Asian Journal of Chemistry; Vol. 25, No. 11 (2013), 6209-6212

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14320

Adsorption of 2-Chlorophenol on Hypercrosslinked Resins

J.P. WANG[1,2,*], J. CHEN[1,2], Y.F. SUN[1,2], J.T. DAI[1,2] and Y.Y.WEI[2]

[1]Jiangsu Provincial Key Laboratory of Coastal Wetland Bioresources and Environmental Protection, Department of Chemistry, Yancheng Teachers University, Xiwang Road, Yancheng 224051, Jiangsu, P.R. China
[2]Institute of Applied Chemistry & Environmental Engineering, Department of Chemistry, Yancheng Teachers University, Yancheng 224051, Jiangsu, P.R. China

*Corresponding author: Tel./Fax: +86 515 88233188; E-mail: wjp-22@163.com

(*Received*: 16 July 2012; *Accepted*: 2 May 2013) AJC-13437

Two kinds of hypercrosslinked resin ZH-01 and ZH-03 were prepared in this study. The batch static experiments were conducted to investigate the adsorption characteristics of 2-chlorophenol on the hypercrosslinked resins. The equilibrium adsorption data was fitted to Freundlich adsorption isotherm model to evaluate the related parameters. The results considering the changes of enthalpy, free energy, entropy indicated an exothermic, spontaneous and disorder decreasing process happens in the adsorption. The adsorbents prepared here are better than the Amberlite XAD-4 for removing the 2-chlorophenol in aqueous solutions, based on the adsorption capacity.

Key Words: Hypercrosslinked resins, 2-Chlorophenol, Adsorption.

INTRODUCTION

Chlorophenols, a group of compounds had been widely used as important raw material in the production of petrochemicals, synthetic resins, pharmaceuticals, paints, herbicides and insecticides[1]. Nowadays, the importance of chlorophenols is proved by its ever increasing global consumption[2]. During the production and application, chlorophenols were introduced into the environment, inevitably. Owing to their toxicity and unpleasant odour, the chlorophenols presence threatens the use and reuse of water resources. Many chlorophenols are considered as the priority pollutants for their negative impacts on organisms and human health[3]. Increasing concern for public health and environmental quality has led to the establishment of rigid limits on the chlorophenols regulation. Thus, the removal of chlorophenols from workshop or waste streams becomes a great concern.

Various methods are feasible in the treatment of chlorophenols[4,5], among these methods, adsorption has been proven to be one of the most promising candidates for separating low concentration of organic pollutants from large volumes of aqueous solutions. The application of adsorption can recover re-usable chemicals effectively, besides the removal of pollutants[6,7].

Thus, resins are widely employed in the treatment of effluent contaminated by organic pollutants[8,9]. Here, we prepared two hypercrosslinked adsorbents ZH-01 and ZH-03, modified by 2-carboxybenzoyl and benzoyl functional group, respectively and investigated their absorption properties for 2-chlorophenol in the aqueous solution.

EXPERIMENTAL

Styrene and divinylbenzene (purity: 50.4 %) were purchased from Dongda Chemical Co. (Shandong province, China). Chloromethyl methylether was obtained from Langfang Chemical Co. (Hebei province, China). Acetone, methanol, zinc chloride, 2-chlorophenol, dibenzoyl peroxide and benzoyl chloride were purchased from Shanghai Chemical Reagent Plant (Shanghai, China) and used without further purification. The spherical Amberlite XAD-4 resin was purchased from Rohm & Haas Company (Philadelphia, USA).

ZH-01 and ZH-03 were synthesized as the method mentioned in the literature[10]. The monomer structures of them were illustrated in Fig. 1. Infrared spectra of the polymeric adsorbent before and after the post-crosslinking reaction were obtained from a Nicolet 170 SX IR spectrometer (USA) with a pellet of powdered potassium bromide and resin.

