Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.770595

51 (2013) 6755–6760
October

Taylor & Francis
Taylor & Francis Group

Adsorption of phenol with the crosslinked polymer of P(MMA-MAh)-PEG_{33}

Yun Huang[a,b,*], Haijun Cao[c,*], Yuanhua Lin[a,b], Xu Wang[b], Zhe cheng[b]

[a]*State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China*
Tel. +86 28 8303740; Fax: +86 28 83037406; email: huangyun213@swpu.edu.cn
[b]*School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, China*
[c]*Institute of Blood Transfusion, Chinese Academy of Medical Sciences, Chengdu 610052, China*

Received 12 July 2012; Accepted 20 January 2013

ABSTRACT

The adsorption of phenol with the crosslinked polymer of P(MMA-MAh)-PEG_{33} was studied. Through the research, it was found the adsorption was favored in acidic aqueous solution and almost needed 35 h to reach the equilibrium. The calculated thermodynamic parameters suggested that the adsorption of phenol onto P(MMA-MAh)-PEG_{33} was spontaneous and exothermic in nature. From the kinetic research, the adsorption of phenol with the crosslinked polymer belonged to the first-order reaction. The adsorption isotherms of phenol with polymer well accorded with the Freundlich model.

Keywords: Phenol; Adsorption; Polymer adsorbent; Wastewater treatment

1. Introduction

Phenol is present in a great variety of waste effluent from different industries, such as paper mill, chemical industry, producing herbicide, fungicide, etc. It is considered to be very toxic to human through oral exposure, with ingestion of 1 g reported to be lethal. Inhalation and dermal exposure to phenol are highly irritating to the skin, eyes and mucous membranes in humans. Acute local effects are severe tissue irritation and necrosis. So it is very important to get some certain adsorbents to remove phenol from waste water because of the toxicity.

The removal of phenol has attracted considerable research interests over the years. Adsorption process has been used widely for the high efficiency removal of solute from aqueous solution. For the method of adsorption, adsorbent is the key point to achieve satisfactory efficiency. From the research reports, the most common types of adsorbents for phenol removal applications are plants [1–4], clays [5–10], activated carbons [11–13], and synthetic polymers [14–18] in which, clays and activated carbons were the better efficient materials to remove phenol in aqueous solution. But in these adsorbents, polymer adsorbent is easier to gain by synthesis method, while other adsorbents are natural resources and limited in origin. So based on the point, polymer considered as adsorbent will be the most important and potential substance in the far future. In addition, with the design idea of composition and structure, the polymer adsorbent can be synthesized by introducing a few certain functional groups to satisfy the effective removal of phenol

*Corresponding author.

under different condition [14–21]. The use of adsorption process has been expanding recently due to the innovation and development of new polymer adsorbent [19–21]. Polymer adsorbents are formed by linking long chains that have a variety of functional groups. The polyacrylate applied widely is one kind of common polymer, while oxyethylene chains (–CH_2–CH_2–O–) produces attraction for phenol in acid aqueous solution. So based on the points, one kind of new crosslinked polymer of P(MMA-MAh)-PEG_{33} was synthesized. In the research, the crosslinked polymer synthesized was adopted as the potential adsorbent to remove phenol. This work is an outgrowth of our attempts to understand the adsorption role of phenol with the crosslinked polymer of P(MMA-MAh)-PEG_{33}.

2. Materials and methods

2.1. Materials

Phenol was obtained from Kelong Chemical Reagent Co. The crosslinked polymer of P(MMA-MAh)-PEG_{33} presented in Scheme 1 was previously synthesized in our laboratory [22].

2.2. Adsorption process

Batch-mode adsorption experiments were carried out by placing the adsorbent into a conical flask which contain amount of phenol solution with a known concentration at certain pH and agitating the mixture using a temperature-controlled water bath shaker. The research of effect of the initial phenol solution pH, adsorbent dose, agitation time, and temperature on the adsorption efficiency was carried out.

