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INFLUENCE OF pH ON ADSORPTION KINETICS OF MONOCHLOROPHENOLS FROM AQUEOUS SOLUTIONS ON GRANULAR ACTIVATED CARBON

WPŁYW pH NA KINETYKĘ ADSORPCJI MONOCHLOROFENOLI Z ROZTWORÓW WODNYCH NA GRANULOWANYM WĘGLU AKTYWNYM

Abstract: Adsorptive removal of 2-, 3- and 4-chlorophenol from aqueous solutions by granular activated carbon was studied. The influence of different experimental parameters like initial concentration, carbon dosage and pH on the adsorption of monochlorophenols were evaluated. The influence of type of acid and base used for water acidification or alkalization was also tested. The results indicate that acidic pH is favorable for the adsorption of chlorophenols; however the type of acid or alkali used for the change of pH has a little influence and did not significantly affect the adsorption efficiency. The pH played an important role in the adsorption kinetics of chlorophenols at pH values above the pKa values of the compounds, while little influence on adsorption rate was observed if pH was decreased below the pKa values.

Keywords: adsorption kinetics, activated carbon, chlorophenols

Introduction

Chlorophenols are a group of chemical compounds that are produced by adding chlorine to phenol. They are used in a number of industries as wood, fibers, paints and leather preservatives and for the manufacturing of resins and pesticides. As a result, chlorophenols are found commonly in air, soil, wastewater, surface and ground waters [1], and in drinking water because they may be generated as by-products in the disinfection of water [2]. Because most of them are highly toxic and might produce disagreeable taste and odor to drinking water at concentrations below 0.01 mg mg/dm³ [3, 4] chlorophenols are classified as priority pollutants by the European Union [5] and US Environmental Protection Agency [6]. Therefore it is very important to reduce the input of toxic chemicals into the environment and to study methods for their removal from contaminated sites.

Chlorophenols are removed from environment by biodegradation [7-9], advanced oxidation processes (AOPs) [10-15] or adsorption, especially on activated carbon [16-20]. These processes have been applied successfully in water treatment to degradation of

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chlorophenols, but most of them do not lead to the complete mineralization of phenols, or are either expensive or time-consuming. An interesting solution for an effective elimination of chlorophenols from water seems to be a combination of advanced oxidation processes with adsorption on granular activated carbon (GAC). Because an oxidative removal of these compounds by AOPs is strongly pH dependent [11], there is a need to fully understand the effect of pH on adsorption kinetic and efficiency. Selection of optimal conditions for simultaneous oxidation and adsorption will enable for rapid and effective degradation of chlorophenols.

The aim of this work is evaluation of the influence of pH on adsorption of monochlorophenols on granular activated carbon in view of the simultaneous application of adsorption and advanced oxidation processes. Influence of the type of acid and base used for water acidification or alkalization was also tested.

Materials and methods

Chemicals and reagents

2-Chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP) and organic acids (formic, acetic and trifluoroacetic acid) were from Sigma (St Louis, MO, USA). Inorganic acids (HCl, H_2SO_4 and H_3PO_4), sodium hydroxide and ammonia were obtained from POCH (Gliwice, Poland). HPLC-grade acetonitrile was from Acros Organics (Geel, Belgium).

Adsorbent

The granular activated carbon Norit R3-ex (The Netherlands) has been used. Prior to use, the carbon was pretreated by ash removal with use HF and HCl concentrated acids and washing in distilled water several times. Finally, the activated carbon was dried in an oven at 120°C for 6 hours and stored in a desiccator until use. The main properties characterizing so prepared carbon are as follows: the BET surface area of the carbon = 1390 m²/g, $V_{mi} = 0.46 \text{ cm}^3/\text{g}$, $V_{me} = 0.081 \text{ cm}^3/\text{g}$, $S_{me} = 52 \text{ m}^2/\text{g}$ (all these parameters from N₂ adsorption), NaOH uptake 0.212 mmol/g, HCl uptake 0.183 mmol/g and surface oxygen content 4.2 at % (from XP spectra) [21].