Adsorption experiments: The isotherms were obtained by variation of concentration and temperature in the adsorption. For each sample, resin (0.100 g) and aqueous solutions was mixed and agitated *ca.* 24 h, in a horizontal shaker operated at 130 r/min to reach the equilibrium. Three kind of adsorbents, including macroporous Amberlite XAD-4, ZH-01 and ZH-03, were employed in adsorbing 2-chlorophenol from the aqueous solutions with the initial concentration 200,

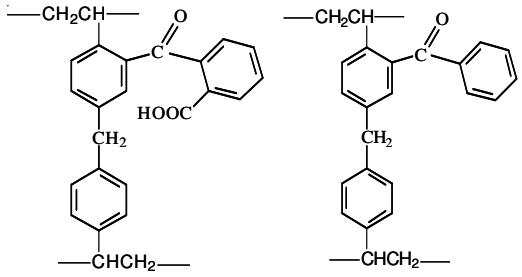


Fig. 1. Monomers structure of ZH-01 and ZH-03

400, 600, 800 and 1000 mg/L at 303 K, to compare their adsorption capacities. Adsorption kinetics was described based on the concentration varation of 2-chlorophenol at corresponding time intervals at 303 K, with the 2-chlorophenol initial concentration about 600 mg/L.

The concentrations of 2-chlorophenol were measured by gas chromatography (Agilent HP 6890 series II, USA) with a Flame ionization Detector. The column was a 30 m × 0.32 mm I.D. fused-silica capillary column HP-5 and a stationary phase thickness of 0.25 μm (Agilent USA). The oven temperature was programmed as follows: 40 ºC for 3 min, increasing to 80 ºC at 10 ºC/min and holding for 2 min. The injector and detector temperatures were set at 200 and 250 ºC, respectively. Nitrogen (99.999 %) was used as carrier gas and make-up gas.

RESULTS AND DISCUSSION

Comparing the IR spectra before and after the post-crosslinking reaction, the C-Cl bands at about 670 cm^{-1} of ZH-01 and ZH-03 decreased obviously. The band presented at 1645.95 cm^{-1} in ZH-01 and 1699.54 cm^{-1} in ZH-03 suggested that the 2-carboxylbenzeoyl and benzeoyl groups have been successfully bonded onto ZH-01 and ZH-03 resins, respectively (Fig. 2). And the typical properties of the polymeric resins were listed in Table-1.

TABLE-1
TYPICAL PROPERTIES OF THE POLYMERIC RESINS

Property	XAD-4	ZH-01	ZH-03
Polarity	Nonpolar	Moderate polar	Moderate polar
Specific surface area (m^2/g)	880	1118	883.4
Average diameter (nm)	5.8	1.2	1.33
Micropore area (m^2/g)	3	686	492.6
Average particle size (mm)	0.5	0.5	0.5
Porosity (mL/g)	1.0	0.69	0.224
Residual chlorine content (%)	0	2.8	4.4
Colour	White	Brown	Brown

The equilibrium adsorption isotherms of 2-chlorophenol from water on Amberlite XAD-4, ZH-03 and ZH-01 resins at 303 K were shown in Fig. 3. And it was found that the adsorption capacities of ZH-01 and ZH-03 are relatively higher than those of Amberlite XAD-4.

Batch equilibrium adsorption dates of 2-chlorophenol were fitted to Freundlich adsorption isotherm equations, which may be expressed as:

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e \quad (1)$$

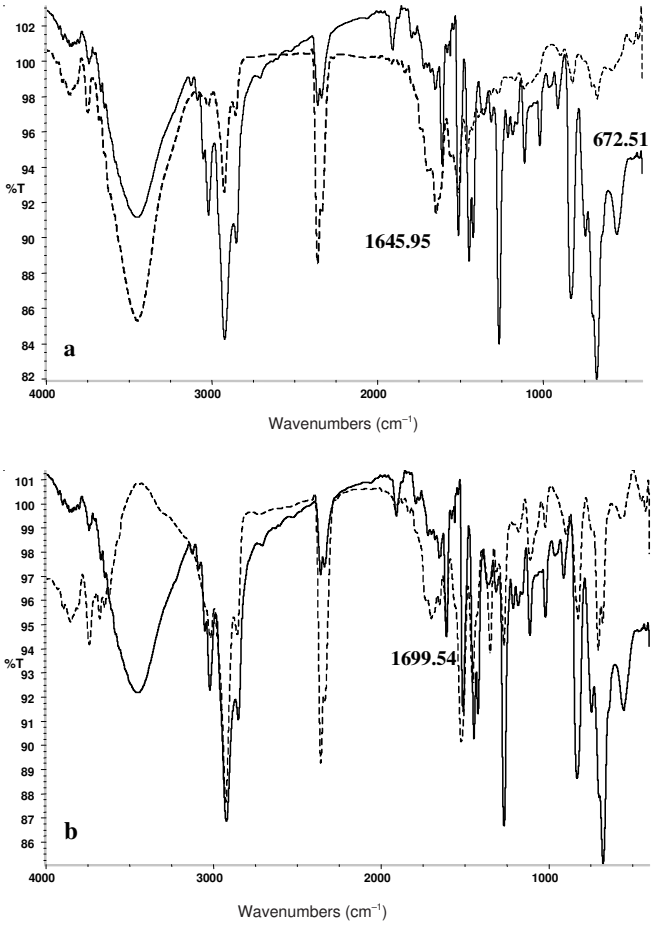


Fig. 2. IR Spectra before(solid line) and after(dotted line) the post-crosslinking reaction (a was for ZH-01 resin and b was for ZH-03 resin)

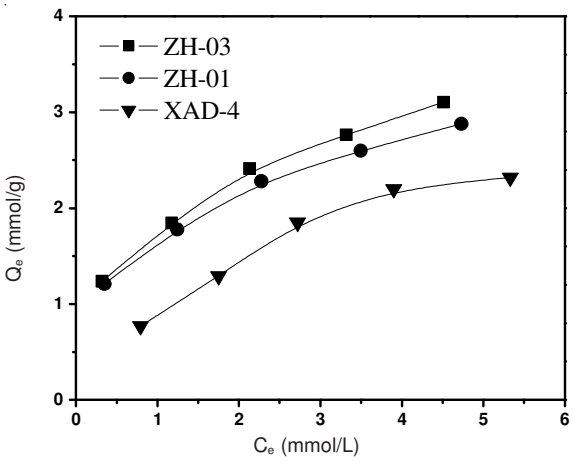


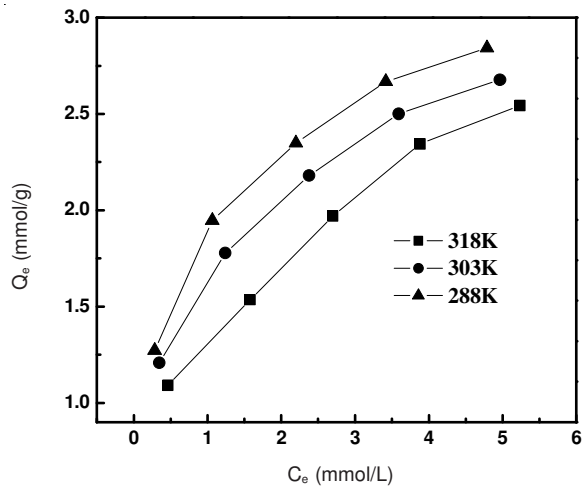
Fig. 3. Adsorption isotherms of 2-chlorophenol on Amberlite ZH-01, ZH-03 and XAD-4 at 303 K

where Q_e was the equilibrium adsorption capacity (mmol/g), C_e was the equilibrium concentration (mmol/L), K_f and n were the characteristic constants. The experiments data were fitted well to the Freundlich isotherm model ($R^2 > 0.95$) and the parameters were listed in Table-2.

