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Removal of 2,4-dichlorophenol and pentachlorophenol from waters by sorption using coal fly ash from a Portuguese thermal power plant

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Abstract

Chlorophenols are one of the most important groups of priority pollutants, due to their high toxicity, mutagenicity and carcinogenicity. Although activated carbon has been the preferred choice for the removal of such pollutants from wastewaters, the search for cheaper alternative sorbents became common in the last years. Fly ash, a by-product from coal burning power plants, has a surface composition that may enable the sorption of specific organic compounds. Therefore, this feasibility study presents the optimization of the operating parameters of a fixed-bed column containing fly ash particles, percolated by aqueous solutions of 2,4-dichlorophenol (2,4-DCP) and pentachlorophenol (PCP) with concentrations of 1 and 100 μg/ml. Both chlorophenols were analysed by gas chromatography with electron capture detection (GC-ECD), after solid-phase microextraction (SPME), with limits of detection (LODs) of 7.28 μg/l for 2,4-DCP and 1.76 μg/l for PCP. Removal efficiencies above 99% were obtained for an initial concentration of 10 μg/ml of chlorophenols. Column saturation was achieved after 7 h of continuous operation for 2,4-DCP and 10 h for the PCP for feed levels of 10 μg/ml. Fly ash exhibited more affinity towards the sorption of PCP, in comparison to 2,4-DCP.
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Keywords: Coal fly ash; Sorption; Pentachlorophenol; Dichlorophenol; Solid-phase microextraction; Tapada do Outeiro thermal power plant

1. Introduction

The generalized use of organochlorine compounds, persistent and highly water-soluble pollutants, and their presence in industrial and urban wastewater, led to accumulation in the environment, and therefore, a serious pollution problem. Chlorophenols are highly toxic, poorly biodegradable and present carcinogenic and recalcitrant properties [1,2], having been used as wood preservatives, herbicides, insecticides, fungicides, flame retardants, solvents, paint, glue and in the paper industry. For instance, 2,4-dichlorophenol (2,4-DCP) and 4-chlorophenol (4-CP) are widely used in the production of pentachlorophenol (PCP), 2,4-dichlorophenoxiacetic acid and 2,4,5-trichlorophenoxiacetic acid [1,2].

Maximum allowable levels were set for chlorophenols depending on the purpose of the water distribution. While maximum discharge levels of 1 mg/l are permitted for PCP–Na industries, the minimum quality objectives of wastewater impose 20 μg/l for 2,4-DCP and 2 μg/l for PCP [3]. The United States Environmental Protection Agency (US-EPA) set a maximum legal limit for PCP in drinking water of 1 μg/l [4]. Consequently, there is the need to find efficient treatments in order do reduce and/or eliminate chlorophenols in the environment.

Activated carbon is a common material used in the removal of organic micropollutants, due to its highly efficiency. However, sorption into granulated activated carbon (GAC) columns carries high regeneration costs. The efficiency of the sorption process has been attributed to its properties, namely high surface area, porosity and chemical nature of the surface. The functional groups on the surface of the activated carbon depend on the nature and type of the activation technique employed [5,6].

Sorption of chlorophenols using GAC was described by Garcia-Mendieta et al. [7], where sorption capabilities for 4-chlorophenol and phenol were compared. Batch studies were reported, being PCP the most studied chlorophenol [8,9]. Mollah and Robinson [8] studied PCP adsorption in GAC, performing batch assays at 30 °C, with variable PCP concentrations and a sorbent ratio of 1 g GAC per 0.2–1.5 l of solution. They observed a strong pH-dependent interaction of PCP with the sorbent surface, with an average sorption capacity of 157 mg PCP/g GAC,

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using an initial PCP concentration of 1 mg/l. Jung et al. [9] studied the sorption capacity of GAC in batch conditions for five chlorophenols: 2-CP, 4-CP, 2,4-DCP, 2,4,6-TCP and PCP.

