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Research Article

Liquid Phase Adsorption of Phenol and Chloroform by Activated Charcoal

The adsorption equilibria of phenol and chloroform from aqueous solutions on four different particle sizes of activated charcoal were examined at different initial concentrations of the adsorbates. The experimental data were analyzed using the Langmuir and Freundlich isotherm models. Both models fit the adsorption data for phenol. The Freundlich model more accurately fits the adsorption data for chloroform than the Langmuir model. The sorption kinetics for phenol was studied using pseudo-first-order and second-order kinetic models. The adsorption data better fit the second-order model. The results of the study show that activated charcoal can be used as potential adsorbent for phenol and chloroform in drinking water.

Keywords: Charcoal, Chloroform, Phenol, Adsorption

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1 Introduction

The final step of water purification is disinfection, a procedure for protecting water during distribution against external contamination and regrowth of bacteria. Disinfection by chlorination is the most important step in water treatment for public supply as chlorine remains in water as long as it is not consumed. However, chlorine reacts with natural organic matter (NOM) present in water and produces a number of by-products with harmful long-term effects [1–4].

Humic substances are a major fraction of NOM which is very common in surface waters. Fulvic and humic acids (HAs) are well known to be major precursors for the formation of trihalomethane compounds and other disinfection by-products [5–10]. Humic acids (HAs) contain many organic functional groups such as carboxyl, phenol, hydroxyl, amine and quinone groups [11]. Trihalomethanes (THMs), i.e., bromoform, dichlorobromomethane, dibromochloromethane, and chloroform, are the major by-products of chlorination [12]. They are recognized as potentially hazardous and carcinogenic substances [13, 14]. Chloroform is found in all chlorinated tap waters. This compound is formed by the reaction of chlorine with organic precursors, typically naturally occurring substances like humic acids [8–10, 14, 15]. Humic acids (HAs) are

natural polyelectrolytes widely occurring in soil and natural waters as a result of the decay of plants and animals and other biological activities of microorganisms in the environment [8, 16, 17]. HAs largely influence the formation of THMs rather than HAAs (haloacetic acids), and also higher yields of THMs resulted from the chlorination of HS with higher phenolic content [9]. On the other hand, phenol belongs to a group of common environmental contaminants. This toxic weak acid causes an unpleasant taste and odor even at low concentrations in water [18–23]. Activated carbon adsorption has been recommended by the USEPA as one of the best available technologies (BAT) in the removal of organic compounds [23]. Granular activated carbon (GAC) has been of a special interest due to its ability to remove a wide range of compounds such as odor, color causing compounds, NOM, THMS, HAAs and other toxic compounds [24–29]. Chloroform can be adsorbed by activated carbon [30]. The objective of this research was to evaluate the removal efficiency of granular activated charcoal for chloroform and phenol. Adsorption batch and kinetic studies were performed.

2 Materials and Methods

All reagents and chemicals were purchased from Merck. Stock solutions were prepared by dissolving the desired amount of phenol and chloroform in double distilled water. The adsorbent was commercial activated charcoal (0.2–0.6 mm) purchased from POCH SA (Poland). The specific surface area of the carbons was evaluated from the N_2 isotherms by applying the Brunauer, Emmett and Teller (BET) equation: it was $800 \text{ m}^2\text{g}^{-1}$.

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2.1 Sorption Procedure

2.1.1 Phenol

Sorption studies were performed by the batch technique to obtain rate and equilibrium data. For isotherm studies, a series of 500-mL Erlenmeyer flasks, each containing 100 mL of adsorbate (phenol) solution of different concentrations (20, 30, 40, 50, 60 ppm) and a definite amount of adsorbent (0.1 g), and another series of 50-mL Erlenmeyer stoppered conical flasks, each containing 50 mL of adsorbate (chloroform) solution of different concentrations (0.5, 1, 2, 5, 10, 15 ppm) and a definite amount (0.05 g) of adsorbent, were used. The contact time was selected on the basis of preliminary experiments, which demonstrated that equilibrium for phenol was established within 24 h and for chloroform within 10 h. After this period the solutions were filtered. Phenol was determined spectrophotometrically ($\lambda_{\max} = 211$ nm) and chloroform was determined according to the liquid-liquid extraction gas-chromatographic method. According to this method, 10 mL of the sample was extracted with 2 mL of *n*-pentane by shaking for one minute in a separation funnel of 25 mL volume. The sample and pentane were added to a funnel by syringes of 10 mL and 2 mL volume, respectively, to avoid the loss of chloroform during sampling. Phase separation occurred within two minutes and the upper phase was collected in 2-mL vials with PTFE septa screw caps. Samples of 1 μ L volume were injected into a gas chromatography (GC) column by an autosampler. The GC was equipped with an electron capture detector.

