

Journal of Hazardous Materials A90 (2002) 229-234



www.elsevier.com/locate/jhazmat

Short communication Adsorption of *p*-chlorophenol from aqueous solutions on bentonite and perlite

B. Koumanova*, P. Peeva-Antova

Department of Chemical Engineering, University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Blvd., Sofia 1756, Bulgaria

Received 30 July 2001; received in revised form 24 October 2001; accepted 6 November 2001

Abstract

The adsorption of *p*-chlorophenol (*p*-CP) from aqueous solutions on bentonite and perlite was studied. These materials are available in large quantities in Bulgaria. Model solutions of various concentrations $(1-50 \text{ mg dm}^{-3})$ were shaken with certain amounts of adsorbent to determine the adsorption capacity of *p*-CP on bentonite and perlite as well. The influence of several individual variables (initial adsorbate concentration, adsorbent mass) on the rate of uptake of the studied compound on the adsorbert was determined by carrying out experiments at different contact times using the batch adsorber vessel designed according to the standard tank configuration. Rapid adsorption was observed 20–30 min after the beginning for every experiment. After that, the concentration of *p*-CP in the liquid phase remained constant. The adsorption equilibrium of *p*-CP on bentonite and perlite was described by the Langmuir and the Freundlich models. A higher adsorption capacity was observed for bentonite (10.63 mg g⁻¹) compared to that for perlite (5.84 mg g⁻¹). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Bentonite; Perlite; p-Chlorophenol; Isotherms

1. Introduction

The usage of natural mineral sorbents for wastewater treatment is increasing because of their abundance and low price. There are many papers in the literature concerning the adsorption of low molecular organic compounds on bentonite and organobentonites [1–7]. Both, the natural material perlite and the modified perlite are used for the treatment of oily wastewaters [8–10] and also as a carrier of biomass in reactors for the treatment of synthetic

^{*} Corresponding author.

E-mail address: bogdana@uctm.edu (B. Koumanova).

^{0304-3894/02/\$ –} see front matter © 2002 Elsevier Science B.V. All rights reserved. PII: S0304-3894(01)00365-X

and municipal wastewaters [11–13]. There are no data available in the literature concerning the adsorption capacity of bentonite and perlite for *p*-chlorophenol (*p*-CP).

Experimental results on the kinetics of adsorption of p-CP onto yellow bentonite and expanded perlite from aqueous solutions are presented in this paper. This is a part of the author's investigations on the adsorption of chlorinated phenols [14,15]. The influence of the initial concentration of p-CP in model aqueous solutions and the sorbent mass on the adsorption rate were both studied. The adsorption isotherms of p-CP on yellow bentonite and expanded perlite were determined and the constants in the Langmuir and Freundlich models calculated.

2. Experimental

The bentonite and the perlite used for the investigations were taken from deposits in the southern part of Bulgaria. Their chemical composition and specific area are presented in Table 1. The surface area was determined by the use of a mercury porosimeter Sorptomatic 1900, FISONS Instruments. The particle size distribution of both materials is given in Table 2. The kinetics and equilibrium adsorption of *p*-CP was carried out using the model aqueous solutions of *p*-CP (Fluka, purity 99%) at 20 ± 2 °C and pH 7 \pm 0.2. The pH measurements were made with a pH-meter, model LPH 403T TACUSSEL. The concentrations of *p*-CP in the solutions were determined using a Perkin-Elmer 323 UV–VIS–NIR spectrophotometer by absorption measurements at $\lambda = 280$ nm. An adsorption contact system with standard configuration—a vessel with a stirrer having a volume of 2 dm³ and internal diameter 0.13 m was used for the kinetic study [16]. The volume of the liquid phase was 1.7 dm³ and the depth 0.13 m. The intensive mixing (*P*, rpm) of the adsorbent particles in the liquid was performed by a stirrer Heidolph RZR 2100. The isotherms were determined

