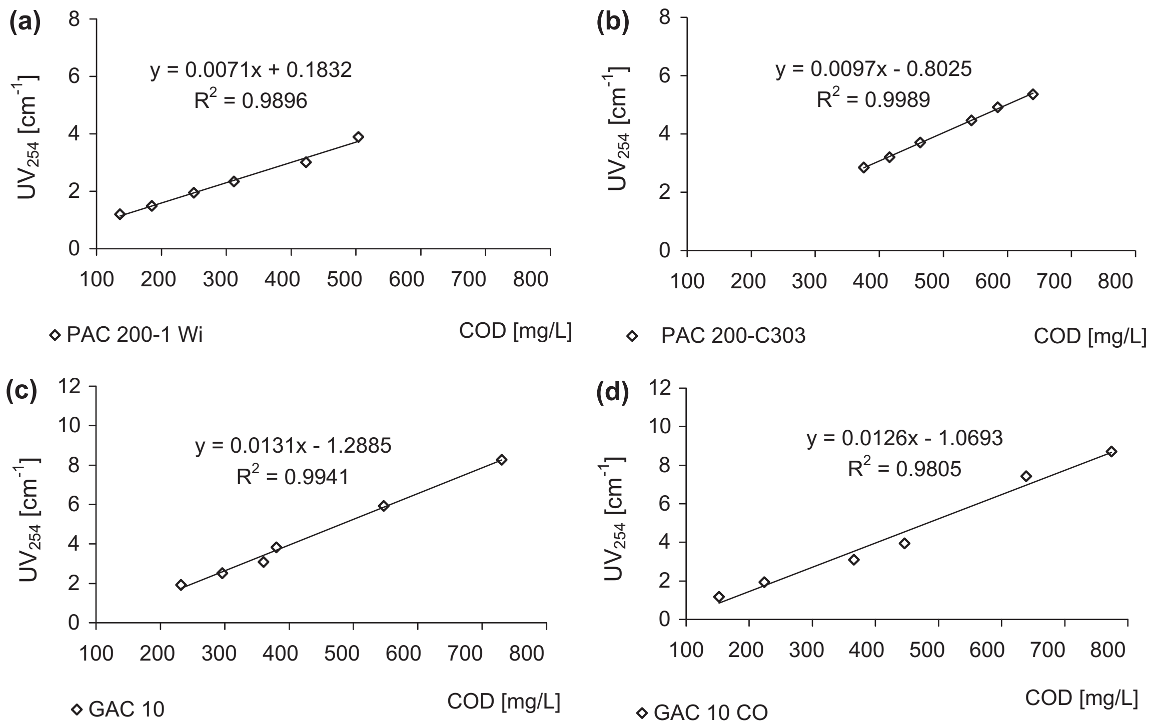

Fig. 3. Relationship between COD concentration and UV_{254} in leachate after adsorption onto PACs and GACs. (a, b) PACs and (c, d) GACs.

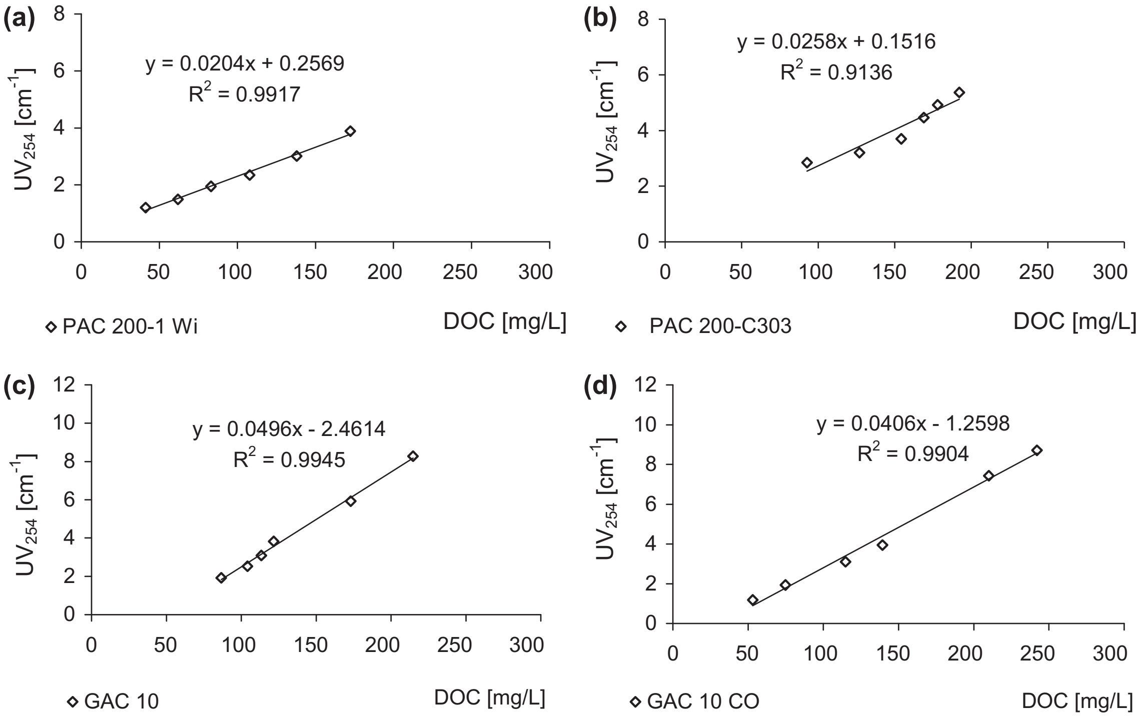

Fig. 4. Relationship between DOC concentrations and UV_{254} in leachate after adsorption onto PACs and GACs. (a, b) PACs and (c, d) GACs.