2.1.2 Chloroform

A series of 50-mL glass stoppered Erlenmeyer flasks containing 50 mL of adsorbate (chloroform) solution of varied concentrations (0.5, 1, 2, 5, 10, 15 ppm) and a definite amount (0.05 g) of adsorbent (granular activated charcoal) were used, and this series was repeated for each particle size of activated charcoal (A, B, C, D). The Erlenmeyer flasks containing adsorbate solution and adsorbent were placed in an electric shaker. The contact time was selected on the basis of preliminary experiments, which demonstrated that equilibrium was established within 10 h. After this period the solution was filtered, 10 mL of the filtrate was placed in a separation funnel and 2 mL of *n*-pentane was added. The mixture was shaken for one minute, phase separation occurred within two minutes and the upper phase was collected in 2-mL vials with PTFE septa screw caps. Samples of 1 μ L volume were injected into a gas chromatography (GC) column by an autosampler. To quantify the evaporation loss of chloroform, control experiments were performed following the same procedure except for the absence of commercial activated charcoal. The assay of chloroform was performed on a gas chromatography Shimadzu model (2010) equipped with an electron capture detector and a capillary column.

2.2 Kinetic Studies

The adsorption kinetics of the adsorbate (phenol) on the adsorbent (activated charcoal) was studied by the batch technique. The batch kinetic studies were performed at different adsorbate concentrations and with different particle sizes of the adsorbent. Activated charcoal was crashed and separated on molecular sieves into four different particle sizes: A (1–2 mm), B (0.5–1 mm), C (0.25–0.5 mm), and D (0.125–0.25 mm). A number of stoppered conical flasks containing a definite volume (100 mL) of phenol solution were placed in a shaking assembly. The amount of adsorbent (1 g L^{-1}) was retained in all subsequent studies. At determined intervals of time, the phenol solutions of the specified conical flasks were separated from the adsorbent and analyzed spectrophotometrically ($\lambda_{\max} = 211$ nm) to verify the uptake of adsorbate (phenol).

2.3 Modeling

2.3.1 Equilibrium Isotherm Models

The Langmuir and Freundlich models were used to fit the adsorption isotherms to evaluate the isotherm parameters. The Langmuir isotherm is based on the assumption of monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the pores of the adsorbent surface. The Langmuir equation may be written as:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0} C_e \quad (1)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mol g^{-1}), C_e is the equilibrium concentration (mol L^{-1}), Q^0 is the monolayer adsorption capacity (mol g^{-1}), and b is the constant related to the free energy of adsorption ($b \propto e^{-\Delta G/RT}$). It is the reciprocal value of the concentration of which half the saturation of the adsorbent is attained. The model parameters Q^0 and b can be determined from the linear plots of C_e/q_e and [31–34, 21].

The Freundlich model assumes heterogeneous surface energies, in which the adsorption energy varies as the function of the surface coverage due to variation in the heat of adsorption [31–34]. The Freundlich equation may be written as:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0} C_e \quad (2)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mol g^{-1}), C_e is the equilibrium concentration (mol L^{-1}), k_f is the constant indicative of the relative adsorption capacity of the adsorbent (mol g^{-1}), and $1/n$ is the constant indicative of the intensity of adsorption. The model parameters k_f and $1/n$ can be determined from the linear plots of $\log q_e$ and $\log C_e$. The Freundlich model is widely applied in heterogeneous systems, especially of organic compounds and highly interactive species on activated carbon and molecular sieves.

2.3.2 Kinetic Models

To analyze the adsorption rate of phenol onto the adsorbent (activated charcoal), two kinetic models (pseudo-first-order and pseudo-second-order) were used.

The pseudo-first-order kinetic equation [35] may be written as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

where q_e and q_t are the amounts adsorbed at equilibrium and at t , respectively, and k_1 is the first-order rate constant. The adsorption rate parameter k_1 can be calculated by plotting $\log(q_e - q_t)$ versus t .

