Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1192494

57 (2016) 28560–28569
December

Taylor & Francis
Taylor & Francis Group

Usability of powdered activated carbon for landfill leachate treatment—continued research

Dorota Kulikowska

Faculty of Environmental Sciences, Department of Environmental Biotechnology, University of Warmia and Mazury in Olsztyn, Sloneczna St. 45G, 10-907 Olsztyn, Poland, Tel. +48 895234145; email: dorotak@uwm.edu.pl

Received 9 February 2016; Accepted 12 May 2016

ABSTRACT

Adsorption onto activated carbon (AC) is an effective method for the treatment of leachate from mature landfill. However, in order to limit an excessive AC consumption, it is very important to determine the range of doses at which the organics and color removal efficiency increases to the greatest extent. This study compared the usability of two powdered activated carbons (PACs) (CWZ-22 and CWZ-14 with specific area 850 and 750 m^2/g, respectively) in organics (expressed as COD and UV_{254} as index of humic substance concentration) and color (UV_{410}) removal from landfill leachate. CWZ-22 was more efficient than CWZ-14. In both PACs, the highest process efficiency was where doses were between 1 and 3 g/L; higher doses (5–20 g/L) proved less efficient because high PAC consumption yielded several times lower increase in organics and color removal than lower doses. In 1–3 g/L ranges, a 1 g/L increase in CWZ-22 gave an increase of 12.5% (COD), 13.1% (UV_{254}), and 20.0% (UV_{410}) removal efficiency. In higher doses, increases were 1.4, 0.5, and 0.7%, respectively. With both PACs, organics adsorption followed pseudo-second-order kinetics. With CWZ-22 and lower doses, a kinetics constants of adsorption was 1.5–1.9 times higher than CWZ-14.

Keywords: Activated carbon; Adsorption; Landfill leachate; Organic compounds; UV_{254}; UV_{410}

1. Introduction

Composition and quantity of pollutants in landfill leachate varies from site to site depending on the nature of solid wastes, active microbial flora, rainfall patterns, and the volume of water which infiltrates the landfill and directly affects the natural processes occurring inside it [1]. Moreover, characterization of leachate is complicated by the fact that its composition may vary as a result of landfill age [2]. However, it is generally assumed that leachate from young landfills contains a high concentration of organic substances, although, because the organics are highly biodegradable, these "young" leachates are usually more easily treated, mainly with biological methods, than "old" ones from stabilized landfill. "Old" leachate is characterized by relatively low organics and high ammonium content, in comparison with "young" leachate. However, the organics are poorly biodegradable, as the main organic fraction is composed of refractory substances (i.e. humic substances, HS). According to Artiola-Fortuny and Fuller [3], humic substances may contain up to 60% dissolved organic carbon (DOC). Significant content of humic and fulvic acids in the leachate is also confirmed by Trebouet et al. [4]. For this

reason, leachate from stabilized landfill cannot be effectively treated using biological processes. As a consequence, physicochemical treatments seem to be promising alternative technologies, e.g. coagulation/flocculation, advanced oxidation, or membrane methods [5–7]. Among the physicochemical treatment methods, adsorption has proved to be one of the most effective in removing refractory compounds such as HS. As adsorbent activated carbon (AC) is commonly used due to its large specific surface area, thermostability, and fast adsorption kinetics. Furthermore, AC is highly effective in the removal of a wide range of organic and inorganic pollutants regardless of their concentrations [8]. However, the major limitations of using AC in leachate treatment process are (i) high cost of commercially available carbons and (ii) large consumption of AC. In order to overcome these flaws (i) adsorbents from non-conventional material such as agricultural waste and industrial byproduct that are locally available are used, (ii) the modification of AC or the use of multi-step technologies are applied. A literature review by Shehzad et al. [9] showed that AC may be prepared from different waste, e.g. almond's shell, banana frond, coconut husk, corn cobs, hazel nuts, oil palm fronds, olive seed waste, olive stone, orange peel, palm shell, peach stones, peanut hulls, rice husk, sugarcane bagasse, and waste tea. For the removal of COD, heavy metals, color, and other contaminants from leachate, such low-cost adsorbents as peat, fly ash, bone char, tamarind, and bagasse have already been utilized (after [10]).

In order to reduce the large consumption of AC, many authors use modified AC. This treatment aims to reduce AC dose to simultaneously achieve high process efficiency. For example, Kaur et al. [10] compared cow dung ash (DA) obtained after the complete combustion of cow dung cakes and dung ash (ADA) that was modified using acetic acid (acetic acid was used for activation of sites). The authors showed that at dosage of 20 g/L, COD removal was 66 and 79% for DA and ADA, respectively. Scanning electron microscope images show that after the activation, carbon particles disintegrate and surface of particles become more rough and porous, indicating the reason for high adsorption efficiency of ADA. Wang et al. [11] used different methods for the treatment of landfill leachate, such as granular activated carbon (GAC), GAC impregnated with Mn and Ce oxides (MnCe-AC), ozone process (O_3), and MnCe-AC integrated with ozone process (MnCe-AC/O_3). They showed that humic acids, TOC, and COD removal efficiencies in MnCe-AC/O_3 process were about 90, 68, and 72%, respectively, which were significantly higher than those of ozone, GAC, and MnCe-AC processes alone. Oloibiri et al. [12] showed that removal efficiencies with GAC adsorption as a single technique did not exceed 8 and 20% for λ 254 and COD removal. Overall removal of 90% (λ 254) and 77% (COD) was achieved when applying ozonation prior to GAC, and 99 and 53%, respectively, by applying $FeCl_3$ coagulation–flocculation prior to adsorption. Moreover, pretreatment of leachate before GAC polishing increases both the adsorption capacity and operation time of a GAC column toward COD removal.