Table	1
тарие	

Typical chemical analysis of the natural sorbents

Constituents (% mass)	Bentonite	Perlite	
SiO ₂	59–75	70-80	
Al ₂ O ₃	12–16	10-15	
Fe ₂ O ₃	1–6	<1.5	
CaO	1.8–5	<1.5	
MgO	0.9–3	<1	
K ₂ O, Na ₂ O	0.5–1	<10	
TiO ₂	0.1–0.8	_	
Loss at ignition	_	<5	
Surface area $(m^2 g^{-1})$	57.99	5.83	

Table 2	

Particle size distribution (%) of bentonite and perlite

			-				
Fraction size (µm)	<63	63–100	100-160	160-200	200-315	315-400	400-500
Yellow bentonite	15.8	5.3	64.2	10.9	2.3	0.2	1.3
Perlite	79.17	14.58	6.25	-	_	_	-

by shaking 50 cm^3 model solutions with $1-50 \text{ mg dm}^{-3}$ concentrations of *p*-CP and definite sorbent quantity (*W*, g) in screw cap jars for 7 days, which was more than ample time for adsorption equilibrium.

3. Results and discussion

3.1. Influence of the initial concentration

The influence of the initial concentration of *p*-CP in the solutions on the rate of adsorption on bentonite was studied. The experiments were carried out at 300 rpm, mass of sorbent 2 g and initial concentrations of *p*-CP 5, 15, 25, 40 and 50 mg dm⁻³. An increase of the initial concentration C_0 leads to a lower adsorptive reduction of the *p*-CP concentration (Fig. 1). The kinetic experiments showed that the necessary time for the equilibrium to be reached was about 30 min.

The influence of the initial concentration on the adsorption rate of *p*-CP on perlite was studied for 12, 25 and 50 mg dm⁻³ at 300 rpm and a sorbent mass of 2 g (Fig. 2). The results



Fig. 1. Effect of initial concentration on the adsorption of *p*-CP on bentonite (P = 300 rpm, W = 2 g).



Fig. 2. Effect of initial concentration on the adsorption of *p*-CP on perlite (P = 300 rpm, W = 2 g).



Fig. 3. Effect of adsorbent mass on the adsorption of *p*-CP on perlite (P = 300 rpm, $C_0 = 50$ mg dm⁻³).

were similar to those obtained in the bentonite study. The equilibrium was established quickly within 15 min.

3.2. Influence of the sorbent mass

232

The adsorption rate of *p*-CP on perlite was studied changing the quantity of the sorbent added: 2, 3 and 5 g in 1.7 dm^{-3} while keeping the same initial concentration of 50 mg dm⁻³ and speed of agitation 300 rpm. The amount adsorbed increased when more sorbent was used (Fig. 3).

Langmuir and Freundlich models were used for the description of the isotherms. The basic assumptions of the Langmuir model are well known [17]. The Freundlich model assumes a heterogeneous adsorption surface and active sites with different energy [18].

According to the Langmuir model:

$$q_{\rm e} = \frac{k_{\rm L}C_{\rm e}}{(1 + a_{\rm L}C_{\rm e})}$$
 or in linear form $\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{k_{\rm L}} + \frac{a_{\rm L}}{k_{\rm L}}C_{\rm e}$;

According to the Freundlich model:

$$q_{\rm e} = k_{\rm f} C_{\rm e}^n$$
 or in linear form $\log q_{\rm e} = \log k_{\rm f} + n \log C_{\rm e}$

where q_e is equilibrium adsorption capacity (mg g⁻¹); C_e is the concentration of *p*-CP in the solution at equilibrium (mg dm⁻³); k_L , a_L are the constants in the Langmuir equation; k_f , *n* are the constants in the Freundlich equation.

The values of the constants were determined after linearizing the equations through linear regression analysis.

The adsorption isotherms of *p*-CP on bentonite and perlite are shown in Figs. 4 and 5. The calculated values of the constants in Langmuir and Freundlich equations and the regression coefficients (R^2) are given in Table 3. Both the models were found to be suitable for describing the adsorption of *p*-CP by bentonite and perlite.

The bentonite had a higher adsorption capacity for the studied compound than that of perlite.

233



Fig. 4. Equilibrium isotherms for *p*-CP on bentonite.