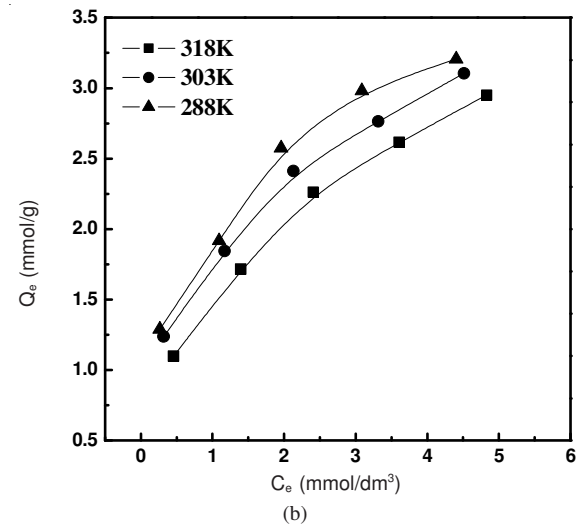
The adsorption capacities on ZH-01 and ZH-03 were significantly higher than that on Amberlite XAD-4, which could be convinced by the value of K_f, a relative indicator of adsorption capacity according to the Freundlich Theory[11]. And the

parameters n drawn from the experiments data also suggested stronger adsorption interactions presented by the surfaces of ZH-01 and ZH-03 than that of Amberlite XAD-4.

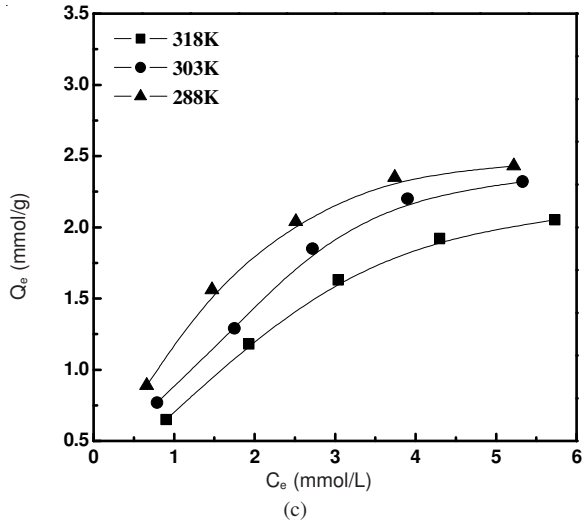
Based on the data presented in Fig. 4, the isomeric enthalpies of adsorption were calculated with a derivative van't Hoff equation[12].



(a)



(b)



(c)

Fig. 4. (a) Adsorption isotherms of 2-chlorophenol on ZH-01, (b) ZH-03, (c) Amberlite XAD-4

$$\log\left(\frac{1}{C_e}\right) = \log(K_0) + \left(-\frac{\Delta H}{RT}\right) \quad (2)$$

where ΔH was the isomeric enthalpy of adsorption when Q_e was a fixed value, R was the gas constant, C_e was the equilibrium concentration of solute at the absolute temperature T. At different temperatures (288, 303 and 318 K), the C_e was obtained from the Freundlich isotherms when Q_e equals to 1.0, 1.5 and 2.0 mmol/g. ΔH was calculated from the slope of line plotted by log ($1/C_e$) *versus* 1/T.

The free energies change of adsorption was calculated with Gibbs equation[13,14].

$$\Delta G = -RT\int_0^X \left(Q_e \cdot \frac{dX}{x}\right) = -nRT \quad (3)$$

where n was the characteristic constant of Freundlich equation. The entropies change of adsorption was calculated with Gibbs-Helmholz equation[10].

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \quad (5)$$

A summary of the calculated values for the change of enthalpy, free energy, entropy about ZH-01, ZH-03 and XAD-4 adsorbing 2-chlorophenol were listed in Table-3.

Little variety of the enthalpy change at different Q_e showed the homogeneous nature of the adsorbent surface[14]. And the heat quantities for ZH-01 and ZH-03 were more than XAD-4's in the exothermic process. Thus, the adsorption abilities of ZH-01 and ZH-03 are stronger than that of XAD-4, in 2-chlorophenol adsorption[10]. Generally, the adsorbate molecular would cover the surface of adsorbent orderly after the adsorption[14], so the disorder and entropy all decreased.