Eq. (1) after linearization takes the following form:

$$\frac{1}{Q_t} = \frac{1}{k_s \cdot Q_e^2} + \frac{1}{Q_e} \cdot t \tag{2}$$

where Q_t—amount of organics COD adsorbed per unit mass of adsorbent after time t (mg/g); Q_e—amount of organics COD adsorbed per unit mass of adsorbent in equilibrium conditions (mg/g); k—rate constant of adsorption (g/mg min for PAC; g/mg h for GAC); t—time (min in case of PAC; h in case of GAC).

The exemplary relationship between organics adsorption and time at dose of 3 g/L PAC and 10 g/L GAC is shown in Fig. 5.

With PACs, the concentration of organic pollutants expressed as COD dropped sharply after 5 min of adsorption, and, in the case of higher doses (5–10 g/L) the amount of organics adsorbed during this time ($Q_{t,5}$) equaled 90–94% of the amount of adsorbed organics in equilibrium conditions. At lower PAC doses (2–3 g/L), $Q_{t,5}$ were lower, 76–82%. Under these conditions, equilibrium was obtained within 30 min in both PACs.

Fast organics adsorption on different kinds of adsorbents is a rather typical phenomena. The study of the adsorption of organics from leachate carried out by Rodríguez et al. [22] showed that after a 10 min adsorption, organic removal corresponded to 59.6, 86, 44.8, and 43.9% of the total amount of adsorbed organics for GAC-40, XAD-8, and XAD-4 IR-120, respectively, and more than 90% was noted after 60 min of the process. According to Li et al. [12] using PAC for landfill leachate treatment in dose 10 g/L the equilibrium could be practically reached in 90 min. Under these conditions, the removal efficiency of COD was about 52%.

Significantly more time to achieve equilibrium conditions was needed when GACs were used as adsorbents. In this study, with higher doses of GAC 10 CO (10–30 g/L), the amount of organics removed during 24 h ($Q_{t,24}$) equaled 87–94%. At lower doses of GAC 10 CO it was about 60%. Using GAC 10, irrespective of doses, the amount of organics removed during 24 h equaled 82–87%. With both GACs equilibrium conditions were obtained in 48 h. Rivas et al. [8] showed that during adsorption of leachates onto three ACs, i.e. Norit 0.8, Chemviron AQ40, and Picacarb 1240, the kinetics of the process indicated a minimum adsorption time which should be in the range of 60–80 h to attain equilibrium.

Kinetic constants (Q_e, k_s) for all ACs, determined from pseudo-second-order kinetic is stated in Table 8 (for PACs) and in Table 9 (for GACs).

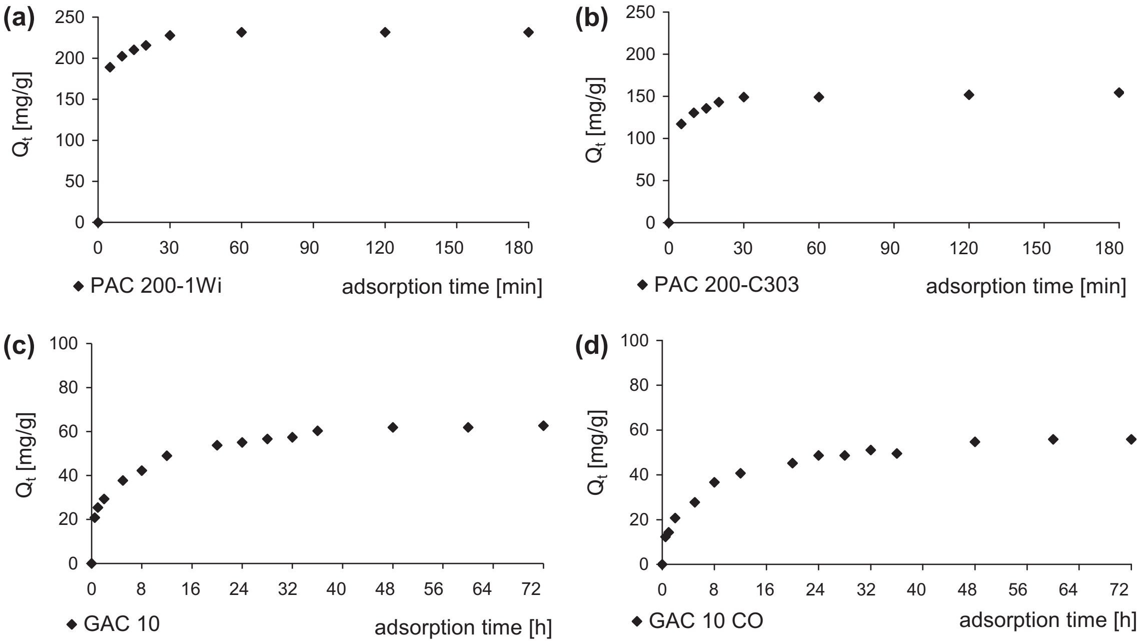

Fig. 5. Changes in organics COD versus adsorption time. (a, b) PACs (at dose of 3 g/L) and (c, d) GACs (at dose of 10 g/L).