Despite attaining the highest efficiencies of removal with GAC sorption, low-cost and abundant materials are being tested as sorbents, with or without previous physical or chemical activation. Pine bark was used to remove organochlorines from aqueous matrices [10–12]; almond shells were tested to remove PCP from contaminated waters [13] and other biomaterials such as rice bark, cactus, olive stone/cake, wool, charcoal and pine needles were used to remove chromium from industrial waters [14].

The utilization of fly ash from coal burning power plants to remove pollutants from aqueous solutions has also been studied by several authors [15–23]. Ugurlu and Salman [20] achieved over 96% efficiency for phosphorous removal in batch and continuous conditions. Aksu and Yener [21] compared sorption capacity of fly ash and GAC towards *o*- and *p*-chlorophenols, concluding that the alternative sorbents may constitute an interesting alternative, once the difference of sorption capacity (for GAC, 380 and 422 mg/g, and for fly ash, 98.7 and 118.6 mg/g, for *o*-chlorophenol and *p*-chlorophenol, respectively) is not significant when compared with the cost of the sorbent.

Kao et al. [22] studied the equilibrium and kinetic parameters for 2-CP and 2,4-DCP sorption in fly ash. Batch and continuous experiments involved average chlorophenols concentrations of 100 mg/l. A relatively fast equilibrium time (about 2 h) and average removal efficiencies of 90% were achieved. Best results were obtained at lower temperature (20 °C) and pH (about 4). Akgerman and Zardkoohi [15] obtained a maximum sorption capacity of 22 mg/g for 2,4-DCP when high concentrations were used (close to the 2,4-DCP water solubility, 5 g/l).

Batabyal et al. [23] introduced another interesting concept for the full removal of micropollutants from waters by sorption with fly ash. As they are mainly constituted by SiO_2, Al_2O_3, Fe_2O_3, CaO, TiO_2 and other metallic complexes, those oxides may act as catalysts in the oxidation of chlorophenols previously sorbed to the fly ash surface, with H_2O_2. Hence, 2,4-DCP batch sorption was performed in fly ash and the contaminated sorbent was successfully treated afterwards by oxidation with hydrogen peroxide.

To our knowledge, no studies were yet conducted on the direct employment of fly ash as sorbent for PCP removal using continuous experiments. Thus, this work was intended as a feasibility study to evaluate the ability of this material to remove 2,4-DCP and PCP from aqueous systems, without any kind of activation treatment.

2. Experimental

2.1. Chemicals

Pentachlorophenol (PCP) (98% purity), 2,4-dichlorophenol (2,4-DCP) (99% purity) and the internal standard 2,4,6-trichlorophenol (2,4,6-TCP) (98% purity) were obtained from Supelco (Bellefonte, PA, USA). Isopropanol (99.8%) used to prepare standards was from Riedel-de Haën (Seelze, Germany) and H_2SO_4 (95–97%) from Fluka (Buchs, Switzerland).

2.2. Sorbent

The fly ash used as sorbent was supplied by the Tapada do Outeiro thermal power plant, located in the north of Portugal and dried at 105 ± 5 °C for 24 h before analysis. The granulometry of the used particles ranged from 125 to 300 μm.

2.3. Standards and sample preparation

Stock solutions (3 g/l of 2,4-DCP and 5 g/l of PCP) were diluted in isopropanol and kept at low temperatures. Working standard solutions of 5.16 mg/l of 2,4-DCP, 5.00 mg/l of PCP and 5.06 mg/l of 2,4,6-TCP, were also prepared in isopropanol. Calibration standards with concentrations ranging from 5.16 to 92.88 μg/l for 2,4-DCP and 2.00 to 30.00 μg/l for PCP (six standards each), were prepared from the latter solutions in deionised water, being the pH adjusted to 2 with H_2SO_4 0.1 M. The pH of the aqueous samples from sorption experiments was adjusted, seemingly, before chromatographic analysis.