Adsorption procedure

The effect of several important parameters like initial concentration of chlorophenols, carbon dosage, type of acid and base used for water acidification or alkalization, and pH were studied. Generally, a fixed amount of the activated carbons (0.06 g) and a 75 cm³ of the solutions containing a initial concentration of 2-CP, 3-CP and 4-CP $C_0 = 1 \text{ mmol/dm}^3$ were placed in an Erlenmeyer flask and shaken at 25°C. The samples were withdrawn at appropriate time intervals and analyzed.

To study the effect of type of acid and base used for acidification or alkalization, solutions containing 1 mmol/dm³ of CPs were adjusted to pH 2 or 12 and, after addition of 0.06 g of adsorbent, shaken for 4 hours. For acidification three organic acids (HCOOH, CH₃COOH, CF₃COOH) and three inorganic acids (HCl, H₂SO₄ and H₃PO₄) were used. For adjustment to pH of 12 sodium hydroxide and ammonia were used.

The effect of pH on the chlorophenol removal was studied over a pH range of 2-12. pH was adjusted by the addition of dilute aqueous solutions of H_2SO_4 or NaOH.

The kinetic studies were performed following a similar procedure at 25°C - the initial concentration was set as 1 mmol/dm³ for each chlorophenols, and the mass of activated carbon was 0.06 g. Concentrations of 2-CP, 3-CP and 4-CP in solutions were measured after 15, 30, 45, 60, 90, 120 and 180 min. The amount of monochlorophenols adsorbed was determined as the difference in concentration between samples withdrawn at two consecutive time intervals during the course of the adsorption experiments. The uptake of the adsorbate at time *t*, *q_t* [mmol/g], was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where: C_0 and C_t are the concentrations of monochlorophenols in solution [mmol/dm³] at time t = 0 and t, respectively, V is the volume of the solution [dm³], and m is the mass of the adsorbent used [g].

Chromatographic analysis

The concentrations of monochlorophenols in solutions were measured by high-performance liquid chromatography with diode array detector (Shimadzu LC-20, Kyoto, Japan). The chromatographic measurements were carried out under isocratic conditions on a Phenomenex Luna C18, 4.6×150 mm, 3 µm column (Torrance, CA, USA) operated at 40°C with acetonitrile and water adjusted to pH 2.2 with acetic acid (30:70, v:v). The mobile phase was pumped at flow rate of 1.0 cm³/min and the peaks were monitored at 281 nm. A typical chromatogram obtained from an aqueous standard solution of 2-CP, 3-CP and 4-CP is shown in Figure 1.



Fig. 1. Chromatogram obtained from an aqueous standard solution of chlorophenols. Concentration of each in final analytical solution 1 mmol/dm³. Peaks: 1 = 2-CP, 2 = 4-CP, 3 = 3-CP

Results and discussion

The adsorption of analytes onto an adsorbent is mainly affected by different factors such as the adsorbent dosage, the adsorbate concentration, as well as the pH of the solution.

Effect of adsorbent dosage

The effect of adsorbent dosage on the uptake of selected chlorophenols on granular activated carbon was studied at three different adsorbent doses (0.03, 0.06 and 0.09 g) for the concentrations of each chlorophenols of 1 mmol/dm³. The results are presented in Figure 2. This figure reveals that the % removal of monochlorophenols increases with increase in adsorbent dosage. The % CP adsorbed from aqueous solution increased from about 30 to 50% and to 70% when 0.03, 0.06 and 0.09 g of activated carbon were used, respectively. An increase in the adsorption with the adsorbent dosage can be attributed to the greater surface area and the availability of more adsorption sites.



Fig. 2. Effect of carbon dosage on the adsorption of chlorophenols

Effect of initial concentration of chlorophenols

The effect of initial concentration on the removal of the monochlorophenols by activated carbon was studied at a mass of 0.06 g. Results are shown in Figure 3. It is clear that increasing the concentration of chlorophenols while keeping the amount of the adsorbent constant leads to the reduction in the % adsorbed. The % of 2-CP adsorbed from

aqueous solution decreased from 67.1 to 40.5% and to 32.9%, when 0.5, 1 and 2 mmol/dm³ solutions were used, respectively. The % of 3-CP decreased from 68.7 to 45.2% and to 34.5%, and the removal of 4-CP decreased from 69.4 to 45.7% and to 37.5%, respectively.