However, regardless of the origin and characteristics of AC, the range of AC doses at which the process efficiency most successfully reduces the AC consumption should be determined.

Although studies about landfill leachate treatment with AC are carried out by various authors, and provide information about organics removal efficiency at different doses of AC, the author of the present study is unaware of other information which establishes the range of AC doses that provides the highest increase in the efficiency of organics removal (in %) with an increase in carbon dose of 1 g/L. A previous study of the author [13] concerning landfill leachate treatment with granular and powdered activated carbon (PAC) showed that process efficiency increased to the greatest extent with lower AC doses (2–3 g/L for powdered AC and 2–10 g/L for granular AC). Higher doses proved to be less efficient because they yielded 8–10 times lower increases in process efficiency than lower doses. This means that it is very important to assess the range of AC doses at which adsorption is most effective. Above this range, despite the marked increase in AC dose, effectiveness of landfill leachate treatment increases slightly.

So, in order to verify whether the findings of the mentioned research can be useful for other kinds of AC, further research is needed. This is more important because, in many cases, although organics removal efficiency has been determined at different doses, the tests are not systematic, i.e. the effectiveness of organics removal was analyzed across a wide range of doses, but there is no determination of an increase in removal efficiency (in %) with a 1 g/L increase in carbon dosage in a specific dose range. Determination of the range of doses at which the process efficiency increases to the greatest extent is very important in order to limit AC consumption.

The aim of the present study was to establish the dose ranges in which organics and color removal from landfill leachate increase to the greatest extent when using two different types of commercially available PAC, CWZ-22, and CWZ-14.

In addition, the kinetics of the adsorption process was investigated with different amounts of PAC.

On the basis of adsorption kinetic constants, the contact time required for the equilibrium can be determined, thus enabling the design of batch adsorption systems.

2. Materials and methods

2.1. Leachate feed

This study used leachate from a 15-year-old municipal landfill located in northern Poland. The landfill site, with the total surface area of 22 ha, operated from 1996. In the research period, waste was landfilled in a second field. The total average amount of solid waste deposited in the landfill in 1996 was estimated at 7,550 tons, in 1997 and 1998—7,970 tons, and 9,120 tons, respectively. Since 1999, it amounted to 11,000–12,000 tons. The landfill received municipal waste without fluid waste, fecal matter, hazardous substances, radioactive, and toxic waste. Approximately, 28–30% of disposed waste was of organic household origin, while glass, paper, plastic, metals, and textiles constituted 12–14%, 12–13%, 3–4%, 3–4%, and 2–3% of the total waste mass, respectively. The rest (about 30–34%) were inorganic remains.

Leachate 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 landfill leachate composition is shown in Table 2 (Section 3).

2.2. AC characteristics

The study used CWZ-22 and CWZ-14, commercially produced PACs, the main characteristics of which are presented in Table 1.

Table 1
Characteristics of AC

Parameter	Value	
	CWZ-22	CWZ-14
Shape	Powdered	Powdered
Specific area (m^2/g)	850	750
Methylene number (ml)	22	14
Iodine number (mg/g)	850	750
Moisture content (%)	<12	<12
Ash (%)	<8	<8
Bulk density (g/L)	290–320	290–380
Size (mm)	<0.12	<0.12

2.3. Process configuration and system design

The batch adsorption experiment was carried out using eight samples for each PAC in 2 L jar test beakers. The following doses of AC were tested for each PAC (1.0, 1.5, 2.0, 3.0, 5.0, 10.0, 15.0, 20.0 g/L). Doses of applied AC were used on the basis of the literature review [14,15] and this author's own preliminary studies. All samples were stirred with magnetic stirrers.

To determine the time needed for adsorption equilibrium, a fixed dose of carbon and 1.5 L of leachate were placed in 2 L reaction vessels. The samples were collected at prescribed time intervals: 0, 0.083, 0.167, 0.33, 0.5, 1.2, and 3 h to determine the organics' content (COD). The frequency of sampling to obtain data for kinetic analysis was based on the literature [13,16,17].

2.4. Analytical methods

Analysis determined the following characteristics of the raw leachate: pH (pH-meter HI 8818); COD, according to [18]; and BOD, according to DIN EN 1899-1/EN 1899-2 official EPA method using OxiTop WTW Wissenschaftlich-Technische Werkstätten GmbH, D-82326 Weilheim, Germany. Standard methods were also used to determine Kjeldahl nitrogen, ammonia-N, and total phosphorus. Measurements of both total- and volatile-dissolved solids were carried out according to [19]. UV optical density at $\lambda = 254$ nm (for aromatic and unsaturated organic compounds [20] and at $\lambda = 410$ nm for color was analyzed using a Cary UV/vis spectrophotometer in 1-cm path length quartz cuvettes. Suspended and particulate matter which might have interfered with measurements of UV absorption was removed via Millipore membranes. Distilled water was used as a blank.