The pseudo-second-order equation based on equilibrium adsorption may be expressed as [36]:

$$\frac{t}{q_t} = \frac{1}{q_0} + \frac{1}{k_2} t \quad (4)$$

where q_0 is the initial sorption rate, q_e is the amount adsorbed at equilibrium, and k_2 is the pseudo-second-order rate constant. The values of q_0 , q_e , k_2 can be calculated by plotting t/q_t versus t .

3 Results and Discussion

3.1 Phenol

3.1.1 Sorption Studies

According to the Giles classification, the isotherms may be classified as H-type for the adsorption of phenol. This H-type suggests a high affinity of the adsorbent towards the adsorbate and that there is no strong competition from the solvent for sorption sites (see Fig. 1).

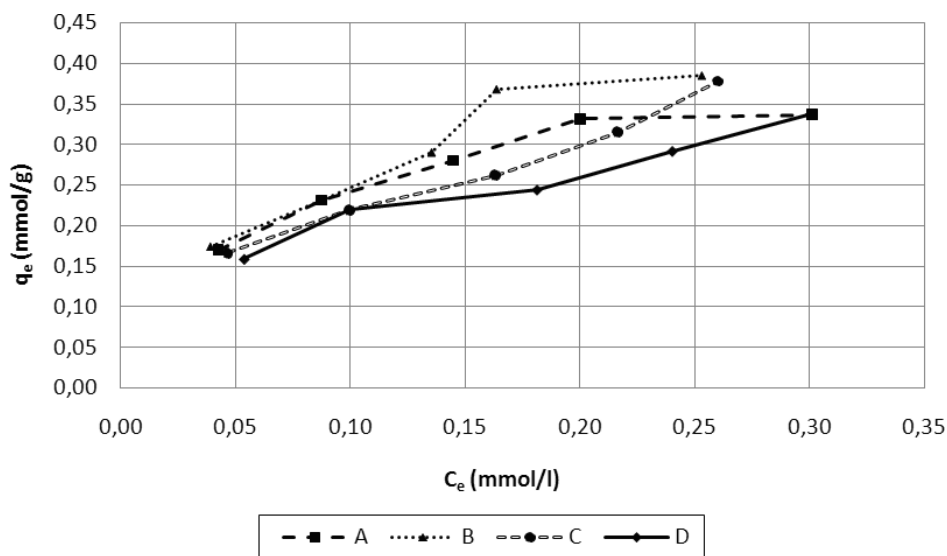


Figure 1. Adsorption isotherms of phenol for different particle sizes (A, B, C, D).

The Langmuir and Freundlich isotherms for the adsorption of phenol on four different particle sizes of commercial activated charcoal (A, B, C, D) are shown in Figs. 2 to 5. The linear plots of $\log(q_e)$ versus $\log C_e$ show that the adsorption of phenol also follows the Freundlich isotherm model (see Figs. 1b) to 4b)). The corresponding Freundlich isotherm parameters along with the correlation coefficients are given in Tab. 1. The values of $0 < 1/n < 1$ exhibit the favorability of adsorption onto activated charcoal [19]. The monolayer adsorption capacity Q^0 was found to be higher for particle size B, presumably because the best mixing conditions were achieved for this particle size; the constant b reflects the affinity of the adsorbent for the solute, found to be higher for the granular size A indicating a more stable bond/complex with the carbon surface (see Tab. 2). The adsorption capacities of activated charcoal of different particle sizes (A, B, C, D) were compared with other

Table 1. Freundlich isotherm constants for adsorption of phenol.

Adsorbent	1/n	R ²	k _f [mmol g ⁻¹]
A	0.37	0.97	0.56
B	0.46	0.95	0.75
C	0.45	0.96	0.64
D	0.40	0.97	0.52

Table 2. Langmuir isotherm constants for adsorption of phenol.

