Simulatneous Adsorption of Phenol and 2,4,6-Trichlorophenol onto Nano Porous Carbon from Binary Mixture: Multicomponent Adsorption, Thermodynamic and Kinetic Study

R Subha[1] and C Namasivayam[2]
[1]Karpagam Institute of Technology, Coimbatore, India
[2]Environmental Chemistry Division, Department of Environmental Sciences, Bharathiar University, Coimbatore, India

Abstract: *During this investigation, simultaneous removal of phenol and 2,4,6-trichlorophenol(TCP) onto nano porous ZnCl₂ activated carbon prepared from coir pith using (ZnCPC) is studied in batch recator by HPLC C-18 column. Nano porous carbon was characterized using standard physio-chemical methods, BET surface area, pore diameter, SEM and FTIR studies. Adsorption of TCP in bisolute systems showed that 2-CP were adsorbed preferentially, but phenol was adsorbed competitively. This result was further confirmed by η_1 and η_2 values obtained from extended Langmuir model. The cost of ZnCPC is economically effective compared to commercial activated carbon.*

Keywords: *Nano porous activated carbon, Bisolute system, Modified competitive Langmuir model.*

1. INTRODUCTION

Phenolic compounds are released into the environment as part of many industrial effluents including pharmaceutical, petrochemical and steel industries, domestic wastewaters and chemical spillage [1]. Phenol presence in natural water can lead further to the formation of chlorophenols during disinfection and oxidation processes, which are carcinogenic compounds[2]. 2, 4, 6-trichlorophenol (TCP) is a common constituent of wood preservative formulations [3] and is often found as a contaminant in soil [4]. Chlorophenols are listed as priority environmental pollutants by US EPA because of their higher toxicity, carcinogenicity and recalcitrant properties [5]. Long term ingestion of water containing phenols in the human body causes protein degeneration, tissues erosion and paralysis of the central nervous system, and also damages the kidney, liver and pancreas [6]. The World Health Organization (WHO) guideline for maximum admissible concentration in drinking water is 0.01 µg/L for 2,4,6-trichlorophenol (TCP) and phenol 1mg/L[7]. In India, Coir pith is a lignocellulosic light fluffy biomaterial generated as a byproduct during separation of fiber from ripened coconut husk contains mainly cellulose, lignin and pentosans. The production of coir pith in India is estimated to be about 7.5 million tons annually and this often causes serious disposal problems [8].Usually, the industrial effluents present a mixture of phenols which compete between it for the active adsorbed sites, that is important for a determination of the phenols selectivity in the solution by adsorbent material. The conventional treatment method available for the treatment of mixture of phenols are sol –gel method [9] and competitive adsorption [10].

Studies of competitive adsorption reveals that different adsorbates compete for adsorption sites characterized by maximum heat of adsorption and minimum free energy of adsorption [11]. Very few adsorbents are reported in literature for the simultaneous adsorption of phenol and TCP such as hydrophobic FAU zeolites[12], Amberlite XAD-4 and NDA-100[13], granular activated carbon[10], layered

hexaniobate [14], montmorillonite modified with hexadecyl trimethylammonium cation [15], polymeric resin MN200[16], CF$_2$, a pure powdered activated carbon [17] and Duolite ES – 86 [18], respectively. The objective of the work is to explore the feasibility of using the ZnCl$_2$ activated nano porous coir pith carbon as an adsorbent for the removal and recovery of toxic phenol and 2,4,6-trichlorophenol (TCP) as binary adsorbate from water using HPLC C-18 column.

2. Material & Methods

Coir pith was dried in sunlight for 5 h. The dried coir pith (200 g) was stirred in a boiling solution of anhydrous ZnCl$_2$ (100 g in 1 liter of distilled water) for 1h, then the remaining solution was drained off and dried at 60° C for 12 h. The whole set up was placed in a muffle furnace at 700°C and carbonization was done for 1 h. After cooling the excess zinc chloride present in the carbonized material was leached out by immersing in 1 M HCl solution for 24 h in an oven at 80°C. Then the carbon was repeatedly washed with water to get rid of traces of HCl and ZnCl$_2$.The carbonized material was sieved to 250 to 500 μm size and characterized using physico-chemical methods and used for adsorption studies [8].