Post adsorption measurements of leachate included COD, UV_{254}, and UV_{410}. Before analysis, all samples were filtered using Millipore membranes to minimize the interference of AC fines with the analysis.

3. Results and discussion

3.1. Landfill leachate characteristics

The leachate came from stabilized landfill, which is demonstrated by the high pH (8.62) and low concentrations of COD (874 mg/L) and BOD_5 (76 mg/L) (Table 2). Such results suggest that the majority of organics in the waste had been converted to methane, thereby diminishing both the organics concentration in leachate and their biodegradability, which was also confirmed by BOD_5/COD ratio (0.09).

Table 2
Characteristics of raw landfill leachate (bdl—below detection limit)

Parameter	Unit	Value
pH	–	8.62
COD	mg/L	874
BOD_5	mg/L	76
BOD_5/COD	–	0.09
Kjeldahl nitrogen	mg/L	914
Ammonia nitrogen	mg/L	864
Total phosphorus	mg/L	21.6
Total dissolved solids	mg/L	7,524
Organic dissolved solids	mg/L	1,140
Inorganic dissolved solids	mg/L	6,384
UV_{254}	cm^{-1}	4.55
UV_{410}	cm^{-1}	0.92
Zinc	mg Zn/L	0.31
Chromium	mg Cr/L	0.04
Cadmium	mg Cd/L	0.019
Cooper	mg Cu/L	0.011
Nickel	mg Ni/L	bdl
Lead	mg Pb/L	bdl
Mercury	mg Hg/L	bdl

The leachate used in the present study contained low concentrations of organic compounds expressed as COD and BOD_5 compared to leachate from other landfills. For example, Foo et al. [17] showed that, in leachate collected from a municipal semi-aerobic landfill, the concentration of COD varied between 2,060 and 2,700 mg/L. Similarly, Rivas et al. [14] found an even higher concentration of COD (3,600 mg/L). However, it should be emphasized that while in the above studies the COD contents were higher than in the present study, the BOD_5/COD ratios were similarly low (<0.1), which indicates the stabilized nature of the organics in the leachate. Low biodegradability of organic compounds present in the leachate is related to the type of compounds present. These are mainly substances with a high molecular weight (MW), i.e. humic substances. For example, Calace et al. [21] showed that, in leachate from old landfill, the fraction with MW > 100,000 Da constituted 19%; those with MW from 50,000 to 10,000 Da constituted 20%, whereas those with MW < 500 Da, 28%. Zhang et al. [22] found that landfill leachate contained DOC in concentration of 2,742 mg/L, and HA and FA constituted 40.86% and 34.15 of DOC. However, other authors found a lower share of HS in organics as COD. For example, Kang et al. [23] shows that in leachate from landfill that has been in operation for over 10 years, the organics concentration as COD was 863 mg/L, and HS was 6.9–14.4% of COD. In another study in which the humic and fulvic acid content in the leachates were determined, it was found that fulvic acids may represent 59% of the initial COD of the landfill leachate [17 after 16].

In this study, UV_{254} was used as an index of HS concentration in leachate. However, the value of UV_{254} was rather low and equaled to 4.55 cm^{-1}. This may be connected with the low concentration of COD as HS constitutes only a part of the organics present in leachate. Comstock et al. [24] showed that in leachate from different active and inactive cells from MSW landfills that had been in operation from 1988, values of UV_{254} varied in a wide range from 7.2 to 90.4 cm^{-1}. Similarly, different values of UV_{254} were obtained by Zhao et al. [25]. They showed that the values of UV_{254} depended on the kind of landfill unit and unit age. The authors obtained the following values of UV_{254}: 4.2–5.3 cm^{-1} in leachate from an inactive landfill unit that was not receiving waste (solid waste disposal for 30 years); 5.8–8.2 cm^{-1} in leachate from the unit that had had no input for over a decade, but was operated as a bioreactor landfill for a period of time (16 years); 20.2–23.0 cm^{-1} from a unit that was closed in 2005 and was operated as a bioreactor landfill (9 years); and 30.1–39.5 cm^{-1} in leachate from a unit which was an active permitted landfill (2.5 years). However, it should be emphasized that leachate from these units was characterized by very different COD concentrations, from 712–903 mg/L in leachate from a 30-year-old unit to 6,602–6,856 mg/L in a 2.5-year-old unit.

In leachate, in this study, the metal concentrations were low (Table 2). However, low concentrations of heavy metals in leachate from old landfills are rather a typical phenomenon. For example, a review of 106 Danish landfills showed that metal concentrations for all were: 0.006 mg Cd/L, 0.13 mg Ni/L, 0.67 mg Zn/L, 0.07 mg Cu/L, 0.07 mg Pb/L, and 0.08 mg Cr/L [26]. Higher metal concentrations are observed in leachate from young landfills, which is connected with a high degree of metal solubilization as a result of low pH caused by the production of organic acids in the acidification stage. As the landfill's age increases, pH values cause a certain decrease in metal solubility.

3.2. The efficiency of organics and color removal using PACs

The landfill leachate was treated with two kinds of PAC (CWZ-22 and CWZ-14) at doses from 1 to 20 g/L. Table 3 shows the concentrations of organic substances (expressed as COD), index of humic substances content (UV_{254}), and color (UV_{410}) after adsorption onto both PACs.