2.4. Chlorophenols analysis and quantification

Samples were pre-concentrated by solid-phase microextraction (SPME), prior to the analysis by gas chromatography with electron capture detection (GC-ECD), using a 85 μm polyacrylate (PA) fibre and a SPME fiber holder, both from Supelco (Bellefonte, PA, USA). A PC-240 heating/stirring plate from Corning (Corning, NY, USA) with a thermometer and a water bath controlled the 750 rpm stirring and the temperature. Samples were extracted in 5 ml amber vials. Optimal conditions for SPME, adapted from Ribeiro et al. [24], included: fiber immersion sampling at 40 °C for 15 min, sample volume of 4 ml and sample pH adjusted to 2.

Analyses were performed on a Finnigan 9001 gas chromatograph from Finnigan Corporation (Austin, TX, USA), with a split–splitless injection port and a ^{63}Ni Electron Capture Detector. The column was a DB-5 MS (30 m × 0.32 mm × 1 μm) from J&W Scientific (Folsom, CA, USA). The temperature of the detector was set to 350 °C. For carrier and make-up gas was used nitrogen 5.0 (99.999%) from Air Liquide (Maia, Portugal) with respective flow rates of 3 and 15 ml/min.

The fiber was previously conditioned in the GC injector for 2 h at 300 °C. This procedure was repeated whenever needed for fiber cleanup. Before sample extraction, blank runs (3 min in the GC injector at 280 °C) were performed to look for possible fibre contamination or carry-over.

After the extraction, the fiber was introduced in the injector at 280 °C for 3 min (desorption time) with the split valve closed. The initial oven temperature was 150 °C, held for 1 min, and then increased to 280 °C, at 10 °C/min. This temperature was kept for 1.5 min, to complete a total analysis time of a single run of 15.50 min.

Chlorophenols were quantified by peak area using 2,4,6-TCP as internal standard. Calibration curves were obtained

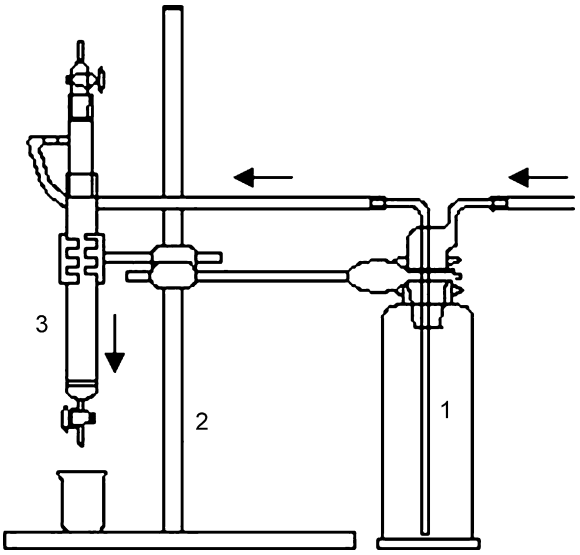

Fig. 1. Schematic diagram of fly ash adsorption column (1, flask containing 2,4-DCP or PCP solution; 2, support; 3, column for adsorption studies).

with standards extracted in the same conditions as the samples.

2.5. Sorption experiments

These experiments were performed with fly ash and carried out using a glass column (2 cm diameter × 23 cm height), filled up to 6 cm with about 10 g of ashes (Fig. 1). This column, previously washed with 150 ml of deionised water, was exposed to different bed contact times (flow rates ranging from 3 to 6 ml/min), using different feed concentrations of chlorophenols (10 and 100 μg/ml for 2,4-DCP and 10 μg/ml for PCP). Solutions were fed from a 4-l reservoir in co-current, with compressed air.