Fig. 5. Equilibrium isotherms for *p*-CP on perlite.

The extent of the removal of p-CP using bentonite was up to 50% for low initial concentrations and decreased at higher concentrations to 33%. When perlite was used these values decreased to 40 and 22%, respectively.

The monolayer adsorbent capacity defined as k_L/a_L [19] was 10.63 mg g⁻¹ for bentonite and 5.84 mg g⁻¹ for perlite.

Table 3 Values of the constants in Langmuir and Freundlich models

Adsorbent	Langmuir			Freundlich		
	k _L	aL	R^2	$\overline{k_{\mathrm{f}}}$	n	R^2
Bentonite	0.478	0.0450	0.997	0.5018	0.74	0.987
Perlite	0.257	0.0441	0.984	0.3058	0.70	0.994

4. Conclusions

The kinetics and the equilibrium of *p*-CP adsorption on yellow bentonite and perlite were studied. Based on the study, the following conclusions were made:

- 1. The rate of adsorption of *p*-CP on bentonite as well as that on perlite was influenced by the initial concentration of the adsorbate. The equilibrium was reached in 30 min with bentonite and 15 min with perlite.
- 2. Both the Langmuir and the Freundlich adsorption models were found suitable for the adsorption of *p*-CP by bentonite and perlite.

References

- [1] T. Viraraghavan, F. de Maria Alfaro, J. Hazard. Mater. 57 (1998) 59-70.
- [2] L. Zhu, Y. Li, J. Zhang, Environ. Sci. Technol. 31 (5) (1997) 1407-1410.
- [3] I.M.C. Lo, C.H. Lee, H.M. Liljestrand, in: Proceedings of the 18th Biennial Conference of the International Association of Water Quality, 1996, pp. 319–325.
- [4] L. Zhu, J. Zhang, Y. Li, X. Shen, W. Qi, Environ. Sci. China 8 (3) (1996) 378-383.
- [5] T.A. Wolfe, T. Demirel, E. R Baumann, J. WPCF 58 (1) (1986) 68–76.
- [6] J.A. Smith, A. Galan, Environ. Sci. Technol. 29 (3) (1995) 685-692.
- [7] S.K. Dentel, A.I. Jamrah, D.L. Sparks, Water Res. 32 (12) (1998) 3689-3697.
- [8] J.I. Tarasevich, Natural Sorbents in Wastewater Treatment, Nauk. Dumka, Kiev, 1981, p. 175 (in Russian).
- [9] J.I. Tarasevich, A.A. Krupa, O.V. Bezorudko, Water Chem. Technol. 3 (2) (1981) 148–152 (in Russian).
- [10] A.T. Pilipenko, A.A. Pashchenko, J.I. Tarasevich, A.A. Krupa, K.A. Zabela, V.A. Sviderskii, Water Chem. Technol. 3 (3) (1981) 242–247 (in Russian).
- [11] D. Garsia-Calderon, P. Buffiere, R. Molleta, S. Elmaleh, Biotechnol. Bioeng. 57 (2) (1998) 136-144.
- [12] C. Joseph, C. Rodier, Environ. Technol. 17 (2) (1996) 2 157–165.
- [13] C. Joseph, C. Rodier, Environ. Technol. 15 (7) (1994) 631-643.
- [14] B. Koumanova, P. Peeva, in: Proceedings of the 14th International Congress of Chemical and Process Engineering CHISA 2000, Praha, August 2000.
- [15] P. Peeva-Antova, B. Koumanova, J. Univ. Chem. Technol. Metall., Sofia 36 (book 1) (2001) 73-80.
- [16] T. Furusawa, J.M. Smith, Ind. Eng. Chem. Fund. 12 (1973) 2.
- [17] J.M. Smith, Chemical Engineering Kinetics, McGraw-Hill, New York, 1970.
- [18] E.H. Smith, Water Res. 25 (2) (1991) 125–134.
- [19] G. McKay, Use of Adsorbents for the Removal of Pollutants from Wastewaters, CRC Press, Boca Raton, 1996, p. 137.