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Adsorption, desorption and bioregeneration in the treatment of 2-chlorophenol with activated carbon

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Abstract

This study aims to clarify the effect of activated carbon type on the extent of adsorbability, desorbability, and bioregenerability in the treatment of 2-chlorophenol. Four different activated carbon types; thermally activated and chemically activated powdered carbons (PAC), and their granular countertypes (GAC) with similar physical characteristics were used. Thermally activated carbons adsorbed 2-chlorophenol much better than chemically activated ones. However, adsorption was more reversible in the case of chemically activated ones. The use of powdered and granular activated carbon countertypes resulted in comparable adsorption and desorption characteristics. For each activated carbon type, 2-chlorophenol exhibited higher adsorbability and lower desorbability than phenol. Biodegradation of 2-chlorophenol took place very slowly when it was used as the sole carbon source in acclimated and non-acclimated activated sludges. Bioregeneration occurred only via desorption due to an initial concentration gradient and no further desorption took place due to low biodegradability. Bioregeneration of activated carbon loaded with 2-chlorophenol was not a suitable option when 2-chlorophenol was the only carbon source. It is suggested to remove 2-chlorophenol via adsorption onto activated carbon rather than applying biological treatment. Also in such cases, the use of thermally activated carbons with higher adsorption and lower desorption capacities is recommended rather than chemically activated carbons.

Keywords: Activated carbon; Activation method; Bioregeneration; 2-Chlorophenol; Irreversible adsorption

1. Introduction

The available adsorption sites become exhausted with adsorbed pollutants and the activated carbon loses its adsorptive capacity in all activated carbon applications. Therefore, activated carbon used in activated carbon filters needs regeneration. One method for the regeneration of spent activated carbon is bioregeneration. Bioregeneration is defined as the renewal of the adsorptive capacity of activated carbon by biodegradation of previously adsorbed organic matter for further adsorption [1].

In biological systems combined with activated carbon, bioregeneration is dependent on the adsorbability of the pollutant and reversibility of adsorption [2–4]. Bioregeneration requires that a compound should be initially adsorbed onto the carbon's surface where microorganisms reside. Consequently, adsorption concentration rises more than the equilibrium adsorption concentration through the decrease of bulk concentration by biological activity and the adsorbed organic matters are desorbed due to the concentration gradient between the activated carbon surface and bulk liquid [1,5,6]. The mechanism of bioregeneration of activated carbon includes subsequent biodegradation. The second theory mentioned in literature is about desorption of organic matter as a result of exoenzymatic reactions [4,6,7].

Bioregeneration is controlled by the reversibility of adsorption [1,5]. For example, activated carbons loaded with non-desorbable compounds could not be bioregenerated [5,8]. Such apparent irreversibility is commonly referred to as hysteresis or nonsingularity [9]. Desorbability or reversibility of adsorption is very much related to the activated carbon type, particularly to the activation method of the carbon [10]. There are two possible mechanisms leading to irreversible adsorption. One of them is the high energy bonding of adsorbate molecules to specific functional groups on the active sites of carbon surface resulting in covalent bonding [9,10]. This phenomenon is called chemisorption and appears to be the most logical explanation for irreversible adsorption [11]. Second is the oxidative poly-

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Table 1
Properties of activated carbons

Activated carbon	SA4	CA1	PKDA	CAgran
Physical form	Powdered	Powdered	Granular	Granular
Activation method	Thermal	Chemical	Thermal	Chemical
Apparent density (g/L)	545	370	295	225
Moisture (%)	2	11	2	12
Ash content (%)	8	2	8	3
Molasses number	525	180	–	165
Methylene blue adsorption (g/100 g)	11	29	–	29
Iodine number (mg/g)	700	–	750	–
Total surface area (BET) (m^2/g)	800	1400	850	1400
Particle size distribution	D_{10} = 3 μm, D_{50} = 29 μm, D_{90} = 161 μm	D_{10} = 7 μm, D_{50} = 28 μm, D_{90} = 75 μm	0.5% > 2 mm, 99% > 0.59 mm	1% > 1.7 mm, 2% < 0.84 mm
Porosity				
Total pore volume (cm^3/g)	0.80	1.55	1.19	1.64
Micro (Φ < 2 nm)	0.25	0.45	0.30	0.40
Meso (Φ 2–50 nm)	0.19	0.75	0.19	0.70
Macro (Φ > 50 nm)	0.36	0.35	0.70	0.54

merization of phenolic compounds onto activated carbon due to the presence of oxygen [2,10].

Aromatic compounds are major target compounds in wastewater treatment systems, since they are usually poorly degraded in conventional wastewater treatment systems. However, they can be very effectively removed by activated carbon adsorption [3]. Therefore, combination of biological treatment with activated carbon adsorption is a promising method for the removal of aromatic compounds. Particularly, bioregenerability of activated carbon facilitates their removal without increasing costs. Chlorinated phenols are an important class of aromatic pollutants that exist in industial wastewaters because of their wide use in the production of preservers, pesticides and biocides. If they are not treated properly in industial wastewater treatment plants, their strong toxicity, persistence in the environment and suspected carcinogenecity may pose serious environmental problems [12].