Procedure

Equilibrium isotherms in two component system Phenol+2,4,6-trichlorophenol at a constant pH was determined using simultaneous adsorption method[19] as follows: To 100 mg of the adsorbent, added 50 ml of mixed solution containing phenol and chlorophenol at pH 2.0 at required concentrations and agitated for 2 h.

The supernatant was separated from the adsorbent by centrifugation at 10,000 rpm for 20 min. Then the supernatant was analyzed both for phenol and 2,4,6-trichlorophenol using HPLC at 270 and 290 nm, respectively. The mobile phase was methanol-water-acetic acid in the ratio 60:39:1. The analysis was carried out in an elution gradient mode with 60 % methanol using a flow rate of 1 ml/min at 35 °C [18]. The residual concentrations of phenol and chlorophenol were obtained from calibration curves. The same procedure was repeated for other combinations of phenol and 2, 4, 6-trichlorophenol (120 mg/L of P+40 mg/L of TCP; 40 mg/L of TCP +120 mg/L of P) in two component system.

3. Results and Discussions

The physio-chemical characteristics of ZnCl$_2$ activated coir pith nano porous carbon in comparison with coir pith carbon in the absence of ZnCl$_2$ activation have already been reported [20].

SEM Study

In SEM studies, ZnCl$_2$ activated coir pith carbon before adsorption (250 X magnifications) revealed honeycomb voids with a large number of pores (Fig.1a). After adsorption the pores were filled by TCP and phenol (Fig. 1b). Coverage of the surface of the adsorbent due to adsorption of the adsorbate molecule presumably leading to formation of a monolayer of the adsorbate molecule over the adsorbent surface is evident from the formation of white layer (molecular cloud) of uniform thickness and coverage (spread).The preparation of activated carbon from Tectona grandis sawdust with 10% ZnCl$_2$ after mixing and subjected to vaccum drying with 1000 times magnification reveals pores of different size and shapes and there was a scattering of salt particles on the surface of the activated carbon [21].

FTIR Study

IR spectra of the ZnCl$_2$ activated carbon before adsorption of phenols showed peaks at 3400 cm^{-1}, 2910 cm^{-1}, 2350 cm^{-1}, 1580 cm^{-1}, 1150 cm^{-1} and 674 cm^{-1} (Fig. 3a). Peak at 3400 cm^{-1} is assigned to OH stretching vibration. Band at 2910 cm^{-1} is ascribed to symmetric C-H stretching vibrations. Peak at 2350 cm^{-1} corresponds to strong O=C=O stretching vibrations. Asymmetric COO- vibration occurs at 1580 cm^{-1}. The 1150 cm^{-1} band may have contributions from both C-O stretching and O-H bending modes in phenolic groups [22].

Batch Mode Studies

(i) 60 mg/L of P + 120 mg/L of TCP

In this case, the maximum uptake of phenol as sole adsorbate (24.69 mg/g) was reduced in the presence of TCP in binary mixture to 17.13 mg/g. On the other hand, the adsorbed quantity of TCP (21.04 mg/g) in binary mixture slightly decreased compared to the sole adsorbate (23.98 mg/g)[23]. This shows that adsorption of phenol on the surface of ZnCPC was reduced in the presence of TCP for the active sites, whereas TCP got preferentially adsorbed in the presence of phenol occupying most of vacant sites. The greater electron density on TCP molecule supplies more π-electrons to interact with the ZnCPC resulting in a larger adsorption capacity.

(ii) 60 mg/L of TCP + 120 mg/L of P

The per cent adsorption of TCP in binary mixture slightly decreased (77.24 %) compared to the sole adsorbate (84.73 %) when low concentration of TCP was mixed with higher concentration of phenol. On the other hand, the uptake of phenol was suppressed to greater extent in the binary mixture (33.25 mg/g) compared to that of sole adsorbate (38.24 mg/g). This is due to lower solubility, greater electron density and lower pK_a value of TCP over phenol.