Adsorbent	Q ⁰ [mmol g ⁻¹]	Q ⁰ b [g ⁻¹]	b [mmol ⁻¹]	R ²
A	0.41	6.53	15.93	0.99
B	0.53	5.57	10.46	0.95
C	0.51	4.18	8.17	0.91
D	0.43	4.18	9.79	0.96

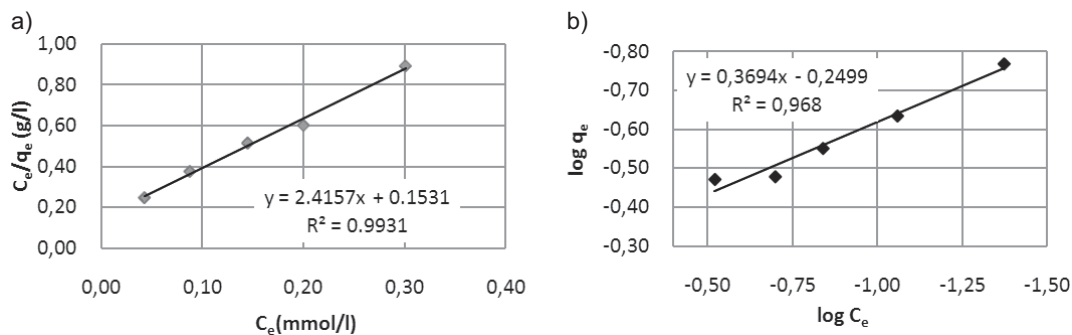


Figure 2. Adsorption isotherms of phenol on charcoal size A: (a) Langmuir, (b) Freundlich.

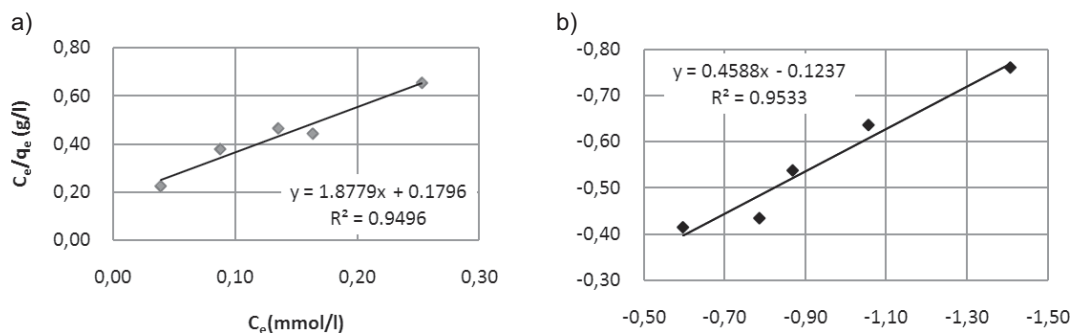


Figure 3. Adsorption isotherms of phenol on charcoal size B: (a) Langmuir, (b) Freundlich.

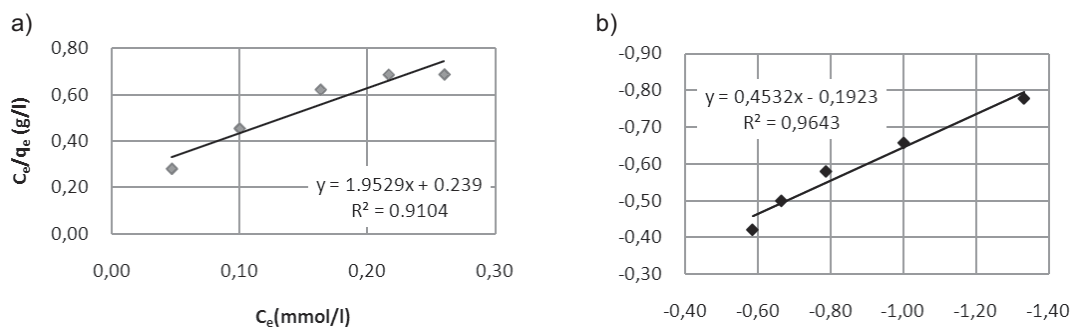


Figure 4. Adsorption isotherms of phenol on charcoal size C: (a) Langmuir, (b) Freundlich.