There is a lack of knowledge in literature about the effect of both carbon activation type and physical form (PAC or GAC) on adsorbability, reversibility of adsorption and bioregeneration. Hence, this study aims to clarify the effect of activated carbon type on the extent of adsorbability and desorbability of aromatic compounds and bioregeneration of activated carbon. For this purpose, two different PACs; thermally activated Norit SA4 and chemically activated Norit CA1, and their granular countertypes with similar physical characteristics, thermally activated Norit PKDA and chemically activated Norit CAgran were used for determination of the extent of adsorbability, reversibility of adsorption and bioregeneration. 2-Chlorophenol was used as the model compound because chlorophenols are known to be well adsorbable on activated carbon [13], but less biodegradable than phenol [14] which was usually used in studies regarding bioregeneration [4,9,15]. Adsorbability, desorbability and biodegradability of 2-chlorophenol was compared with phenol which was used as a model compound in previous studies [3,4]. This will enable us to investigate the effect of the target aromatic compound on bioregenerability of different activated carbon types.

2. Materials and methods

2.1. Activated carbon characteristics

Norit SA4 and its granular countertype PKDA are steam activated carbons. Norit CA1 and its granular countertype CAgran are produced by chemical activation using the phosphoric acid process. Both carbons (CA1 and CAgran) have a very open (macro/meso) pore structure which results in a high adsorption capacity for higher molecular weight organics and an effective regeneration. The characteristics of the four commercial carbon types can be seen in Table 1. All activated carbon samples were obtained from the Norit Company, the Netherlands. The micro- and mesopore volumes, dominating the adsorptive capacities, do not differ very much between the powdered and granular countertypes (Table 1). However, in the production of powdered carbons, the larger macropores are milled away, resulting in significant differences compared to the granules. It should also be noted that most of the total surface area is found in the micropores. Typical surface area data for activated carbon are: 1000 m^2/g in micropores, 10–100 m^2/g in mesopores and 1 m^2/g in macropores. Therefore, particularly macropores make small contribution to the surface area.

2.2. Adsorption studies

The first step in the experimental work was the determination of the adsorbabilities of 2-chlorophenol for each activated carbon type in batch adsorption tests. Adsorption studies were performed in 100 mL flasks shaken at 140 rpm and 25 °C. For determination of the adsorption isotherms, different masses of activated carbon (100–1600 mg/L) were contacted with fixed concentrations of 2-chlorophenol (200 mg/L) and the mixture was agitated until reaching equilibrium. The time required for reaching an equilibrium 2-chlorophenol concentration is the equilibrium time for adsorption. The equilibrium time was determined for estimating the shaking time required for adsorption isotherm tests. For this purpose, 2-chlorophenol values in

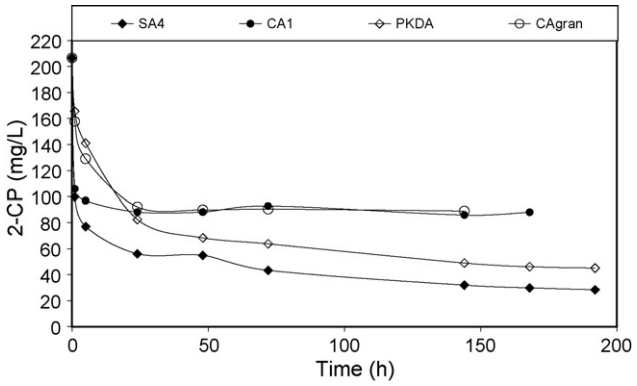

Fig. 1. 2-Chlorophenol profiles during adsorption at an initial 2-CP concentration of 207 mg/L and 1 g/L of activated carbons SA4 (powdered, thermally activated), CA1 (powdered, chemically activated), PKDA (granular, thermally activated) and CAgran (granular, chemically activated).

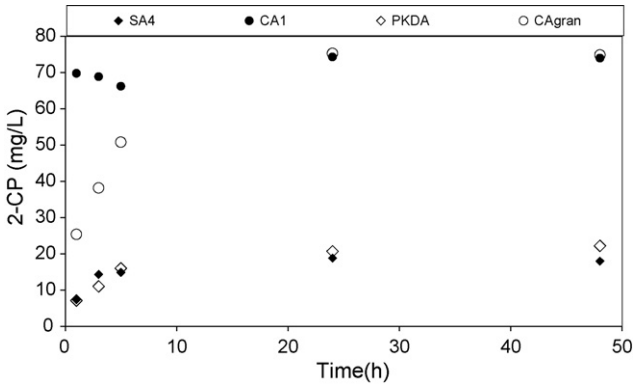

Fig. 2. 2-Chlorophenol profiles during desorption at a dose of 2 g/L of activated carbons SA4 (powdered, thermally activated), CA1 (powdered, chemically activated), PKDA (granular, thermally activated) and CAgran (granular, chemically activated).

250 mL stoppered flasks with different activated carbon concentrations were analyzed with respect to time until reaching equilibrium concentrations. Equilibrium time was described as the time when the 2-chlorophenol concentration reached a constant value, and was determined as 7 days for SA4 and PKDA, and 1 day for CA1 and CAgran as seen in Fig. 1. Initial and final equilibrium concentrations in the adsorption flasks were measured and used for the construction of adsorption isotherms.