2.6. Safety procedures and hazardous waste disposal

Chlorophenols are dangerous compounds (risk phrases 22-24-34-36/38-40-50/53) and therefore must be handled with precaution, assuring the necessary ventilation and wearing gloves (safety phrases 26-36/37/39-45-60/61). All the material used in contact with chlorophenols was washed with acetone and the residues placed in a container labelled as 'Danger-Organic Compounds-Chlorophenols'. The isopropanolic solutions were recycled by fractional distillation and reused on other less accurate applications. The residues remaining from the distillation (chlorophenols) were placed in a proper container, as mentioned above.

3. Results and discussion

3.1. Validation of the analytical method

An in-house validation of the analytical methodology was performed, not only to establish the main characteristics of the method (linearity range, detection limits, accuracy and precision), but also to assess the global uncertainty associated to the results. This last parameter is important to distinguish between the variation of the results that may be attributed to the method of analysis or to the sorption experiments. Sorption studies usually do not include validation parameters for the analytical methodology employed, but such data is particularly important when it is known that the molecular structure of the chlorophenols assumes different forms according to the pH (either protonated or as the derivating salt – fenoxide form). For instance, once the molar absorptivity depends on the structure of the compounds, when HPLC with UV detection is used, so will the detected amount.

The limits of detection (LODs) calculated from the calibration curves [12], were 7.28 μg/l for 2,4-DCP and 1.76 μg/l for PCP.

The intermediate precision, expressed as the coefficient of variation (CV%), was evaluated for standards with concentrations of 41.28 and 15.00 μg/l, for 2,4-DCP and PCP, respectively, analysed in six different days. Results for accuracy, checked through recovery assays, were determined by eight independent extractions of the same standards. The results of the main validation parameters are shown in Table 1.

Global uncertainty was calculated according to the EURACHEM/CITAC Guide [25] and following the considerations about its main contributions described by Ratola et al. [12]. Fig. 2 presents the variation of the global uncertainty with the standard concentration levels. The global uncertainty is 15%

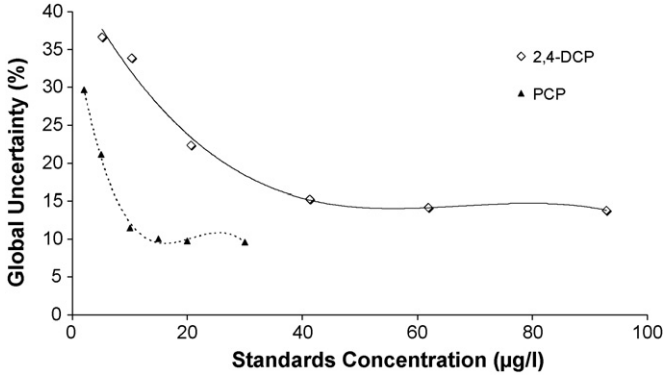

Fig. 2. Global uncertainty for the analysis of 2,4-DCP and PCP by SPME/GC-ECD.

Table 1
Main validation parameters of the analytical method (SPME/GC-ECD)

Compound	R^2	Linearity range (μg/l)	Limit of detection (μg/l)	Intermediate precision (%)	Mean reproducibility CV (%) ($n = 6$)	Mean recovery (%)
2,4-DCP	0.991	5.16–92.88	7.28	12.0 (41.28 μg/l)	26.82 ± 12.00 (41.28 μg/l)	119.90 ± 5.06 (41.28 μg/l)
PCP	0.995	2.00–30.00	1.76	1.4 (15.00 μg/l)	3.95 ± 1.40 (15.00 μg/l)	85.20 ± 8.89 (15.00 μg/l)

and 10% for concentrations higher than 40 μg/l of 2,4-DCP and 10 μg/l of PCP, respectively. For lower concentrations these values increase significantly to values up to 40% in the vicinity of the LODs. Although the sorption experiments were designed for initial concentrations much higher than the linearity range, such as 10 μg/ml, there is a need to measure extremely low concentrations in the end, given the sorption efficiencies close to 99%. This was the main reason for the validation of the analytical method within such low linearity range of concentrations. Whenever that range is exceeded, the dilution of the samples is always possible without significant increase of uncertainty.