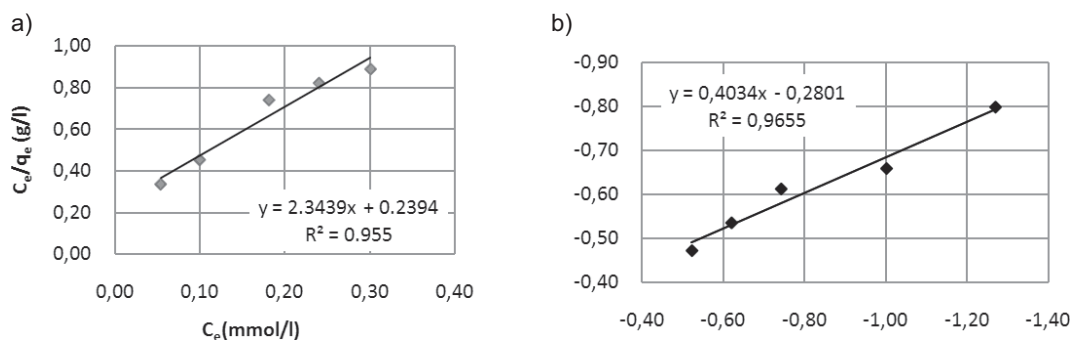


Figure 5. Adsorption isotherms of phenol on charcoal size D: (a) Langmuir, (b) Freundlich.

adsorbents derived from different raw materials. The adsorption capacities of activated charcoal of different particle sizes have higher values for the adsorption of phenol as compared to those of carbons derived from oil shale (KOH-OS, ZnCl₂-OS), bagasse fly ash, carbonized bark (data1, data2), and coconut shells (SAC), and they are comparable with those of activated carbon derived from acid-treated coconut shells (ATSAC) (see Tab. 3).

Table 3. Adsorption capacities of various adsorbents for phenol.

Adsorbent	Temperature [°C]	Q^0 [mmol g ⁻¹]	Ref.
Oil shale (KOH-OS) ^a	–	0.049	[44]
Oil shale (ZnCl ₂ -OS) ^b	–	0.081	[44]
Bagasse fly ash ^c	30	0.007	[45]
Carbonized bark ^d	23.26	0.43	[46]
Conconut shells (ATSAC) ^e	25	0.53	[32]
Conconut shells (SAC) ^f	25	0.36	[32]
Activated charcoal (A)	25	0.41	present study
Activated charcoal (B)	25	0.53	present study
Activated charcoal (C)	25	0.51	present study
Activated charcoal (D)	25	0.43	present study

^achemically activated oil shale pretreated with KOH as impregnating agent; ^bchemically activated oil shale pretreated with ZnCl₂ as impregnating agent; ^cwaste generated in sugar industries; ^dslash pine bark carbonized by slow heating in nitrogen for 6.5 h to 672 °C; ^eactivated carbon developed through thermal activation of coconut shells; ^factivated carbon developed through acid treatment of coconut shells.

The mechanism of phenol adsorption is determined by so-called π - π interactions and donor-acceptor complex formation. The adsorption of phenol from aqueous solution involves the interaction between the π -electron system of the aromatic ring with the graphitic carbon surface. It suggests that the benzene ring remains parallel to the surface at low concentrations [28, 37–41]. The second postulates that the adsorption mechanism is based on the formation of a donor-acceptor complex between the surface carbonyl groups (electron donor) and the aromatic rings of phenol acting as acceptor [42, 43].

3.1.2 Kinetic Studies

Concentration-time profiles for the adsorption of phenol onto different particle sizes of commercial activated charcoal (A, B, C, D) at different initial concentrations of the adsorbate (phenol) (see Fig. 6) show that the particle size B of activated charcoal has a higher uptake rate at different initial concentrations of the adsorbate (phenol). The adsorption rate data for the studied adsorbate onto different particle sizes of commercial activated charcoal (A, B, C, D) were analyzed by using two kinetic models, namely, pseudo-first-order and pseudo-second-order equations.