2.3. Desorption studies

The second step in the experimental work was the determination of the desorbabilities of 2-chlorophenol for each activated carbon type in batch desorption tests. Desorption studies were performed in 100 mL flasks shaken at 140 rpm and 25 °C. Desorption of the target compound was conducted to determine the degree of reversibility of adsorption for each activated carbon. Desorption isotherms were constructed according to a batch-displacement technique [2,9,10]. A known weight of activated carbon (2000 mg/L) was initially contacted with a known concentration of phenol and was agitated until equilibrium was reached as in adsorption batches. After adsorption equilibration, the supernatant was removed by centrifugation and the sorbate concentration in the supernatant was measured. The supernatant was replaced by distilled water. Desorption of 2-chlorophenol from activated carbon occurred until equilibrium. Desorption equilibrium was determined as 24 h for each carbon type as seen in Fig. 2. Upon equilibration, the concentration in the liquid phase was measured. Desorption was conducted successively until 2-chlorophenol concentration in the supernatant was under the detection limit (<0.1 mg/L). A succession of desorption steps produced a desorption isotherm. After each successive desorption step, the new hypothetical activated carbon loading for the following desorption step (q_i) was calculated by substracting the amount of desorbed 2-chlorophenol from the activated carbon loading at the beginning of the desorption step as shown by Eq. (1):

$$q_i = \frac{X_a - \sum (X_d)_i}{M} \quad (1)$$

where X_a is the initial 2-CP loading on the carbon (mg), X_d the mass of 2-CP desorbed after each *i*th desorption step (mg) and M is the mass of activated carbon used in each desorption experiment (g).

2.4. Biodegradation and bioregeneration studies

Biodegradability and bioregenerability of 2-chlorophenol were studied in simultaneously operated batch reactors. The experimental set-up consisted of 2 L plexiglass batch reactors provided with four baffles to prevent vortex formation and thereby obtain proper mixing conditions. The reactors were placed in a hood and were surrounded by a water jacket for temperature control. The tops of the reactors were closed by conic covers. Spent air was removed by a hose and passed through a gas-wash bottle which contained water or methylene chloride. Air was supplied by a compressor to provide sufficient oxygen. Mixing was obtained by magnetic stirrers instead of excessive aeration to prevent volatilization of 2-chlorophenol. The temperature in the reactors ranged between 22 and 25 °C, and dissolved oxygen concentrations were always above 4 mg/L. A mineral salts solution was prepared and added to the reactors to provide the necessary nutrients for microorganisms. The stock mineral salts solution was composed of 5000 mg/L $(NH_4)_2SO_4$, 2000 mg/L KH_2PO_4, 2000 mg/L K_2HPO_4, 2000 mg/L $MgSO_4{\cdot}7H_2O$, 500 mg/L $CaSO_4{\cdot}2H_2O$, 200 mg/L $FeSO_4{\cdot}7H_2O$, and 3000 mg/L $NaHCO_3$. This solution was suitable for a wastewater with a COD of 10,000 mg/L and was diluted in 2-chlorophenol biodegradation and bioregeneration reactors in proper amounts to compensate for the nutrient requirement. Throughout the study, 2-chlorophenol was used as the sole carbon source in biodegradation and bioregeneration reactors.

In batch bioregeneration studies, activated carbon was initially loaded with 2-chlorophenol (loading amounts can be seen in Table 2) as in adsorption experiments. The supernatant was removed by centrifugation. Then, by measuring the amount of 2-chlorophenol remaining in the supernatant, the loading on activated carbon was calculated. Loaded activated carbon was mixed with 1 L activated sludge and a proper

Table 2
Main characteristics of biodegradation and bioregeneration experiments with 2-chlorophenol (2-CP) as the target compound

Run	Reactor type	Activated carbon	Biomass	Carbon dose (mg/L)	Initial 2-CP loading (mg /g)	Initial bulk 2-CP (mg/L)	Initial MLSS (mg/L)
1a	Biodegradation	–	Non-acclimatted	–	–	384	1200
1b	Bioregeneration	SA4	Non-acclimatted	2000	212.5	–	1200
2a	Biodegradation	–	Acclimated	–	–	139.6	550
2b	Bioregeneration	SA4	Acclimated	2000	74.5	–	550

SA4: powdered, thermally activated.

amount of mineral salts was added. The biodegradation reactors were operated in parallel to the bioregeneration reactors. The control biodegradation reactor was fed with an amount of 2-chlorophenol (Table 2) equal to the amount of 2-chlorophenol loading on the activated carbon in the bioregeneration reactor. Also a proper amount of mineral salts and 1 L activated sludge were added to the biodegradation reactors as in bioregeneration reactors. The operational conditions in biodegradation and bioregeneration reactors in seven runs are shown in Table 2.

In biodegradation-bioregeneration run 1 with 2-chlorophenol, non-acclimated biomass was used. This biomass was obtained from a laboratory-scale batch activated sludge reactor which was semi-continuously fed with a synthetic wastewater at a daily loading rate of 500 mg COD/L day as in other studies [16,17]. In run 2 with 2-chlorophenol acclimated biomass was used. Before starting run 2, biomass was obtained from the semi-continuously fed batch activated sludge reactor mentioned above. This biomass was acclimated by feeding with phenol and 2-chlorophenol. Acclimation in a batch reactor was started with 200 mg/L phenol as the only carbon source. 2-Chlorophenol in mixture was increased gradually up to 140 mg/L (as phenol was decreased to 80 mg/L) in a period of 40 days. Batchwise feeding was repeated every 2–3 days. During this acclimation period, at the end of a 48 h aeration period, almost all of the phenol and 2-chlorophenol were removed and biological activity was determined by oxygen uptake rates as high as 20 mg/L h.