Fig. 3. Effect of initial concentration of 2-CP, 3-CP and 4-CP on the adsorption onto activated carbon

Choice of acids and bases for pH changes

Three organic acids, three inorganic acids and two bases were used to study the effect of type of acid and base used for pH modification on removal of chlorophenols. Samples were adjusted to pH 2.0 by addition of HCOOH, CH_3COOH , CF_3COOH , HCl, H_2SO_4 and H_3PO_4 or to pH 12 by NaOH and NH₄OH. All the other parameters like carbon dosage (0.06 g) and initial concentration of CPs (1 mmol/dm³) were kept constant. Results are shown in Figures 4 and 5. Based on these results it is clear that type of acid or alkali used for the change of pH has a little influence and did not significantly affect the adsorption of chlorophenols from water. However, slightly the best adsorption of chlorophenols was

observed when sulfuric acid (from mineral acids) or acetic acid (from organic acids) and sodium hydroxide were used.



Fig. 4. Effect of type of acid used for pH modification on removal of chlorophenols from aqueous solution



Fig. 5. Effect of type of base used for pH modification on removal of chlorophenols from aqueous solution

Effect of pH

The effect of the solution pH on the adsorption equilibrium of selected chlorophenols is shown in Figure 6. The contact time was fixed at 180 min for the rest of the batch experiments to make sure that equilibrium was reached in all cases. The adsorption of 2-CP, 3-CP and 4-CP is more or less constant in acidic and neutral pH (from 2 to 7), whereas the removal of chlorophenols decrease significantly when the pH of the solution is more than 8 (nearing or more then their pKa values). The pKa values for chlorophenols reported in the literature [1] were 8.3-8.6 for 2-CP, 8.8-9.1 for 3-CP and 9.1-9.4 for 4-CP.

For organic acids and organic bases, the occurrence of the protonated and deprotonated species depends on the solution pH in relation to the dissociation constant (pKa) of the compound. When pH < pKa, the nondissociated species and the dissociated species (bases form cations by protonation at pH) are dominated for organic acids and organic bases, respectively; whereas when pH > pKa, the dissociated species (anion) is dominant for organic acids and the nondissociated species is dominant for organic bases. Chlorophenols are weak organic acids, therefore, when solution pH is less than their pKa values, they are

present in aqueous solution as protonated form. Deprotonated species are formed if pH is higher than their pKa values.

At pH 2 the adsorption was 47, 51 and 52% for 2-CP, 3-CP and 4-CP, respectively. When the pH of the solution was increased above the pKa value, most of the chlorophenol molecules were present as negative ions. This leads to the significant decrease in the adsorption - from about 50% at pH 2 to 3, 5 and 10% at pH 12 for 2-CP, 3-CP and 4-CP, respectively. This decrease was mostly due to the repulsion between the carbon surface and the anionic chlorophenolide ions as well as the competition between the adsorption on the solution at such high pH, for the adsorption on the carbon active sites. These observations are in agreement with the results presented in the literature [16, 19, 22-25]. Effect of pH on the adsorption of the chlorophenols is similar in the case of the Norit R3-ex carbon used in this experiment, as well as in the case of other activated carbons [16, 19], natural zeolite [22], polymers [23] and carbon nanotubes [24] or fibers [25].



Fig. 6. Effect of pH on the percentage removal of selected monochlorophenols from aqueous solution

Although influence of pH on adsorption of chlorophenols is well described, information on the adsorption kinetics are inadequate. Therefore, the effect of pH on the adsorption kinetic of chlorophenols onto activated carbon was also studied. In order to investigate the kinetics of adsorption of monochlorophenols on granular activated carbon, the rate constants were determined in terms of the pseudo-first order and pseudo-second order models. If the sorption follows pseudo-first order mechanism, the equation has the form [26]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$
(2)

where: q_e and q_t are the amounts of adsorption at equilibrium [mmol/g] and at time t [min], respectively, and k_1 the rate constant of adsorption [1/min]. Values of k_1 were calculated from the plots of $\log(q_e - q_t)$ versus t for different concentrations of selected adsorbates. The pseudo-second order kinetic model is expressed as [27]:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$$
(3)

where q_e and q_t are the amounts of adsorption at equilibrium and at time *t*, respectively, and k_2 is the rate constant of second-order adsorption [g/mmol·min]. Values of k_2 were calculated from the intercept and slope of the plots of t/q_t versus *t*.