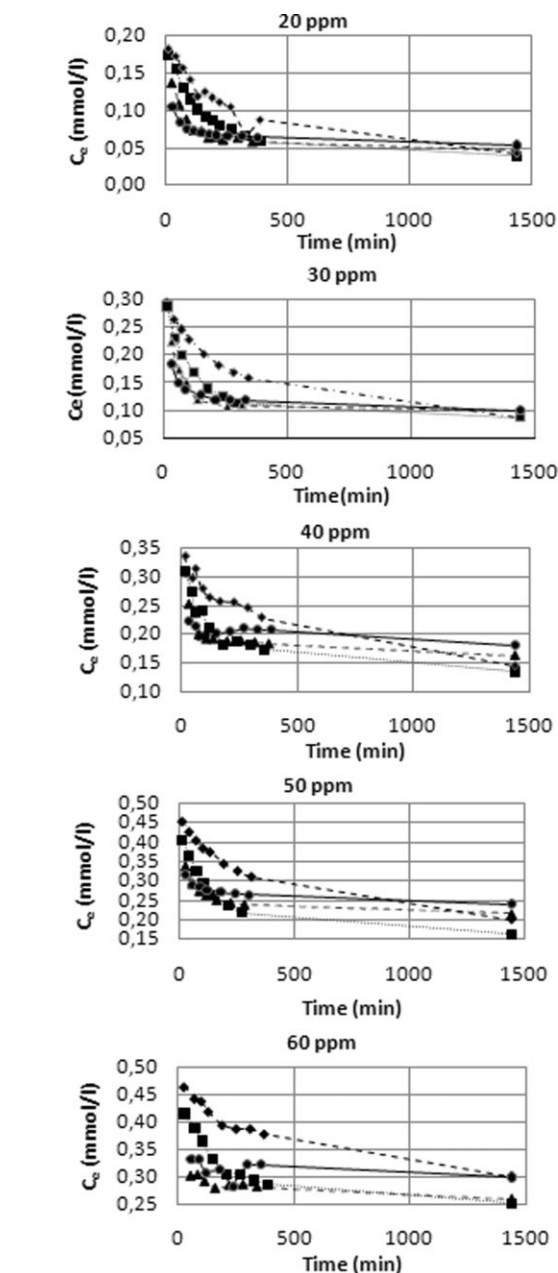


Figure 6. Time- C_e profiles at initial concentrations (20, 30, 40, 50 and 60 ppm) of adsorbate (phenol) on four different particle sizes (A, B, C, and D) of adsorbent (activated charcoal).

Both models were studied at different initial concentrations of adsorbate (phenol).

The q_e values were calculated using pseudo-first and second-order rate equations; it was observed that the theoretical q_e values calculated by the second-order equation at different adsorbate concentrations agree more accurately with the experimental q_e values (see Tab. 4). These observations suggest that the studied sorption system follows the second-order rate equation instead the first-order one. In addition, the coefficients for pseudo-second-order were higher than those for

Table 4. Comparative evaluation of q_e as calculated experimentally and by using first and second-order rate equations.

Initial conc. [ppm]	A			B			C			D		
	q_e (pse-1)	q_e (pse-2)	q_e (exp)	q_e (pse-1)	q_e (pse-2)	q_e (exp)	q_e (pse-1)	q_e (pse-2)	q_e (exp)	q_e (pse-1)	q_e (pse-2)	q_e (exp)
20	0.149	0.170	0.17	0.133	0.184	0.174	0.071	0.168	0.166	0.037	0.153	0.160
30	0.202	0.220	0.231	0.993	0.279	0.231	0.118	0.240	0.219	0.069	0.212	0.219
40	0.170	0.210	0.28	1.470	2.700	2.896	0.062	0.249	0.262	0.025	0.216	0.244
50	0.255	0.257	0.332	0.256	0.360	0.368	0.087	0.311	0.320	0.067	0.275	0.292
60	0.168	0.277	0.34	0.172	0.378	0.380	–	0.360	0.378	–	0.321	0.337

pseudo-first-order (see Tab. 5), also indicating the suitability of the second-order rate equation for the adsorption of phenol onto different particle sizes of commercial activated carbon. The pseudo-second-order equation predicts the behavior over the whole range, strongly supporting the validity, and agrees with chemisorptions being rate-controlling because it is based on the adsorption capacity [47].

3.2 Chloroform

The amount of chloroform adsorbed in the equilibrium state was plotted against the concentration of chloroform in solution in logarithmic scale. A linear relationship was obtained, indicating that the adsorption reaction was a Freundlich type reaction (see Figs. 7 and 8). The Freundlich isotherm parameters along with the correlation coefficients for the four particle sizes of commercial activated charcoal (A, B, C, D) are given in Tab. 6.

The value of the constant k_f was higher for particle size A. The value of $1/n$ was highest for particle size A (see Tab. 6).