2.5. Analysis

The analytical methods used in the experiments followed the *Standard Methods* [18]. COD analyses were carried out by the closed reflux method. The soluble COD (SCOD) of the final liquids were determined after filtering through 0.45 μm Millipore filters to remove activated carbon particles. 2-Chlorophenol concentrations of the filtered samples were measured colorimetrically according to the 4-amino antipyrene method. Mixed liquor suspended solid (MLSS) analysis was carried out by drying the residue on 0.45 μm Millipore filters for one hour at 103 °C. Chloride concentrations were determined according to the argentometric method. Oxygen uptake rates (OUR) in the activated sludge reactors were measured automatically in terms of mgO_2/L h by WTW Microprocessor Oximeter Oxi 3000.

3. Results and discussion

3.1. Adsorption studies

The adsorption isotherm data for 2-chlorophenol are plotted in Fig. 3. The adsorption isotherm data was found to fit the Freundlich equation below:

$$q = K_f C^{1/n} \quad (2)$$

q is the adsorption capacity of the activated carbon (mg phenol adsorbed/g activated carbon), C the equilibrium phenol concentration (mg/L), and K_f and $1/n$ are the Freundlich constants (Freundlich exponent and slope).

The Freundlich adsorption isotherm constants obtained by regression analysis for 2-chlorophenol are shown in Table 3.

The K_f value, which is an indicator of adsorption capacity, was found to be higher for the thermally activated carbons compared to the chemically activated carbons (Table 3). The thermally activated carbons were obviously better adsorbers for 2-chlorophenol as in the case of phenol [3]. Smaller K_f values obtained for the chemically activated carbon reveal that these carbons are not very suitable for adsorption of 2-chlorophenol. Lower $1/n$ values for the thermally activated carbons indicate that an increase in the activated carbon dose was more effective for thermally activated carbons rather than in the case of chemically activated carbons with steeper isotherm curves (Fig. 3). This effect can be seen more clearly in Fig. 4, which illustrates

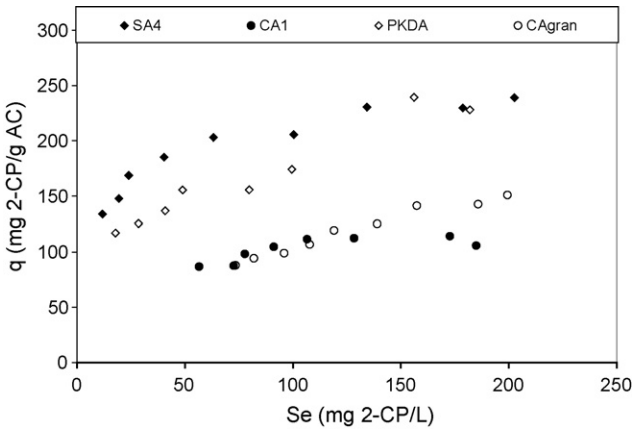

Fig. 3. 2-Chlorophenol adsorption isotherms for activated carbons SA4 (powdered, thermally activated), CA1 (powdered, chemically activated), PKDA (granular, thermally activated) and CAgran (granular, chemically activated).

Table 3
Freundlich isotherm constants for 2-chlorophenol adsorption

Carbon type	Physical form	Activation method	K_f [(mg/g) (L/mg)$^{1/n}$]	1/n	R^2
Norit SA4	Powdered	Thermal	86.5	0.195	0.96
Norit CA1	Powdered	Chemical	13.6	0.406	0.97
Norit PKDA	Granular	Thermal	60.4	0.227	0.93
Norit CAgran	Granular	Chemical	8.2	0.553	0.98

the effect of carbon dose on equilibrium bulk 2-chlorophenol concentrations.

The diffence in adsorption capacities between the thermally and chemically activated carbons was certainly caused by their activation method, which eventually results in different surface characteristics. Equilibrium pH values obtained in adsorption isotherm studies pointed out that the surface characteristics of the two thermally activated carbons SA4 and PKDA (pH between 7.1 and 8.4 depending on the carbon dose) were basic, and surface characteristics of the two chemically activated (with phosphoric acid) carbons CA1 (pH between 3.9 and 5.5) and CAgran (pH between 5.4 and 6.9) were acidic. Chemical treatment of activated carbon increases the quantity of acidic surface functional groups, whereas thermal treatment results in a decrease in the number of acidic surface functional groups [19]. Also in the previous study with phenol [3] the inverse relationship between adsorption capacity and surface acidity had been investigated.

Fig. 4 shows that the powdered and granular countertypes (SA4–PKDA and CA1–CAgran) do not differ very much in terms of 2-chlorophenol adsorption, although powdered carbons exhibited slightly better adsorption. Considering that the granular activated carbons have higher macropore volumes than their powdered countertypes (Table 1), the similar adsorption characteristics for both powdered–granular countertypes shows that 2-chlorophenol adsorption on the macropores was much less significant compared to meso- and micropores as in the case of phenol. The lesser adsorption of 2-chlorophenol on macropores was mainly due to very low surface area in macropores compared with micro and mesopores. During the first few hours of adsorption (Fig. 1) before reaching adsorption equilibrium, the powdered activated carbons (SA4 and CA1) adsorbed more 2-CP compared to their granular countertypes (PKDA and CAgran). Adsorption was faster onto PACs, probably due to higher intraparticle diffusivity through PAC compared to GAC with a higher diameter.