With both PACs, COD, UV_{254}, and UV_{410} values in treated leachate decreased with the increase in PAC

Table 3
Organics (COD, UV_{254}) and color (UV_{410}) in leachate after adsorption onto PACs

	CWZ-22			CWZ-14		
PAC dose (g/L)	COD (mg/L)	UV_{254} (cm^{-1})	UV_{410} (cm^{-1})	COD (mg/L)	UV_{254} (cm^{-1})	UV_{410} (cm^{-1})
0.0	874	4.55	0.92	874	4.55	0.92
1.0	528	4.31	0.68	632	4.48	0.83
1.5	440	3.67	0.48	624	4.23	0.78
2.0	353	3.17	0.47	598	4.11	0.73
3.0	312	2.31	0.32	531	4.00	0.69
5.0	280	1.36	0.26	460	3.31	0.44
10.0	208	0.91	0.17	352	1.68	0.25
15.0	128	0.78	0.16	242	1.21	0.20
20.0	112	0.74	0.16	202	1.11	0.19

dosage. However, according to all indices, CWZ-22 was more effective than CWZ-14. This may be connected with PACs surface area, as adsorption is a surface phenomenon. In this study, the specific area of CWZ-22 was higher (850 m^2/g) than CWZ 14 (750 m^2/g). However, when considering the effectiveness of organics removal with AC, two aspects should be taken into account: the surface area of the AC and the MW of organics present in the leachate. On the one hand, a larger surface area enables adsorption of higher amounts of organics. On the other hand, large molecules in landfill leachate may be unable to penetrate the smaller pores of this PAC, which would diminish the process efficiency. This phenomenon was observed in a previous study in which lower organics concentrations in the effluent and higher process efficiency were obtained with PAC-200-1Wi (specific area, 900 m^2/g) than with PAC-200-C303 (specific area 1,200 m^2/g) [13]. Lin et al. [27] have observed that the adsorption capacity of PAC, with a surface area 730 m^2/g, depends on the molecular weight of a stock solution of commercial humic acid (HA) (Aldrich). They found that PAC was ineffective in removing MW fractions of humic acid either <300 or >17,000. The large molecules of humic substances were unable to penetrate the smaller pores of the PAC they used. As for the low MW molecules, they were probably of a hydrophilic nature, and hence, not amenable to PAC adsorption. Thus, PAC removed humic substances in the middle MW range. According to Cossu and Rossetti [28], the organic fraction preferentially removed by AC is the fulvic fraction, with a molecular weight of 100–10,000.

The relationship between adsorption efficiency and the particle size of the adsorbate is a common phenomenon that has been noted with other kinds of AC, e.g. fibrous AC (FAC). Brasquet et al. [29] used two kinds of FAC with different specific surface areas (1,500 and 1,300 m^2/g) for adsorption of substances that differed in molecular size, and showed that the capacity of FAC to adsorb high MW compounds (humic substances) was about 3 mg/g, which was much lower than the absorbance of low MW compounds, which was 200 and 400 mg/g for phenol and benzoic acid, respectively. According to the authors, micropollutants adsorption by FAC is selective, due to the high microporosity of the fibers, and to the fact that micropores act as a molecular sieve for macromolecules like humic materials.

The use of AC is an efficient method of landfill leachate treatment because adsorption of pollutants greatly reduces both organics concentration and color. However, the main drawback of the process may be the high consumption of AC when high process efficiency is needed. Therefore, to limit the PAC consumption, it is important to determine the range of doses at which the process efficiency increases to the greatest extent with PAC increase at 1 g/L. In order to avoid excessive use of PAC for further leachate treatment (polishing), another method should be used.

In this study, data on the percent of organics removal with different PAC 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 and color removal efficiency (in %) with an increase in PAC dose of 1 g/L.

The relationship between the PAC doses and landfill leachate removal efficiency in terms of COD, UV_{254}, and UV_{410} (experimental data) is shown in Fig. 1.

In the case of organics expressed as COD, at dosages ranging from 1 to 3 g/L, process efficiency increased 12.5% with a 1 g/L increase of CWZ-22, and 6.5% with the same increase of CWZ-14 (Fig. 1(a)). At higher doses (5–20 g/L), the increases in process efficiency in both cases were smaller and accounted for