According to the Giles classification, the isotherms may be classified as L-type for the adsorption of chloroform on different granular sizes of commercial activated charcoal (see Fig. 9). The L-type isotherms suggest the completion of the monolayer on the surface of the adsorbent. Tab. 7 shows the effect of particle size of commercial activated charcoal and initial concentration of adsorbate (chloroform) on the removal efficiency of activated charcoal. Fig. 10 and Tab. 7 show that the removal efficiency of adsorbent (A) ranged from 70 % to 98 %, of (B) from 61.7 % to 100 %, and of (C) and (D) from 51 % to 100 %. It was observed that the adsorbates (A, B, C,

D) were more effective at low concentrations of the adsorbate (0.0042, 0.0084, 0.0167 mmol L⁻¹) than at higher ones (0.0418, 0.0837, 0.1255 mmol L⁻¹).

4 Conclusions

Granular activated charcoal was studied for the adsorption of phenol and chloroform at different initial concentrations of

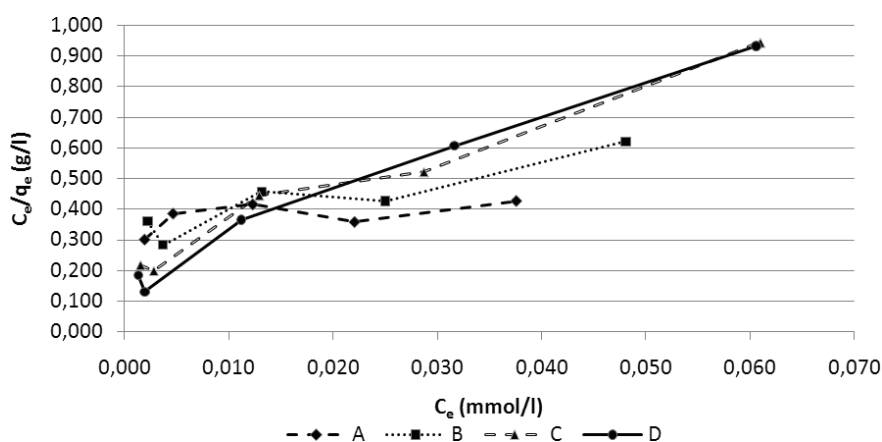


Figure 7. Langmuir adsorption isotherms of chloroform on four particle sizes of commercial activated charcoal (A, B, C, D).

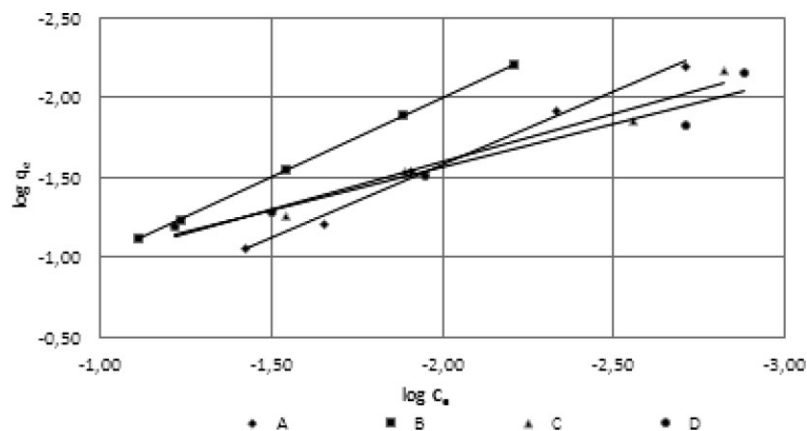


Figure 8. Freundlich adsorption isotherms of chloroform on four particle sizes of commercial activated charcoal (A, B, C, D).

Table 5. Second-order rate constants at different initial adsorbate concentrations.

Initial conc. [ppm]	A			B			C			D		
	q_0	q_e	R^2	q_0	q_e	R^2	q_0	q_e	R^2	q_0	q_e	R^2
20	0.001	0.170	0.912	0.002	0.184	0.991	0.005	0.168	0.998	0.014	0.153	1.000
30	0.002	0.220	0.988	0.027	0.279	0.997	0.006	0.240	0.996	0.013	0.212	1.000
40	0.006	0.210	0.990	0.090	2.700	0.997	0.021	0.249	0.999	0.137	0.216	0.999
50	0.004	0.257	0.976	0.008	0.360	0.987	0.016	0.311	1.000	0.030	0.275	1.000
60	0.009	0.277	0.996	0.011	0.378	0.997	0.076	0.360	1.000	0.392	0.321	0.992

Table 6. Freundlich constants.