Adsorption kinetic studies: The influence of contact time on 2-chlorophenol removal by Amberlite XAD-4, ZH-01 and ZH-03 were presented in Fig. 5. All the adsorbents showed their ability to adsorb 2-chlorophenol with various efficiencies. And the kinetics adsorption data was processed to investigate the dynamics of the adsorption process in terms of the rate constant drawn from the first-order equation[15],

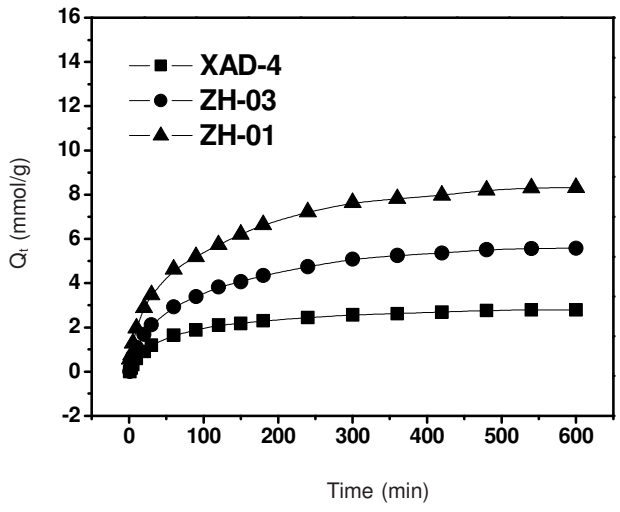


Fig. 5. Influence of contact time on removal of 2-chlorophenol by Amberlite XAD-4, ZH-01 and ZH-03

TABLE-2
EVALUATED CONSTANTS DRAWN FROM FREUNDLICH EQUATION

Adsorbents	T (K)	Freundlich equation	K_f	n	R^2
ZH-01	288	$\log Q_e = 0.3411 \log C_e + 0.3578$	2.2793	2.9317	0.9991
	303	$\log Q_e = 0.4744 \log C_e + 0.2411$	1.7422	2.1079	0.9997
	318	$\log Q_e = 0.3543 \log C_e + 0.1348$	1.3639	2.8225	0.9993
ZH-03	288	$\log Q_e = 0.3878 \log C_e + 0.3342$	2.1587	2.5786	0.9996
	303	$\log Q_e = 0.5204 \log C_e + 0.1717$	1.4849	1.9216	0.9992
	318	$\log Q_e = 0.4921 \log C_e + 0.0665$	1.1654	2.0321	0.9992
XAD-4	288	$\log Q_e = 0.3347 \log C_e + 0.1564$	1.4335	2.2523	0.9996
	303	$\log Q_e = 0.4437 \log C_e + 0.0490$	1.1194	2.006	0.9999
	318	$\log Q_e = 0.5254 \log C_e - 0.1017$	0.7912	1.7185	0.9996

TABLE-3
THERMODYNAMIC PARAMETERS

Adsorbent	Q_e (mmol/g)	ΔH (kJ/mol)	ΔG (kJ/mol)			ΔS (J/mol/K)		
			288 K	303 K	318 K	288 K	303 K	318 K
ZH-01	1.0	-54.41	-7.02	-5.31	-7.46	-165	--162	-148
	1.5	-43.49				-127	-126	-113
	2.0	-37.01				-104	-104	-92.9
ZH-03	1.0	-42.77	-6.17	-4.84	-5.37	-127	-125	-118
	1.5	-37.01				-107	-106	-99.5
	2.0	-32.96				-93.9	-92.8	-86.8
XAD-4	1.0	-38.64	-5.39	-5.05	-4.54	-115	-111	-107
	1.5	-27.43				-76.53	-73.9	--72.0
	2.0	-19.46				-48.9	-48.2	-46.9

$$\ln\left[\frac{Q_e}{(Q_e - Q_t)}\right] = kt \text{ or } -\ln(1-F) = kt \quad (6)$$

where Q_e was the equilibrium adsorption capacity (mmol/g), Q_t was the adsorption capacity when the contact time t (mmol/g), F was the fractional attainment of the equilibrium and k was the overall rate constant (min^{-1}), which showed the intra-particle diffusion would not be the rate limiting for the straight line did not pass through the origin. The values of the rate constant k was calculated from the slope of the plots obtained from -ln (1-F) *versus* the contact of 2-chlorophenol time t were 0.0113, 0.0185 and 0.0111 min^{-1} for ZH-01, ZH-03 and XAD-4, respectively.