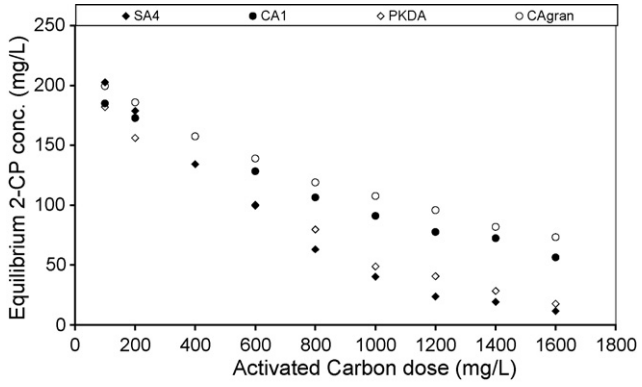

Fig. 4. Effect of activated carbon dose on equilibrium 2-chlorophenol concentrations at an initial 2-chlorophenol concentration of 200 mg/L (SA4: powdered, thermally activated; CA1: powdered, chemically activated; PKDA: granular, thermally activated; CAgran: granular, chemically activated).

The isotherm curves tended to reach saturation as the equilibrium concentrations increased (Fig. 3). The theoretical Langmuir equation was also tested for the adsorption isotherms. Langmuir expression is defined as in Eq. (3):

$$q = \frac{Q^0 bC}{1 + bC} \tag{3}$$

in which C is the measured concentration in solution at equilibrium, Q^0 the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface, q the number of moles of solute adsorbed per unit weight at concentration C, and b is the constant related to the energy of adsorption (Table 4).

The essential characteristics of the Langmuir equation can be expressed [20] in terms of a dimensionless separation factor R_L which is defined by the following equation:

$$R_L = \frac{1}{1 + Q^0 \times b \times C_0} \tag{4}$$

where C_0 is the initial 2-chlorophenol concentration (g/L). The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L (dimensionless separation factor) values for each activated carbon (Table 4) were found to be between 0 and 1 indicating a favorable adsorption of 2-chlorophenol on each carbon type. The adsorption of 2-chlorophenol on two thermally activated carbons was found to be more favorable and closer to the irreversible adsorption edge of $R_L = 0$ as evidenced from relatively lower R_L values [20]. This finding is in agreement with the results of subsequent desorption studies. The R_L values for 2-chlorophenol (Table 4) were lower than the ones for phenol which were 0.268 for SA4, 0.826 for CA1, 0.528 for PKDA and 0.731 for CAgran [3]. This finding indicates that 2-chlorophenol is better adsorbed than phenol and adsorption of 2-chlorophenol is more irreversible than adsorption of phenol.

Table 4
Langmuir adsorption isotherm constants for 2-chlorophenol adsorption

Carbon type	Q^0 (mg/g)	b (L/mg)	R^2	R_L
Norit SA4	250.0	0.075	1.00	0.191
Norit CA1	140.8	0.029	0.98	0.556
Norit PKDA	270.3	0.026	0.95	0.409
Norit CAgran	256.4	0.007	0.98	0.723

Table 5
Freundlich isotherm constants for 2-chlorophenol desorption

Carbon type	Physical form	Activation method	K_f [(mg/g) (L/mg)$^{1/n}$]	1/n	R^2
Norit SA4	Powdered	Thermal	169.2	0.035	0.97
Norit CA1	Powdered	Chemical	39.3	0.258	0.99
Norit PKDA	Granular	Thermal	155.4	0.032	0.95
Norit CAgran	Granular	Chemical	35.4	0.286	0.99

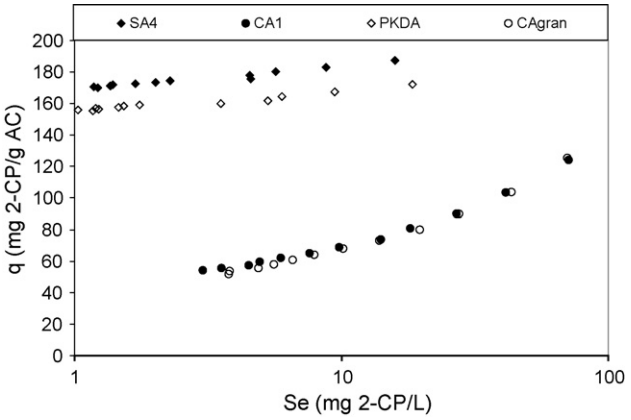

Fig. 5. 2-Chlorophenol desorption isotherms for activated carbons SA4 (powdered, thermally activated), CA1 (powdered, chemically activated), PKDA (granular, thermally activated) and CAgran (granular, chemically activated).