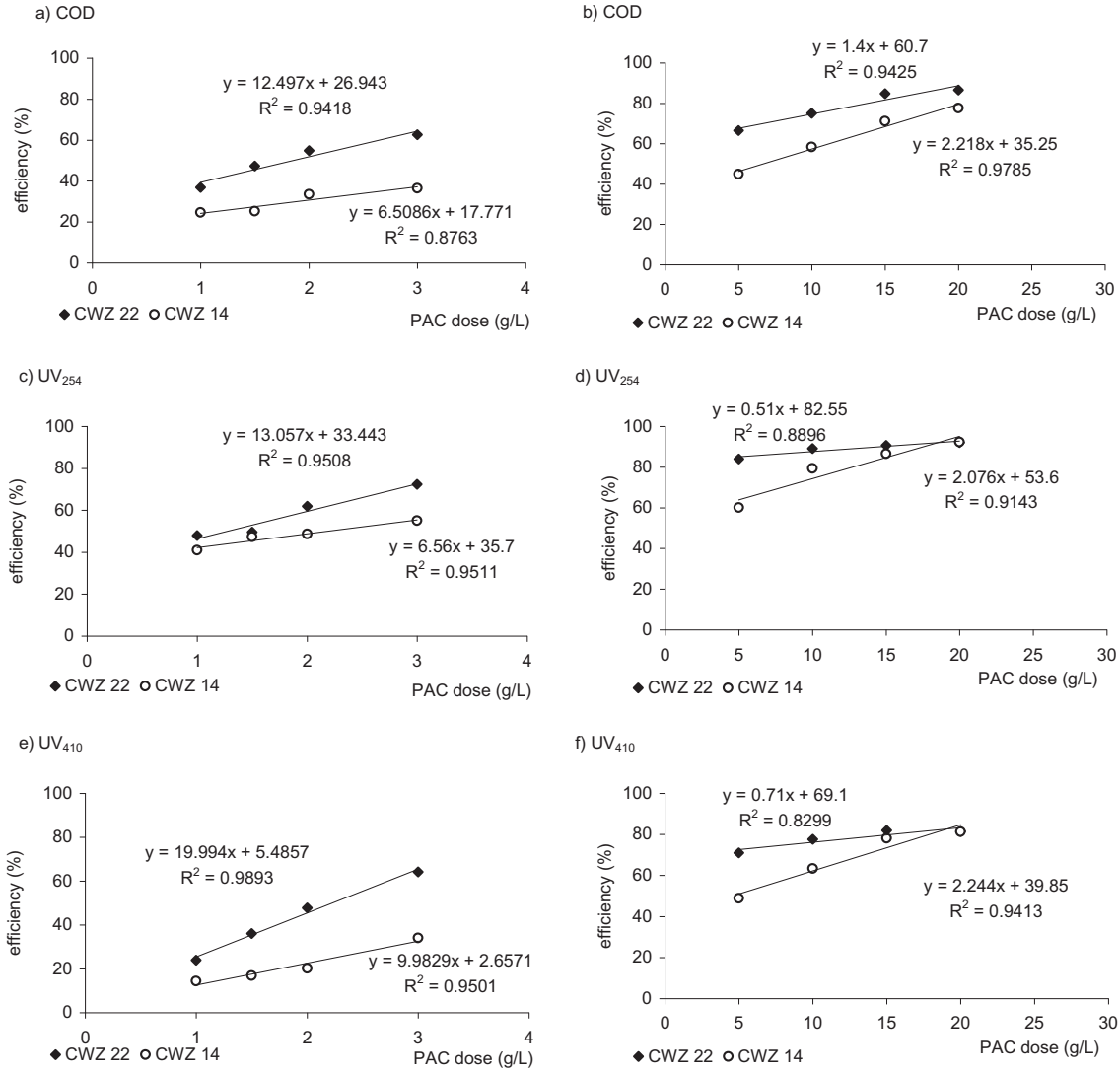

Fig. 1. Increase of landfill leachate treatment efficiency with the increase in PAC dose of 1 g/L.

1.4 and 2.2%, respectively (Fig. 1(b)). The same phenomenon was observed in the case of UV_{254}. Lower doses (1–3 g/L) of CWZ-22 saw a 13% increase in UV_{254} removal efficiency, however in CWZ-14, with lower specific area, it was 6.6% (Fig. 1(c)). At higher doses, the increase of UV_{254} removal was much lower (Fig. 1(d)). A similar phenomenon was noted in the case of color removal (Fig. 1(e) and (f)).

Although reports of the relationship between process efficiency and PAC dosage described in the same manner as in this study are not typical in the literature, other authors have also indicated that adsorption is a dosage-dependent process. They found that obtaining high process efficiency is possible at high AC doses, which causes adsorption to become a costly process. In newer works, therefore, authors have used as an adsorbent-modified AC [30] or AC prepared from waste, e.g. from coconut and almond shells, rice husks, and sugarcane bagasse.

Kalderis et al. [31] used AC from rice husks and sugarcane bagasse that was chemically impregnated with $ZnCl_2$. The ACs obtained was microporous and had surface areas of 811 and 864 m^2/g, respectively. Both ACs were tested for adsorption of arsenic, humic acid, phenol, and landfill leachate from municipal solid waste. They both were most effective at adsorbing phenol, removing around 80% at an equilibrium time of 4 h. The adsorption of arsenic and humic acid were also favorable, although the maximum efficiencies achieved were lower than that of phenol. When treating landfill leachate, 30 g/L of AC removed 70% of COD and 60% of color.

Foo et al. [17] showed that, using GAC derived from tamarind fruit seed (TSAC), removal of both COD and color from landfill leachate increased as adsorbent dosage was raised from 10 to 30 g/L, but further increases in dosage did not appreciably increase the removal of COD and color. The optimum COD and color removal were noted at a carbon dosage of 30 g/L (79.9 and 91.2%, respectively).

However, it should be noted that, in both the above studies, high adsorbent doses (30 g/L) were needed to obtain relatively high process efficiency, which meant the production of large amounts of waste AC. To avoid excessive consumption of AC and to improve the treatability of leachate, Kurniawan and Lo [30] used integrated H_2O_2 oxidation and GAC adsorption. At an initial COD concentration of 8,000 mg/L and with a GAC dose of 15 g/L, this integrated treatment removed substantially more COD (82%) than either H_2O_2 oxidation (33%) or GAC alone (58%).