Modified Langmuir Model in Bisolute System

In the modified Langmuir model, an interaction term η which is a characteristic of each species and depends on the concentrations of the other components [24]. The modified Langmuir isotherm is written as

$$q_{eq,i} = \frac{Q_i^o b_i (C_{eq,i}/\eta_i)}{1 + \sum_{j=1}^{N} b_j (C_{eq,j}/\eta_j)}$$

(1)

where

b_1, b_2 = individual Langmuir adsorption constants of the first and the second solute related to the affinity of the binding sites, respectively, C_{eq1}, C_{eq2} is the unadsorbed concentrations of the first and the second solute, respectively, at equilibrium (mg/L), q_{eq1}, q_{eq2} is the adsorbed quantities of the first and the second solutes per gram at equilibrium, respectively (mg/g), Q_1^o, Q_2^o is the individual Langmuir adsorption capacity of the first and the second solutes respectively and η_1, η_2 is the multicomponent Langmuir adsorption capacity of the first and the second solute, respectively. The η values of chlorophenol (η_2) is higher than that of phenol (η_1) in any combination of phenol and 2,4,6-trichlorophenol. The calculated qe values of Langmuir multicomponent system agreed well with the experimental qe values in P+TCP system. These results show that the competitive, modified Langmuir isotherm provided a more realistic description of the adsorption process in bisolute system.

4. Conclusions

The present study shows that $ZnCl_2$ activated carbon developed from an agricultural waste, coir pith, is an effective adsorbent and phenol adsorption was suppressed to a great extent in the presence of TCP. Adsorption of TCP in bisolute and single solute systems showed that TCP was adsorbed preferentially, but phenol was adsorbed competitively. This result was further confirmed by η_1 and η_2 values obtained from extended Langmuir model. Lower solubility, molecular weight, nature and position of the substituent group, greater electron density and lower pKa value are responsible for preferential adsorption of TCP over phenol. These results would be useful for designing the removal of phenol/2, 4, 6-trichlorophenol from wastewaters in the treatment plants.

References

1. S.Kumar, M. Zafar, J.K. Prajapati, S.Kumar, S.Kannepalli, "Modeling studies on simultaneous adsorption of phenol and resorcinol onto granular activated carbon from simulated aqueous solution", J Haz Mat, vol: 185, pp**:**287-294, 2011.
2. A. Hasanoglu, "Removal of phenol from wastewaters using membrane contactors: Comparative experimental analysis of emulsion protraction", Desal, vol: 309, pp: 171-180, 2013.
3. M.Martinez, A.Campos, A.Garcia, C.L.Gonazalez.," Marine bacteria tolerant to chlorophenol degradative bacteria isolated from river receiving pulp mill discharges", Toxic Environ Microbiol, vol: 63, pp: 4145-4149, 2000.
4. V.M.Dominguez, J.Correa, G.Vidal, A.Lopez, M. Marttinez, "2, 4, 6-trichlorophenol degradation by river sediments exposed to bleached kraft mill discharge", Bull Env Cont Toxic, vol: 69, pp: 463-470, 2002.
5. W.Oh, P.Lim, C. Seng, A.N.A Sujari, "Bioregeneration of granular activated carbon in simultaneous adsorption and biodegradation of chlorophenols", Biores Tech, vol: 102, pp: 9497-9502, 2011.
6. Y.Li, Q.Du, T.Liu, J.Sun, "Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto grapheme", Mat Res Bull, vol: 47, pp: 1898-1904, 2012.
7. WHO. Guidelines for drinking water quality, Third edition incorporating the 1st and 2nd addenda, Geneva, WHO Press, World Health Organisation, Switzerland, 2008.
8. R.Subha, C. Namasivayam, "$ZnCl_2$ - modified activated carbon from biomass coir pith for the removal of 2-Chlorophenol by adsorption process". Bioremediation J, vol: 14, pp: 1-9, 2010.
9. J.M.Palacois-Santander, L.M Cubillana-Aguilera, M. Cocchi, A. Ulrici et al., "Multi component analysis in the wavelet domain of highly overlapped electrochemical signals: Resolution of quaternary mixtures of chlorophenols using a peg-modified Sonogel-Carbon electrode", Chem. Intel Lab Syst, vol: 12, pp: 34-38, 2007.
10. O. Aktas, F. Cecen, "Competitive adsorption and desorption of a bi-solute mixture: effect of activated carbon type", Adsorption, vol: 13, pp: 159-169, 2008.
11. V.M.Gunko, "Competitive adsorption", Thero. Exp. Chem, vol: 43, pp: 139-179, 2007.
12. D.M.Nevskaia, E.Castillejos-Lopez, V.Munoz, Guerrereo-ruiz, "Adsorption of aromatic compounds from water by treated carbon materials", Environ Sci Technol, vol: 38, pp: 5786-5796, 2004.