Table 8
Kinetic constants for PACs determined from pseudo-second-order kinetic

	Kinetic constants			
	PAC 200-1Wi		PAC 200-C303	
Carbon dose (g/L)	Q_e (mg/g)	k_s (g/mg min)	Q_e (mg/g)	k_s (g/mg min)
2	250.0	0.72×10^{-2}	185.2	0.36×10^{-2}
2.5	242.8	0.91×10^{-2}	173.2	0.42×10^{-2}
3	232.6	1.10×10^{-2}	153.8	0.58×10^{-2}
5	151.5	1.67×10^{-2}	108.7	1.15×10^{-2}
8	117.2	4.60×10^{-2}	88.0	1.62×10^{-2}
10	86.9	7.34×10^{-2}	63.3	2.46×10^{-2}

It was shown that Q_e value was dose dependent and was in the range 250–86.9 mg/g for PAC 200-1Wi. However, for PAC 200-C303, the Q_e values were from 1.3 to 1.5 lower.

In the case of GACs, the amounts of organics adsorbed under equilibrium conditions (Q_e) were several times lower than in the case of PACs. However, there were no significant differences between Q_e for GAC 10 and GAC 10 CO (Table 9).

Rodríguez et al. [22] also show that Q_e values depended greatly on the kind of adsorbent used. From the four adsorbents used by the authors (GAC, XAD-8, and XAD-4 IR-120, all at dose 30 g/L), the highest amount of organics removed at equilibrium was obtained with GAC (38.12 mg/g), and the lowest with resin Amberlite IR-120 (14.82 mg/g).

In this study, adsorption proceeded according to pseudo-second-order kinetics. Similarly, Foo et al. [2] showed that the adsorption kinetic was satisfactory fitted to the pseudo-second-order when treated landfill leachate using fruit seed derived GAC kinetic model. In this study, in the case of both types of AC (PACs and GACs) an increase in k_s value was observed with an increase in carbon doses (Tables 8 and 9). In contrast, Rivas et al. [8] proved that Lagergren's equation describes the adsorption regardless of the type and amount of AC used (Norit 0.8, Chemviron AQ40 and Picacarb 1240 in doses 5–30 g/L). The authors showed that in the case of Norit 0.8, kinetic constants increased when carbon dose decreased (from 0.030 to 0.115). This relationship was not found in the case of other carbons and changed in the range 0.023–0.266

Table 9
Kinetic constants for GACs determined from pseudo-second-order kinetic

	Kinetic constants			
	GAC 10		GAC 10 CO	
Carbon dose (g/L)	Q_e (mg/g)	k_s (g/mg h)	Q_e (mg/g)	k_s (g/mg h)
2	140.8	0.40×10^{-2}	138.9	0.30×10^{-2}
5	84.7	0.40×10^{-2}	75.6	0.38×10^{-2}
10	63.7	0.57×10^{-2}	57.1	0.43×10^{-2}
15	42.7	0.89×10^{-2}	43.3	0.78×10^{-2}
20	35.3	1.10×10^{-2}	39.1	1.44×10^{-3}
30	26.3	1.38×10^{-2}	28.7	2.50×10^{-2}

for Chemviron AQ40 and from 0.027 to 0.058 for Picacarb 1240.

4. Conclusions

With PACs, process efficiency increased to the greatest extent with doses from 2 to 3 g/L. In this range, increasing PAC 200-1Wi by 1 g/L increased the removal efficiency of COD (19.1%) and UV_{254} (15.4%). With GACs, process efficiency increased to the greatest extent with doses from 2 to 10 g/L; in this range, an increase of 1 g/L gave smaller increase in removal efficiency of COD (4–4.3%) and UV_{254} (5.4–6.0%).

Organics adsorption followed pseudo-second-order kinetics. With both PACs, equilibrium was reached in 30 min, with both GACs, 48 h. Q_e was 2–3 times higher for PACs than for GACs.

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Nomenclature

PAC — powdered AC
GAC — granular AC
UV_{254} — UV absorption at wavelength 254 nm
UV_{280} — UV absorption at wavelength 280 nm
Q_t — amount of organics COD adsorbed per unit mass of adsorbent after time t (mg/g)
Q_e — amount of organics COD adsorbed per unit mass of adsorbent in equilibrium conditions (mg/g)
k_s — rate constant of adsorption (g/mg min for PAC; g/mg h for GAC)
t — time (min in case of PAC; h in case of GAC)

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