In this study with both PACs, the most effective doses for organics removal were in the range of 1–3 g/L. Higher doses proved less efficient because the high consumption of carbon yields only a low increase in process efficiency. The same phenomenon was observed in earlier research concerning the organics removal from landfill leachate with both PACs and GACs as adsorbent [13]. The authors showed that with PAC doses between 2 and 3 g/L, an increase of 1 g/L (PAC 200-1Wi and PAC 200-C303) gave an increase in COD and UV_{254} removal efficiency of 19.1 and 15.4%, respectively; with GACs (GAC 10 and GAC 10CO), 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.

Although it is known that efficiency of landfill leachate treatment with adsorption is largely dependent on the type of adsorbent and adsorbent dose, the literature lacks data about optimal dosage ranges above which the efficiency of the adsorption process is lessened. However, both in this work and in the author's previous study, it was shown that although the increase of process removal efficiency with PAC dose of g/L were different with different PACs characterized by a different specific area, in all cases, the highest increase in process efficiency was observed at PAC dose up to 3 g/L. Although even at PAC dose 3 g/L, COD concentration in effluent was relatively high (Table 3), further increase in PAC dose is economically unjustified. Therefore, other methods should be used. According to many authors, none of the individual physicochemical methods were universally applicable or highly effective for the removal of recalcitrant compounds from stabilized leachate and not even a single method was effective enough to meet effluent limits for release into surface waters [32]. For example, Li et al. [15] showed that the removal efficiencies of COD, from the stabilized landfill leachate were up to 86%, by the combined coagulation–flocculation (polyferric sulfate 0.3 g Fe^{3+}/L) and adsorption process (PAC dose 10 g/L).

3.3. Adsorption kinetics

In adsorption, it is important to establish the time required to obtain equilibrium concentration of pollutants in the leachate. Therefore, adsorption kinetic experiments of leachate were performed using both PACs, in order to investigate the minimum contact time for the removal of organics.

In addition, the relationship between the amount of adsorbed organics and adsorption time formed the basis for analysis of the kinetics of adsorption. Experimental data (COD) were applied to two different models (pseudo-first-order, pseudo-second-order kinetics), previously reported in the literature. On the basis of R^2 values for linear forms of pseudo-first-order ($R^2 < 0.86$) and pseudo-second-order kinetics (R^2 in the range 0.9912–0.9999), it was assumed that pseudo-second-order kinetics would provide a better description of the adsorption process:

$$\frac{dQ_t}{dt} = k_s(Q_e - Q_t)^2 \quad (1)$$

Eq. (1) after linearization takes the form:

$$\frac{1}{Q_t} = \frac{1}{k_s Q_e^2} + \frac{1}{Q_e}t \quad (2)$$

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

With both PACs, organics concentration dropped significantly after 5 min of adsorption, and in the case of CWZ-22, the amount of organics adsorbed during this time ($Q_{t,5}$) averaged 80% of the amount at equilibrium conditions. With CWZ-14, $Q_{t,5}$ averaged 64% lower than with CWZ-22.

Rapid organics adsorption on different kinds of adsorbents has also been observed by other authors. For example, Rodriguez et al. [16] showed that, after

Table 4
Kinetic constants for PACs determined from pseudo-second-order kinetics

	Kinetic constants			
	CWZ-22		CWZ-14	
Carbon dose (g/L)	Q_e (mg/g)	k_s (g/mg min)	Q_e (mg/g)	k_s (g/mg min)
1.0	312.5	0.11×10^{-2}	208.3	0.71×10^{-3}
1.5	263.2	0.19×10^{-2}	142.9	0.96×10^{-3}
2.0	243.9	0.19×10^{-2}	156.2	0.16×10^{-2}
3.0	175.4	0.25×10^{-2}	105.3	0.25×10^{-2}
5.0	111.1	0.50×10^{-2}	85.6	0.53×10^{-2}
10.0	62.9	1.76×10^{-2}	48.5	0.91×10^{-2}
15.0	46.7	3.44×10^{-2}	39.8	1.08×10^{-2}
20.0	35.9	4.74×10^{-2}	31.6	2.09×10^{-2}

10 min, adsorption of organics on GAC-40, XAD-8, XAD-4, and IR-120 equaled 59.6, 86, 44.8, and 43.9% of the total amount of organics adsorbed. Li et al. [15] showed that during organics removal with PAC (10 g/L), COD removal efficiency reached 52% and equilibrium was reached in 90 min.

Kinetic constants (Q_e, k_s) for both PACs in this study are presented in Table 4. The Q_e value was dose-dependent and was in the range of 312.5–35.9 mg/g CWZ-22. However, with CWZ-14, the Q_e values were from 1.5 times lower with the dose of 1 g/L to 1.13 times lower with the dose of 20 g/L. Moreover, in the case of both PACs, the value of k_s increased with the increase in carbon dose.