3.2. Sorption capacity of fly ash

Fly ashes are small particles of mineral residue resulting from the combustion of ground or powdered coal in electric-generating power plants. Their chemical composition, although dictated by the nature of the burned coal and the combustion temperature, consists essentially of inorganic matter. Since the particles solidify while suspended in the exhaust gases, fly ash particles are generally spherical [26].

Table 2 presents some physical and chemical characteristics of fly ash from two thermal power plants. In fact, physical, chemical and mineralogical properties of coal fly ashes vary in a wide range depend on the nature of the burned coal. However it may be aceeptable to state that the main constituents are silica, alumina and iron oxides, which provide a charged surface prone to sorption. The amount of carbon depends on the extent of the combustion and Kao et al. [22] found that the larger the particles size the higher the carbon content. Fly ash, has a porous structure mainly consisting of macro and mesopores, with a hydrophilic surface although with a relatively low specific area when compared to GAC.

These characteristics are likely to interfere in the kind of compounds that may be easily sorbed to the surface. Low molecular organic compounds, as phenol and monochlorophenols, may exhibit an S type adsorption curve or *cooperative* adsorption, described for adsorption of phenolics on polar surfaces, meaning that adsorption becomes progressively easier as more solutes are taken up [15].

The material used in this work, although not analysed for physical and chemical structure, consisted of particles with diameters ranging from 125 to 300 μm and therefore expected to bear relatively high carbon content. Unburned carbon content generally ranges between 1% and 10%, but for higher particles size it may reach 50% [16]. Regarding cement production, one of the destinations of the fly ash, this fact will lead to loss of efficiency and poor marketability. On the other hand, those particles may be used in the sorption of organic compounds from waters.

To study the adsorption capacity of fly ash, the experiences were carried out with aqueous solutions of chlorophenols. The individual feed concentrations were 10 μg/ml for PCP and 10 and 100 μg/ml for 2,4-DCP.

A low pH was used (pH 2), to assure the presence of the protonated form of both chlorophenols. This decision was based on previous results from literature. When the pH is lower than pK_a, the chlorophenols exist in molecular form, whereas if the pH value is higher than pK_a, the dissociation degree of chlorophenols to form anions increase. The dependence of K_{ow} with pH is described in literature [27]. When pH is slightly above the pK_a, the neutral species are dominant in the octanol phase and the anionic species become dominant in the aqueous phase, which makes the distribution ratio pH-dependent [27,28]. Aksu and Yener [29] studied the adsorption of *o*-chlorophenol and *p*-chlorophenol at different values of pH in fly ash, dried activated slurry and activated carbon and concluded that an increase to the initial pH of over 1.0 led to a reduction of the sorptive capacity towards the mono-chlorophenol for all materials. Kao et al. [22] concluded that a pH increase provokes the increase of negative charges at the surface of the particles of fly ash and causes the sorption of chlorophenols in the anionic form to diminish.

The influence of the flow rate and the contact time in the sorption capacity of 2,4-DCP and PCP was studied at two levels: 4.3 and 6.6 ml/min (Fig. 3). For both compounds the column saturation was achieved earlier for higher flow rates. Comparing the sorption behaviour for different feed concentrations, in the case of 2,4-DCP, the higher concentration led to shorter column breakthrough. Nevertheless, the feed concentrations used in these experiments, as well as those reported in the studies of other authors [15,22] are not expected to happen in naturally contaminated environmental samples, where monitoring results show concentrations only up to 100 μg/l [30–32].