3.2. Desorption studies

The Freundlich type isotherm equation was applied to desorption data (Fig. 5) for each carbon type with satisfactory correlations. Desorption Freundlich isotherm constants are shown in Table 5. High K_f values for thermally activated carbons showed that 2-CP loading was still high after desorption for these carbons. These findings showed that the desorbability of 2-chlorophenol from thermally activated carbons was lower. Desorption capacities were higher for chemically activated carbons CA1 and CAgran as in the previous phenol desorption studies [3]. Also lower 1/n values in the case of thermally activated carbons (SA4 and PKDA) indicated that desorption was more difficult from these carbons and adsorption was highly irreversible. Higher 1/n values obtained for the chemically activated carbons (CA1 and CAgran) indicated that adsorption was more reversible for these carbons. These findings are also supported by Table 6, which shows the total adsorption and desorption efficiencies of 2-chlorophenol for each type of activated carbon.

The isotherm results and the adsorption-desorption efficiencies shown in Table 6 reveal that adsorption of 2-chlorophenol was highly irreversible for thermally activated carbons, and highly reversible for chemically activated ones as in the case of phenol [3]. The previous adsorption studies with phenol had resulted in high differences between the thermally activated carbons and chemically activated ones in terms of adsorption efficiency [3]. In the present study with 2-chlorophenol this difference also existed but it was smaller (Fig. 4). For all carbon types, 2-chlorophenol was adsorbed with a higher efficiency (Table 6) compared to phenol (63.1% for SA4, 50.9% for PKDA, 31.5% for CA1, 32.0% for CAgran) [3]. This difference was higher in the case of chemically activated carbons. On the other hand, reversibility of adsorption was less in the case of 2-chlorophenol (Table 6) compared to phenol (20.3% for SA4, 25.8% for PKDA, 86.6% for CA1, 87.5% for CAgran) [3]. The higher adsorption capacity for 2-chlorophenol was attributed to less polarity and solubility of chlorinated phenols due to substitution of chloride group. Also larger molecules of the chlorinated phenols tend to be more strongly adsorbed than phenol [2]. In addition, *ortho*-substituted phenols are more irreversibly adsorbed compared to phenol or *para*- and *meta*-substituted phenols [11].

Reversibility of adsorption can be expressed [9] as a degree of hysteresis (w) by using Eq. (5):

$$w\,(\%) = \left(\frac{1/n_{ads}}{1/n_{des}} - 1\right) \times 100 \tag{5}$$

where $1/n_{des}$ and $1/n_{ads}$ are the desorption and adsorption intensities obtained from Freundlich isotherms, respectively. The 1/n value in desorption isotherms being smaller than the 1/n value in adsorption isotherms implies that desorption is slower [9] or more difficult than adsorption. The degree of hysteresis is an indicator for adsorption reversibility which bases on the difference between the adsorption and desorption intensities. Higher degrees of hysteresis were calculated for the thermally activated carbons (Table 6). This showed that, chemically activated carbons should be preferred for bioregeneration of activated carbon although their adsorption efficiencies are lower. However, even in the case of chemically activated carbons reversibility of adsorption was below 68% (Table 6).

Table 6
Adsorption and desorption efficiencies of 2-chlorophenol for each activated carbon type

Carbon type	Carbon concentration (mg/L)	Adsorption efficiency (%)	Desorption efficiency (%)	Irreversible adsorption (%)	Degree of hysteresis, w (%)
Norit SA4	2000	80.3	12.9	87.1	459
Norit CA1	2000	65.6	66.0	34.0	58
Norit PKDA	2000	74.5	14.4	85.6	858
Norit CAgran	2000	66.0	67.7	32.3	93

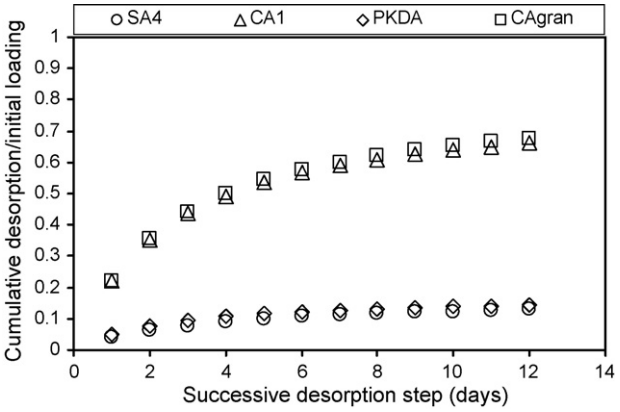

Fig. 6. Cumulative desorption of 2-chlorophenol from loaded activated carbons at the end of each successive desorption step (SA4: powdered, thermally activated; CA1: powdered, chemically activated; PKDA: granular, thermally activated; CAgran: granular, chemically activated).

The desorption equilibrium curves (Fig. 2) showed that during the first 5 h of desorption, more 2-CP was desorbed from PACs compared to their GAC countertypes. Hence, desorption was faster from PACs just as adsorption was faster onto PACs. The differences between PAC and GAC results can be attributed to the effect of particle size. Since GAC particles are much larger than PAC particles, diffusive transport into GAC is slower [15]. Fig. 6 shows the cumulative desorbed 2-CP at the end of each equilibrium desorption step and reflects that comparable desorption is achieved from PAC-GAC countertypes. However, slightly higher desorption (Fig. 6) was obtained for the GACs compared to their powdered countertypes due to their more macroporous structure (Table 1). The differences in cumulative desorption between the powdered and granular countertypes were statistically significant ($p < 0.01$ at 95% confidence level). Since 2-chlorophenol was mainly adsorbed on micro- and mesopores, the difference in macropore volume of PAC and GAC countertypes resulted in only a small difference in desorption as in the case of phenol [3].