Adsorbent	$\log(k_f)$	k_f [mmol g ⁻¹]	$1/n$	R^2
A	0.407	2.553	1.047	0.929
B	-0.071	0.850	0.786	0.952
C	-0.457	0.349	0.583	0.951
D	-0.501	0.316	0.532	0.955

adsorbate (phenol, chloroform) and for different particle sizes of adsorbent. Both the Freundlich and Langmuir isotherm models adequately fit the adsorption data of phenol, the Freundlich isotherm model better fit the adsorption data of chloroform than the Langmuir model. The pseudo-second-order rate model better explained the adsorption kinetics of

phenol compared to the pseudo-first-order rate model. The adsorption capacities of phenol for the adsorbates A, B, C, D were 0.41, 0.53, 0.51, 0.43 mmol g⁻¹, the adsorption capacities of chloroform were 2.553, 0.85, 0.349, 0.316 mmol g⁻¹. The results of this study show that granular activated charcoal of different particle sizes can be used as potential adsorbent for phenol and chloroform in drinking water.

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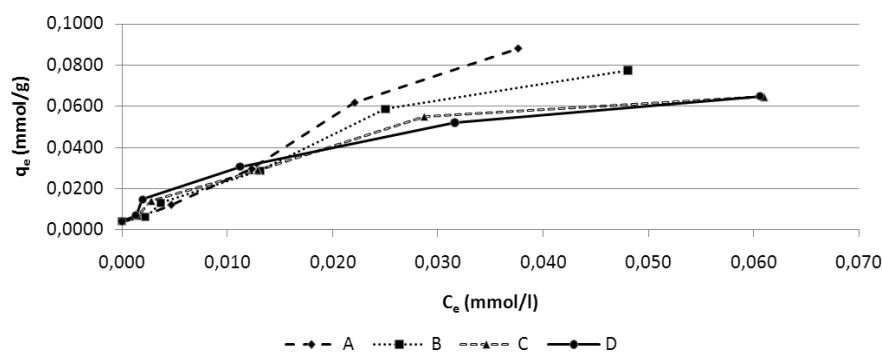
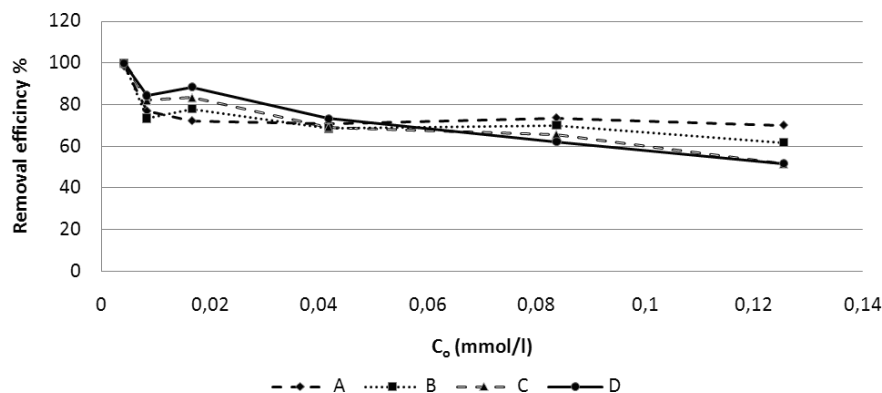
**Figure 9.** Adsorption isotherms of chloroform on different particle sizes of commercial activated charcoal (A, B, C, D).**Figure 10.** Removal efficiency of different particle sizes of activated charcoal adsorption of chloroform.

Table 7. Removal efficiency of chloroform by different particle sizes of activated charcoal.

Adsorbent	Particle diameter [μm]	Initial concentration [mmol L^{-1}]					
		0.0042	0.0084	0.0167	0.0418	0.0837	0.1255
A	1000–2000	98.6 %	76.9 %	72.2 %	71 %	73.6 %	70.0 %
B	500–1000	100 %	73.5 %	77.9 %	69 %	70.1 %	61.7 %
C	250–500	100 %	82.1 %	83.4 %	69 %	65.7 %	51.4 %
D	125–250	100 %	84.4 %	88.4 %	73 %	62.2 %	51.7 %

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