In the conditions of the experiments and for the same flow rate and concentration, the saturation time was achieved much later for PCP (10.0 h) than for 2,4-DCP (7.0 h). As shown in Fig. 4, the removal efficiencies were over 99% for both. The breakthrough time, the point where the outer concentration achieves 5% of the concentration of the initial solution [5], was 7.4 h for PCP and 3.8 h for 2,4-DCP, for the same operating conditions (flowrate of 4.3 ml/min and initial concentration of 10 μg/ml).

The higher affinity of fly ash towards PCP is positive as this chlorophenol is the most detected in environmental media and the strongest "acid" of the phenolic family. This result may probably be explained in terms of the differences in water solubility and log K_{ow} between the two pollutants. According

Table 2
Some physical and chemical characterization of fly ash

Particle size (μm)	Specific surface area (m^2/g)	Chemical composition (wt%)				Carbon content	Reference
		SiO_2	Al_2O_3	Fe_2O_3	CaO		
53–212 (34% mass ratio)	5–40	45–53	24	4–5	0.5–3.2	8–49	[22]
–	1.47	64.5	21.1	3.05	6.87	–	[15]

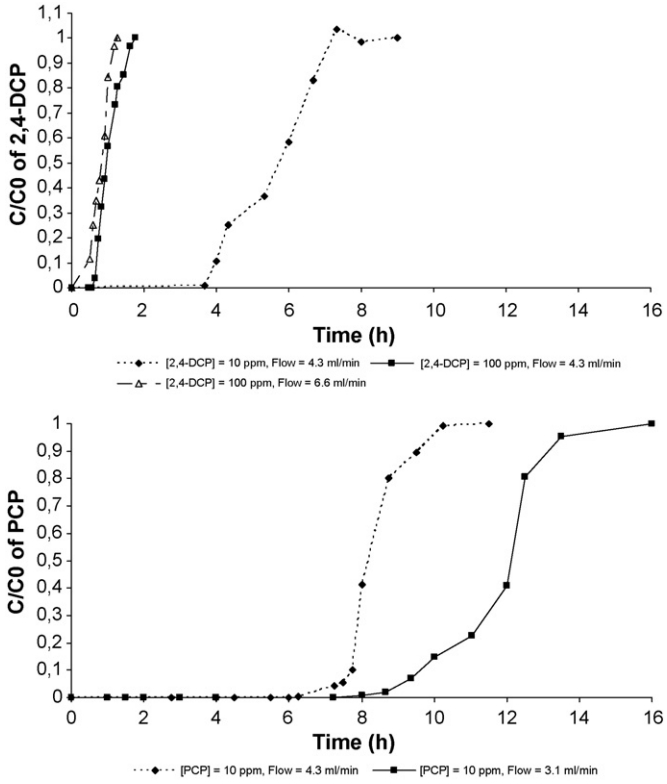

Fig. 3. Effect of flow rate and concentration in the removal of 2,4-DCP and PCP.

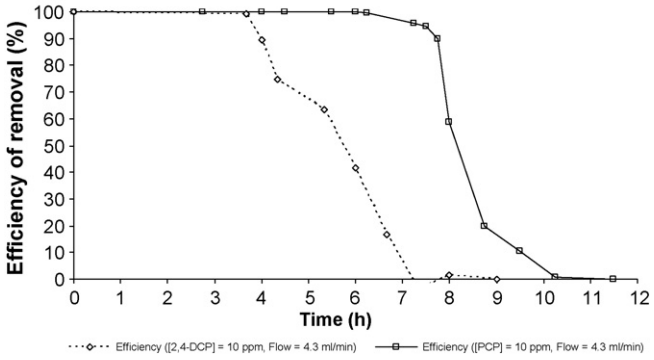

Fig. 4. 2,4-DCP and PCP removal efficiency with time.

to literature, the latter parameter is 3.23 for 2,4-DCP [33], whereas for PCP is between 5.04 [34] and 5.24 [35]. Although for different chlorophenols, qualitatively similar results were obtained by Kao et al. [22], who stated that 2-CP and 2,4-DCP competed for sorption sites, with breakthrough times of about 1 h for the former and 2 h for the latter.