3.3. Biodegradation and bioregeneration studies

3.3.1. The use of non-acclimated biomass

Initially, non-acclimated biomass obtained from the semi-continuously fed batch reactor, was used for biodegradation in run 1a and for bioregeneration in run 1b (Table 2). After 24 h aeration, no 2-chlorophenol removal was observed in the biodegradation reactor of run 1 (Fig. 7a). After 72 h of aeration, the decrease in the initial 2-chlorophenol concentration (384 mg/L) was only 13%, and the decrease in the initial COD concentration (621 mg/L) was only 8%. Between 3rd and 10th days of aeration, 2-chlorophenol and COD concentrations in the biodegradation reactor did not change much. But at the end of 21 days aeration, the decrease in initial 2-chlorophenol concentration was 16%, and decrease in COD was 14% (Fig. 7a). These results showed that, at such high initial 2-chlorophenol concentrations (384 mg/L), biodegradation of 2-chlorophenol by non-acclimated biomass was not possible in the absence of a growth substrate. Removal was very small and slow (Fig. 7a). This very

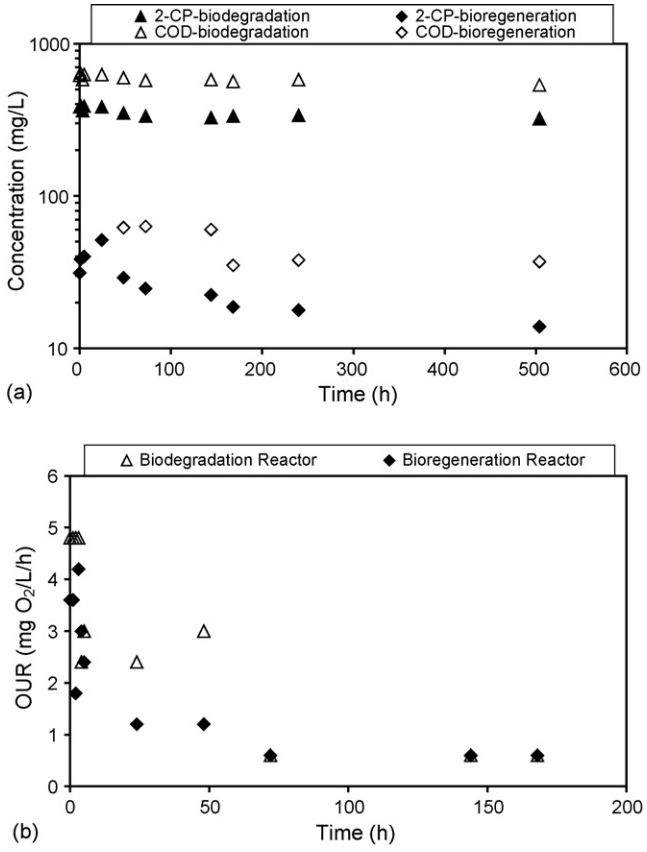

Fig. 7. (a) 2-Chlorophenol and COD profiles and (b) OUR profiles in biodegradation run 1a and bioregeneration run 1b with 2-chlorophenol when non-acclimated biomass and SA4 carbon were used.

small metabolic activity was also concluded from low oxygen uptake rates in Fig. 7b which were always below 5 mg/L h. 2-Chlorophenol and COD profiles in run 1a were almost parallel to each other (Fig. 7a), because the measured COD/2-CP ratio was almost constant (1.66 ± 0.06). This value is very close to the theoretical COD equivalent (1.62) of 2-chlorophenol. This suggested that a small amount of 2-chlorophenol was almost completely mineralized or was removed by sorption to activated sludge. Also further gas chromatographic measurements showed that no phenolic by-product was formed during biodegradation of 2-chlorophenol. During mineralization or oxidation of 2-chlorophenol, dechlorination is an expected mechanism which would lead to an increase of chloride in the bulk solution. Therefore, chloride measurements were performed to determine dechlorination.After 21 days aeration, a 37 mg/L increase in the chloride ion concentration was measured due to dechlorination of 2-chlorophenol. This revealed that 2-chlorophenol was partly removed by biological activity, although very slowly.

In the bioregeneration reactor in run 1b, 52 mg/L 2-chlorophenol was desorbed from the loaded activated carbons during the first 24 h of aeration. This value decreased to 14 mg/L at the end of 21 days aeration (Fig. 7a). This also showed that desorbed 2-chlorophenol was biodegraded very slowly. Chloride accumulation of 19 mg/L in the bioregeneration reactor also showed that only a small amount of 2-chlorophenol was dechlorinated.