Similarly, Foo et al. [17] showed that during the treatment of landfill leachate with GAC derived from fruit seed, the adsorption kinetics followed pseudo-second-order kinetics. However, in their study, k_s and Q_e were 0.035 g/mg h and 61.35 mg/g, respectively. In contrast, Rivas et al. [14] showed that, with Norit 0.8, Chemviron AQ40 and Picacarb 1240 (in doses 5–30 g/L), the adsorption process was better described by Lagergren's equation. The authors showed that with Norit, 0.8, k_s increased as carbon dose decreased (from 0.030 to 0.115). However, this inverse relationship was not found with other ACs, with which the k_s ranged from 0.023 to 0.266 for Chemviron AQ40 and from 0.027 to 0.058 for Picacarb 1240.

Adsorption processes take place in a multi-step mechanism: (i) diffusion across the liquid film surrounding the solid particles (this process is limited by an external mass transfer coefficient), (ii) diffusion within the particle itself via pore diffusion mechanism (intra-particle diffusion), and (iii) physical or chemical adsorption at site [33 after 34]. Halim et al. [34] analyzed organics removal from landfill leachate using three different adsorbents: zeolite, AC, and a new composite media (limestone and rice husk carbon). On the basis of COD, they showed that AC had the highest adsorption capacity (37.88 mg/g), followed by the composite media (22.99 mg/g) and zeolite (2.35 mg/g). According to the authors, both chemical adsorption (dominant) and physical adsorption were involved in the adsorption of organics on the composite adsorbent and zeolite, while physical adsorption was the dominant mechanism with AC. Chemical adsorption refers to ion exchange activity on the adsorbent surface, while physical adsorption refers to physical attachment of non-polar adsorbate on a very large surface area due to the presence of macropores, mesopores, and micropores. With the composite media and zeolite, the combination of chemical and physical adsorption was due to these materials' high cation exchange capacity (CEC) and moderate surface area. With AC, in contrast, an extremely large surface area and a low CEC meant that physical adsorption dominated.

4. Conclusion

CWZ-22 was more efficient than CWZ-14 for the removal of COD, UV_{254}, and UV_{410}. With both PACs, process efficiency increased to the greatest extent while increasing dosage from 1 to 3 g/L. In this range, increasing CWZ-22 by 1 g/L increased the removal efficiencies by 12.5% (COD), 13.1% (UV_{254}), and 20.0% (UV_{410}). At higher dosages (5–20 g/L), this increase in dosage gave an increase in organics and color removal, albeit several times lower.

This study shows that, similar to other PACs examined by the author in a previous study, increasing the dosage of AC is most effective for doses up to 3 g/L during landfill leachate treatment with relatively low concentrations of organics.

Acknowledgment

The study was supported by the Ministry of Science and Higher Education in Poland (Statutory Research, 528-0809-0801).

Nomenclature

PAC	—	powdered activated carbon
UV_{254}	—	UV absorption at wavelength 254 nm
UV_{410}	—	UV absorption at wavelength 410 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)
t	—	time (min)