Table 3 summarizes the main results of this work. The sorption capacity does not differ significantly for different flow rates and feed concentrations. The average sorption capacity for a 10 μg/ml feed, was 1.8 and 2.5 mg/g for 2,4-DCP and PCP, respectively.

Similar results were obtained for PCP sorption in pine bark [11], but using much lower feed concentrations (100 μg/l). The pine bark particles size ranged from 150 to 400 μm, the surface area was 0.74 m^2/g and the sorption capacity was 1.7 mg/g. On the other hand, for GAC removal of PCP, Mollah and Robinson [8] reported values of 157 mg/g obtained from batch experiments. Despite the expected difference in sorption capacity, if cost analysis is considered, fly ash can be a valid alternative for the treatment of wastewaters contaminated with 2,4-DCP and PCP.

Absorbed amount of chlorophenol by fly ash is affected by particle size distribution, carbon content, specific surface area of the ash and pH value of the solution [22]. As this study intends to be a feasibility one, only one class of fly ash was tested. Given the excellent results found, future work will include the determination of the physical and chemical and the check the relationship between coal fly ash characterization and process performance.

In the future and in order to implement a scale-up procedure, leaching interferences from the sorbent must be studied. Iyer [26] stated that the surface layer of the fly ash particles, contains readily leachable material, mainly metallic elements such as Mn, Ba, Co, Cr and Ni, among others, that were volatilised during coal combustion. Therefore, Wang and Wu [16] recommend the testing of the leaching behaviour of the fly ash, and that a forced extraction of the mobile substances and/or the immobilisation of the metals can be performed prior to the application of the sorbent in water systems.

Table 3
Initial set-up and results for the sorption assays in column for 2,4-DCP and PCP

	Column assay numbers				
	1	2	3	4	5
Compound	2,4-DCP	2,4-DCP	2,4-DCP	PCP	PCP
Initial feed concentration (C_0) (mg/l)	100	100	10	10	10
Flow rate (ml/min)	4.3	6.6	4.3	4.3	3.1
Mass of fly ash (g)	10	10	10	10	10
Initial concentration at the column outlet	4.04 μg/l	11.630 mg/l	96.00 μg/l	3.88 μg/l	2.60 μg/l
Initial removal efficiencies (%)	99.99	89.16	99.03	99.97	99.98
Breakthrough time (h) $C = 0.05 \times C_0$	0.7	0.2	3.8	7.4	9.1
Saturation time (h) $C = 0.95 \times C_0$	1.6	1.1	7.0	10.0	13.5
Sorbed amount until saturation (mg)	41.28	43.56	18.06	25.20	25.11
Sorption capacity (mg chlorophenols/g fly ash)	4.128	4.356	1.806	2.520	2.511

4. Conclusions

The main conclusion of the present work, is that fly ash may be a good natural and cheap sorbent for 2,4-DCP and PCP sorption from waters, reaching efficiencies of removal high enough to be considered an excellent alternative to activated carbon or other synthetic materials. The results obtained in the various experiments with a flow rate equal or slower than 4.3 ml/min, yielded removal efficiencies higher than 99.9% for both chlorophenols. The saturation time of the column decreased with the increase of the concentration of the solution. For 2,4-DCP a decrease from 7 to 1.6 h was observed when the concentration went from 10 to 100 μg/ml. However, such levels are not expected to be reached in environmental waters. Average sorption capacities were 2.5 and 1.8 mg/g for PCP and 2,4-DCP, respectively.

Fly ash exhibited more affinity towards PCP sorption comparing to 2,4-DCP, which was probably related to the higher octanol–water partition factor (K_{ow}) and the lower water solubility of the former. Therefore, fly ash may be a valid sorbent for chlorophenols in wastewater treatment, especially when cost-effective solutions are needed.

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