13. B. Koubaissy, G. Joly, P. Manoux, "Adsorption and competitive adsorption on zeolites of nitrophenol compounds present in wastewater", Ind Eng Chem Res, vol:47, pp: 9558-9565, 2008.

14. W.Zhang, C. Hong, B.Pan, Z.Xu, Q.Zhang,L.V. Lu, " Removal enhancement of 1-naphthol and 1-naphthylamine in single and binary aqueous phase by acid-basic interactions with polymer adsorbents" J Haz Mat,vol:158, pp: 293-299, 2008.

15. J.H. Kim,W.S. Shin, D.I.Song, S.J. Choi, "Multi-step competitive sorption and desorption of chlorophenols in surfactant modified montmorillonite" Water Air Soil Poll, vol: 166, pp:367-380, 2005.

16. C.Valderrama, J.I. Barios, M.Caetano, A. Farran, J.L.Cortina, "Kinetic evaluation of phenol/aniline mixtures adsorption from aqueous solutions onto activated carbon and hypercrosslinked polymeric resin (MN200)", React Funct polym, vol:70,pp:142-150, 2010.

17. R. Mihalache, I. Pelanu, I.Meghea, A.Tudorache, "Competitive adsorption models of organic pollutants from bi and tri solute systems on activated carbon" J Radioanalytical Nuclear Chem, vol:229,pp:133-137, 1998.

18. A.Garcia, L.Ferreria, A. Leitao, A.Rodrigues, "Binary adsorption of phenol and m- cresol mixtures onto a polymeric adsorbent" Adsorption, vol: 5, pp: 359-368, 1999.

19. F.Pagnanelli, M.Trifoni, F.Belochini, A.Esposito, L.Toro, F.Veglio,"Equilibrium biosorption studies in single and multi-metal systems", Process Biochem, vol:37, pp:115-124, 2001.

20. R.Subha, C.Namasivayam, "Removal and Recovery of PCP onto low cost nano porous carbon surface: Kinetics and Isotherms", J Solid Waste tech Manage, vol: 37, pp: 168-178, 2011.

21. K.Mohanty, D.Das, M.N.Biswas, "Adsorption of phenol from aqueous solutions using activated carbons prepared from Tectona grandis sawdust by $ZnCl_2$ activation", Chem Eng J, vol: 115, pp: 121-131, 2005.

22. Z.Jiang,Y. Liu, X. Sun, F. Tian, F. Sun, C.Liang, W. You, C. Han, C.Li, "Activated carbons chemically modified by concentrated H_2SO_4 for the adsorption of the pollutants from wastewater and the dibenzothiphene from fuel oils". Langmuir,vol: 19,pp: 731-736, 2003.

23. R.Subha, C. Namasivayam, "Kinetics and isotherm studies for the adsorption of phenol using low cost micro porous $ZnCl_2$ activated coir pith carbon", Can. J Civ. Eng, vol:8,pp: 1-12, 2009.

24. J.C.Bellot, J.S.Condoret, „Modelling of liquid chromatography equlibria. Process Biochem, vol: 28, pp: 365, 1993.