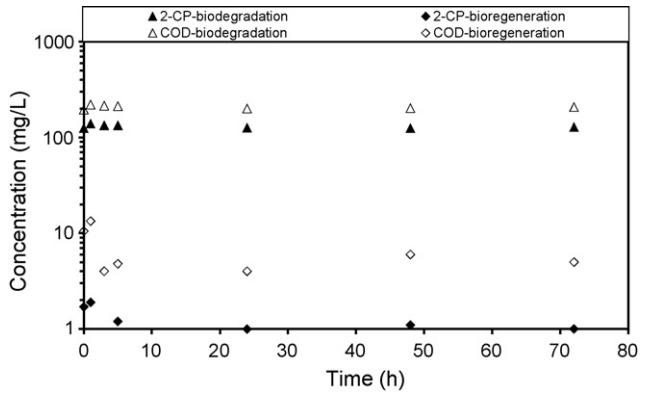

Fig. 8. 2-Chlorophenol and COD profiles in biodegradation run 2a and bioregeneration run 2b with 2-chlorophenol when acclimated biomass and SA4 carbon were used.

Efficiency of bioregeneration was approximately determined using the Freundlich adsorption isotherm constants for 2-chlorophenol as explained in a previous study [4]. During bioregeneration, the amount of adsorbed substrate (mg) left on activated carbon (Q) was determined by Eq. (6):

$$Q(t) = KC_e(t)^{1/n} \quad (6)$$

where $C_e(t)$ is the 2-chlorophenol concentration in the bulk liquid (mg/L) at bioregeneration time t. It was found that 12.3% of the adsorbed 2-chlorophenol was desorbed in the bioregeneration reactor at the end of 24 h aeration. This ratio is very close to the desorbability efficiency of SA4 for 2-chlorophenol in the absence of biological activity (Table 6). During the remaining 20 days of aeration, the desorbed 2-chlorophenol was biodegraded very slowly (Fig. 7a). Very low OUR values (Fig. 7b) and low chloride formation (19 mg/L) showed that no further desorption took place during this period. Thus, under the operating conditions of run 1b, bioregeneration occurred only due to the initial concentration gradient between the loaded activated carbon and the bulk liquid. Bioregeneration due to exoenzymatic reactions did not seem to be plausible when 2-chlorophenol was the only target compound although in a previous study bioregeneration with phenol-loaded thermally activated carbons had indicated exoenzymatic bioregeneration [4]. The low bioregeneration in the case of 2-chlorophenol can be attributed to both the low desorbability from the carbon SA4 and the slow biodegradation of 2-chlorophenol by the non-acclimated biomass.

3.3.2. The use of acclimated biomass

Run 2a (Table 2), in which acclimated biomass was used and 2-chlorophenol was the only carbon source, also resulted in no significant biodegradation (Fig. 8). The low biodegradability was also ascertained by the OUR values below 5 mg/L h. However, 2-chlorophenol had been removed completely in the presence of phenol during the acclimation phase. Kim and Hao [21] extensively investigated the cometabolic degradation of monochlorophenols in the presence of phenol. In that study, biodegradability of chlorophenols decreased as the initial phenol/chlorophenol concentration ratios decreased indicating that chlorophenols were only removed by a cometabolic pathway in the presence of a sufficient amount of phenol.

In run 2b, activated carbon was not fully loaded with 2-chlorophenol. The purpose was to decrease the amount of 2-chlorophenol in the reactors in order to decrease the inhibitory effects of 2-chlorophenol. The 2-CP loading on SA4 carbon was about one third of the loading in run 1b (Table 2). This resulted in much lower desorption in the bioregeneration reactor (Fig. 8). In addition to low desorption in the bioregeneration reactor, biodegradation was very slow. Therefore, in the case of 2-chlorophenol, bioregeneration did not occur even with the acclimated biomass. In the previous study performed with phenol [4], phenol was highly biodegradable even when the same non-acclimated biomass was used as in this study, and all four types of activated carbon were successfully bioregenerated to some extent (58.1% for SA4, 66.6% for PKDA, 93.6% for CA1, 84.8% for CAgran). The results of this study and previous results [4] showed that the type of the target compound is very important for the extent of bioregeneration.

4. Conclusions

The results showed that thermally activated carbons were better 2-chlorophenol adsorbers than chemically activated ones. However, desorbability of 2-chlorophenol was higher in the case of chemically activated carbons compared to thermally activated carbons. Both adsorbability and its reversibility were dependent on the carbon activation method rather than the physical form. Biodegradation and bioregeneration studies showed that biodegradation of 2-chlorophenol alone was very difficult and very slow. Hence, bioregeneration of activated carbon did not occur under the conditions of this study when 2-chlorophenol was the sole carbon source.

When the adsorption and desorption results of this study were interpreted together with those of a previous study on phenol [3], 2-chlorophenol was adsorbed better than phenol. However, its desorption was less and hence its bioregeneration was more difficult. In the treatment of 2-chlorophenol by adsorption processes, which are not going to be combined with biological ones, thermally activated carbons should be preferred. However, in biological processes combined with activated carbon adsorption, chemically activated carbons could be preferred to increase the service life of activated carbon considering bioregeneration of activated carbon. But, it should be noted that this statement is true only if the target aromatic compound can be biologically degraded as in the case of phenol [4]. 2-Chlorophenol was not sufficiently biodegraded in the absence of a growth substrate such as phenol. Therefore, bioregeneration of activated carbon loaded totally with 2-chlorophenol will not be a realistic application. It can be deduced that the type of the target compound was very important on the extent or occurrence of bioregeneration Therefore, for the treatment of 2-chlorophenol alone, thermally activated carbons should be preferred without the need of a combination with biological processes.

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