The constants of the two models are listed in Table 1. The pseudo-first-order model gives poor fitting with low R^2 values. The pseudo-second-order model fits the experimental data quite well for all chlorophenols, the correlation coefficients are greater than 0.98. These indicate that the adsorption system belongs to the second-order kinetic model. The k_2 values are more or less constant over the range of pH from 2 to 8 while, at a pH above 9 (above the pKa) k_2 values decreases.

Table 1

		pH							
		2	4	6	7	8	9	10	12
		Pseudo-first order							
2-CP	k_1 [1/min]	0.023	0.026	0.032	0.035	0.025	0.021	0.018	0.006
	R^2	0.978	0.981	0.961	0.991	0.957	0.963	0.996	0.950
3-CP	k ₁ [1/min]	0.024	0.025	0.032	0.034	0.032	0.031	0.017	0.007
	R^2	0.978	0.974	0.972	0.992	0.962	0.953	0.980	0.975
4-CP	k ₁ [1/min]	0.024	0.026	0.032	0.034	0.036	0.029	0.017	0.009
	R^2	0.979	0.961	0.978	0.991	0.958	0.964	0.995	0.978
		Pseudo-second order							
2-CP	k₂ [g/mmol∙min]	0.108	0.111	0.105	0.097	0.113	0.063	0.043	0.038
	R^2	0.986	0.989	0.996	0.998	0.995	0.987	0.998	0.993
3-CP	k_2 [g/mmol·min]	0.112	0.113	0.099	0.105	0.098	0.091	0.064	0.046
	R^2	0.984	0.992	0.996	0.998	0.994	0.992	0.999	0.985
4-CP	k_2 [g/mmol·min]	0.107	0.119	0.109	0.105	0.104	0.095	0.068	0.042
	R^2	0.991	0.993	0.996	0.997	0.993	0.993	0.997	0.987

The pseudo first and second-order rate constant at selected monochlorophenols on granular activated carbon Norit R3-ex at 25°C; initial concentration 1 mmol /dm³

Conclusions

The granular activated carbon Norit R3-ex is an effective adsorbent for the removal of 2-chlorophenol, 3-chlorophenol and 4-chlorophenol from aqueous solution. Adsorption kinetic follows second-order model. Type of acid or alkali used for the change of pH did not significantly affect the adsorption of monochlorophenols from water. The results show that pH played an important role in the adsorption kinetics of chlorophenols at pH values above the pKa values of the compounds, while little influence on adsorption rate was observed if pH was decreased below the pKa values. Simultaneous application of adsorption and oxidation methods for the removal of chlorophenols from water can be effective only in the case of methods based on hydrogen peroxide. Oxidation of

chlorophenols by H_2O_2 -based methods occurs in an acidic medium (pH~3) [11], in which the adsorption of chlorophenols onto activated carbon takes place also effectively and quickly. Removal of chlorophenols by ozonation is most effective under alkaline pH [11], but at a pH above 9 the adsorption efficiency and kinetic decrease significantly.

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WPŁYW pH NA KINETYKĘ ADSORPCJI MONOCHLOROFENOLI Z ROZTWORÓW WODNYCH NA GRANULOWANYM WĘGLU AKTYWNYM

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Abstrakt: Zbadano absorpcję 2-, 3- i 4-chlorofenolu z wody na granulowanym węglu aktywnym. Sprawdzono wpływ różnych parametrów na adsorpcję, takich jak stężenie początkowe adsorbatów, ilość węgla aktywnego czy pH roztworu, jak również wpływ rodzaju kwasu i zasady użytych do zakwaszenia lub alkalizacji środowiska. Uzyskane rezultaty pokazują, że adsorpcja chlorofenoli zachodzi o wiele lepiej w kwaśnym środowisku, natomiast rodzaj zastosowanego kwasu lub zasady do zmiany pH nie wpływa znacząco na efektywność adsorpcji. pH odgrywa natomiast istotną rolę w przypadku kinetyki adsorpcji chlorofenoli na węglu aktywnym zwłaszcza w pH powyżej wartości ich pKa, natomiast w środowisku o pH poniżej wartości pKa chlorofenoli wpływ ten jest znikomy.

Słowa kluczowe: kinetyka adsorpcji, węgiel aktywny, chlorofenole