Conclusion

Two hypercrosslinked polymeric adsorbent (ZH-01 and ZH-03) for adsorbing 2-chlorophenol from their aqueous solutions was prepared and the equilibrium adsorption capacities for 2-chlorophenol on ZH-01 and on ZH-03 were markedly higher than those on XAD-4, which attributed to its high specific surface area, high micropore area and the right adsorbates molecular volume.

The batch kinetic studies and the adsorption capacities comparisons about XAD-4, ZH-01 and ZH-03 for 600 mg/L 2-chlorophenol indicated the advantages of adsorbent ZH-01 or ZH-03 for adsorbing 2-chlorophenol. Both of the dynamics and the thermodynamics studied draw the same conclusions for adsorbing 2-chlorophenol on ZH-01 or ZH-03 that there were physical adsorption processes and showed the homogeneous nature of the adsorbent surface.

All the isotherm data for 2-chlorophenol on the XAD-4, ZH-01 and ZH-03 could be satisfactorily fitted with the Freundlich equations. The data of the thermodynamics studies for 2-chlorophenol on XAD-4, ZH-01 and ZH-03 showed the adsorption process of an exothermic, spontaneous and disorder decreasing. And the data of the kinetics were fit for the first-order equation. The two hypercrosslinked resins could effectively remove the 2-chlorophenol from aqueous solution. The new feasible measure for resolve 2-chlorophenol was offered in groundwater micropollution.

ACKNOWLEDGEMENTS

The authors express sincere gratitude to Professor Fund Project of Yancheng Teachers University (Grant No. 09YSYJ-B0202), Students' Practice Innovation Training Programs of Universities in Jiangsu Province, China and Jiangsu Provincial Key Laboratory of Coastal Wetland (Grant No. JLCBE 12030) for the financial support. This project is also supported by the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant No:12KJB610006)

REFERENCES

1. A. Dabrowski, P. Podkoscielny, Z. Hubicki and M. Barczak, *Chemosphere*, **58**, 1049 (2005).
2. I. Rodriguez, M.H. Mejuto and R.C. Bollain, *J. Chromatogr. A*, **786**, 285 (1997).
3. C. Long, J.D. Lu, A.M. Li, D.B. Hu and F.Q. Liu, *J. Hazard. Mater.*, **150**, 656 (2008).
4. B. Koumanova and P. Peeva-Antova, *J. Hazard. Mater.*, **90**, 229 (2002).
5. S. Rengaraj, S.H. Moon, R. Sivabalan, B. Arabindoo and V. Murugesan, *J. Hazard. Mater.*, **89**, 185 (2002).
6. A.M. Li, Q.X. Zhang, G.C. Zhang, J.L. Chen, Z.H. Fei and F.Q. Liu, *Chemosphere*, **47**, 981 (2002).
7. R. Kunin, *Pure Appl. Chem.*, **46**, 205 (1976).
8. V.V. Azanova and J. Hradil, *React. Funct. Polym.*, **41**, 163 (1999).
9. P. Li and A.K. SenGupta, *React. Funct. Polym.*, **44**, 273 (2000).
10. A.M. Li, Q.X. Zhang, C. Long, J.L. Chen and Z.H. Fei, *Sep. Sci. Technol.*, **37**, 3211 (2002).
11. P.J. Dumont and J.S. Fritz, *J. Chromatogr. A*, **691**, 123 (1995).
12. R.A. Garcla-Delgado, L.M. Cotouelo-Minguez and J.J. Rodfiguez, *Sep. Sci. Technol.*, **27**, 975 (1992).
13. P.B. John and T. Marios, *J. Water Pollut. Contr.*, **59**, 191 (1987).
14. R.L. Gustafson, R.L. Albright, Joel Heisler, J.A. Lirio and O.T. Reid Jr., *Ind. Eng. Chem. Prod. Res. Develop.*, **7**, 107 (1968).
15. Z.H. Fei, J.L. Chen, G.D. Gao, A.M. Li and Q.X. Zhang, *Chin. J. Polym. Sci.*, **22**, 425 (2004).