References

[1] P.H. Chen, Assessment of leachates from sanitary landfills: Impact of age, rainfall and treatment, Environ. Int. 22 (1996) 225–237.
[2] D. Kulikowska, E. Klimiuk, The effect of landfill age on municipal leachate composition, Bioresour. Technol. 99 (2008) 5981–5985.
[3] J. Artiola-Fortuny, W.H. Fuller, Humic substances in landfill leachates: I. Humic acid extraction and identification, J. Environ. Qual. 11 (1982) 663–669.
[4] D. Trebouet, J.P. Schlumpf, P. Jaouen, F. Quemeneur, Stabilized landfill leachate treatment by combined physicochemical-nanofiltration processes, Water Res. 35 (2001) 2935–2942.
[5] D.M. Bila, A.F. Montalvão, A.C. Silva, M. Dezotti, Ozonation of a landfill leachate: Evaluation of toxicity removal and biodegradability improvement, J. Hazard. Mater. 117 (2005) 235–242.
[6] J.J. Wu, C.C. Wu, H.W. Ma, C.C. Chang, Treatment of landfill leachate by ozone-based advanced oxidation processes, Chemosphere 54 (2004) 997–1003.
[7] T.A. Peters, Purification of landfill leachate with reverse osmosis and nanofiltration, Desalination 119 (1998) 289–293.
[8] N. Turki, D. Belhaj, I. Jaabiri, H. Ayadi, M. Kallel, J. Bouzid, Determination of organic compounds in landfill leachates treated by coagulation–flocculation and fenton-adsorption, IOSR J. Environ. Sci. Toxicol. Food Technol. 7 (2013) 18–25.
[9] A. Shehzad, M.J.K. Bashir, S. Sethupathi, J.-W. Lim, An overview of heavily polluted landfill leachate treatment using food waste as an alternative and renewable source of activated carbon, Process Saf. Environ. Prot. 98 (2015) 309–318.
[10] K. Kaur, S. Mor, K. Ravindra, Removal of chemical oxygen demand from landfill leachate using cow-dung ash as a low-cost adsorbent, J. Colloid Interface Sci. 469 (2016) 338–343.
[11] J.-M. Wang, Ch.-S. Lu, Y.-Y. Chen, D.T. Chang, H.-J. Fan, Landfill leachate treatment with Mn and Ce oxides impregnated GAC–ozone treatment process, Colloids Surf., A 482 (2015) 536–543.
[12] V. Oloibiri, I. Ufomba, M. Chys, W.T.M. Audenaert, K. Demeestere, S.W.H. Van Hulle, A comparative study on the efficiency of ozonation and coagulation–flocculation as pretreatment to activated carbon adsorption of biologically stabilized landfill leachate, Waste Manage. (Oxford) 43 (2015) 335–342.
[13] D. Kulikowska, K. Bernat, K. Parszuto, P. Sułek, Efficiency and kinetics of organics removal from landfill leachate by adsorption onto powdered and granular activated carbon, Desalin. Water Treat. 57(10) (2016) 4458–4468.
[14] F.J. Rivas, F.J. Beltran, O. Gimeno, J. Frades, F. Carvalho, Adsorption of landfill leachates onto activated carbon. Equilibrium and kinetics, J. Hazard. Mater. 131 (2006) 170–178.
[15] W. Li, T. Hua, Q. Zhou, S. Zhang, F. Li, Treatment of stabilized landfill leachate by the combined process of coagulation/flocculation and powder activated carbon adsorption, Desalination 264 (2010) 56–62.
[16] J. Rodríguez, L. Castrillón, E. Marañón, H. Sastre, E. Fernández, Removal of non-biodegradable organic matter from landfill leachates by adsorption, Water Res. 38 (2004) 3297–3303.
[17] K.Y. Foo, L.K. Lee, B.H. Hameed, Batch adsorption of semi-aerobic landfill leachate by granular activated carbon prepared by microwave heating, Chem. Eng. J. 222 (2013) 59–264.
[18] A.E. Greenberg, L.S. Clesceri, A.D. Eaton (Eds.), Standard Methods for the Examination of Water and Wastewater, eighteenth ed., APHA-AWWA-WEEF, Washington, DC, 1992.
[19] W. Hermanowicz, W. Dożańska, J. Dojlido, B. Koziorowski, Fizyczno-Chemiczne Badanie Wody i Ścieków (Physical-chemical analysis of water and wastewater), Arkady, Warszawa, 1999.
[20] Y.P. Chiang, Y.Y. Liang, Ch.N. Chang, A.C. Chao, Differentiating ozone direct and indirect reactions on decomposition of humic substances, Chemosphere 65 (2006) 2395–2400.
[21] N. Calace, A. Liberatori, B.M. Petronio, M. Pietroletti, Characteristics of different molecular weight fractions of organic matter in landfill leachate and their role in soil sorption of heavy metals, Environ. Pollut. 113 (2001) 331–339.
[22] L. Zhang, A. Li, Y. Lu, L. Yan, S. Zhong, C. Deng, Characterization and removal of dissolved organic matter (DOM) from landfill leachate rejected by nanofiltration, Waste Manage. (Oxford) 29 (2009) 1035–1040.
[23] K.H. Kang, H.S. Shin, H. Park, Characterization of humic substances present in landfill leachates with different landfill ages and its implications, Water Res. 36 (2002) 4023–4032.
[24] S.E.H. Comstock, T.H. Boyer, K.C. Graf, T.G. Townsend, Effect of landfill characteristics on leachate organic matter properties and coagulation treatability, Chemosphere 81 (2010) 976–983.
[25] R. Zhao, A. Gupta, J.T. Novak, C.D. Goldsmith, N. Driskill, Characterization and treatment of organic constituents in landfill leachates that influence the UV disinfection in the publicly owned treatment works (POTWs), J. Hazard. Mater. 258–259 (2013) 1–9.
[26] T.H. Christensen, P. Kjeldsen, P.L. Bjerg, D.L. Jensen, J.B. Christensen, A. Baun, H.-J. Albrechtsen, G. Heron,

Biogeochemistry of landfill leachate plumes, Appl. Geochem. 16 (2001) 659–718.
[27] C.F. Lin, Y.J. Huang, O.J. Hao, Ultrafiltration processes for removing humic substances: Effect of molecular weight fractions and PAC treatment, Water Res. 33 (1999) 1252–1264.
[28] R. Cossu, R.R. Raga, The PAF model: An integrated approach for landfill sustainability, Waste Manage. (Oxford) 23 (2003) 37–44.
[29] C. Brasquet, E. Subrenat, P. Lecloirec, Selective adsorption on fibrous activated carbon of organics from aqueous solution: Correlation between adsorption and molecular structure, Water Sci. Technol. 35(7) (1997) 251–259.
[30] T.A. Kurniawan, W.-H. Lo, Removal of refractory compounds from stabilized landfill leachate using an integrated H_2O_2 oxidation and granular activated carbon (GAC) adsorption treatment, Water Res. 43 (2009) 4079–4091.
[31] D. Kalderis, D. Koutoulakis, P. Paraskeva, E. Diamadopoulos, E. Otal, J. Valle, C. Fernández-Pereira, Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse, Chem. Eng. J. 144 (2008) 42–50.
[32] A.Ž. Gotvajn, T. Tišler, J. Zagorc-Končan, Comparison of different treatment strategies for industrial landfill leachate, J. Hazard. Mater. 162 (2009) 1446–1456.
[33] M.S. Chiou, H.Y. Li, Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads, J. Hazard. Mater. 93 (2002) 233–248.
[34] A.A. Halim, H.A. Aziz, M.A.M. Johari, K.S. Ariffin, Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment, Desalination 262 (2010) 31–35.