2.3. Characterization

In order to calculate the concentration from each experiment, the calibration curve was first prepared. The concentration of phenol was determined spectrophotometrically using UNICO UV-2100 spectrophotometer (China). The value of λ_{max} was 269 nm for phenol. The amount of phenol adsorbed by the adsorbents was calculated.

$$\text{Removal } \% = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{C_0 - C_e}{m_s} \quad (2)$$

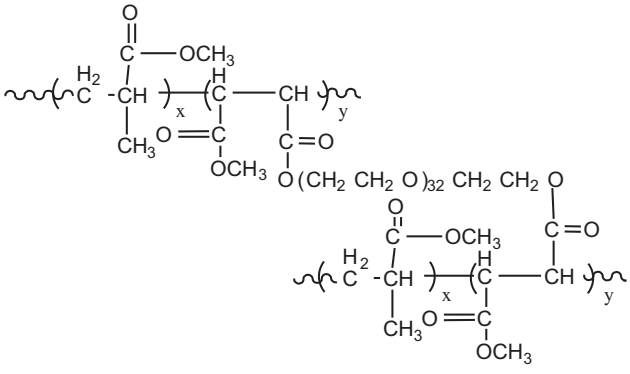
$$q_t = \frac{C_0 - C_t}{m_s} \quad (3)$$

C_0 and C_e (mg L^{-1}) denote the initial and equilibrium concentrations of phenol solution, respectively. m_s (g L^{-1}) is the adsorbent dose added into phenol solution. q_e and q_t (mg g^{-1}) are the phenol adsorption amount on adsorbent at equilibrium and time t, respectively.

3. Results and discussion

3.1. Effect of pH

Fig. 1 shows the removal of phenol as a function of pH between 3.0 and 9.0 for the adsorbent of crosslinked polymer. It can be seen that the optimum pH at which maximum removal of phenol occurred is observed over the range of 3.0–6.0. When pH is over the range of 6–9, adsorption gradually falls with



Scheme 1. Structure formula of crosslinked polymer (x:y = 8:1).

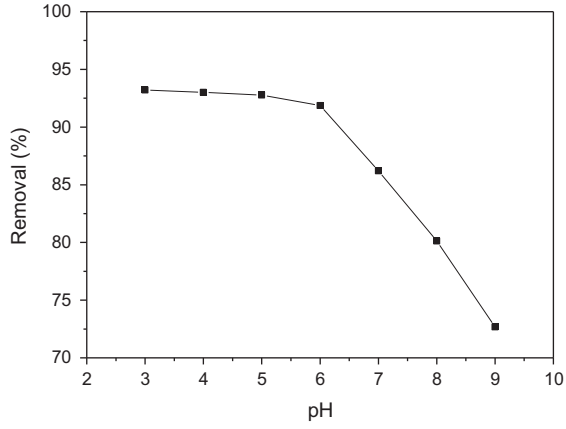


Fig. 1. The effect of initial solution pH on the removal (%). C_0 = 300 mg L^{-1}, m_s = 10 g L^{-1}, T = 25 °C, $t \geqslant 35$ h.

increasing basicity of the solution. But even in the basic solution of pH 7.0–9.0, the removal efficiency was larger than 70.0%. The phenomenon can be explained as that the crosslinked polymer produces organic phase which has better affinity with phenol molecule. The maximum removal of 93.21% was observed at pH 3.0, and the removal was 91.87% at pH 6.0. The effect of pH on phenol removal depends on the species of phenol in solution. In the low pH solution, the phenol molecule became cation and produced hydrogen bonding interaction with the oxygen atom in the long chain of $–CH_2–CH_2O–$ of the crosslinked polymer, which was presented in Scheme 2. So the hydrogen bonding between phenol molecule and adsorbent was the main driving force of phenol sorption onto P(MMA-MAh)-PEG_{33}. Considered both the application of wastewater treatment and the removal efficiency of phenol, the crosslinked polymer of P(MMA-MAh)-PEG_{33} was used as adsorbent to adsorb phenol in aqueous solution at the fixed pH 6 in the following experiments.

3.2. Effect of adsorbent dose

As shown in Fig. 2, the effect of adsorbent dose on both the removal (%) and the adsorption amount q_e ($mg\,g^{-1}$) of phenol was indicated. It was obvious that with the increasing of adsorbent dose (m_s) from 2.0 to 10.0 $g\,L^{-1}$, the phenol removal efficiency (%) and the equilibrium adsorption amount q_e increased and decreased from 30.27% to 91.87% and from 45.29 to 27.96 $mg\,g^{-1}$, respectively.

3.3. Effect of agitation time

The agitation time was one important influence factor to obtain satisfying result of adsorption. From Fig. 3, the initial drastic removal of phenol increased

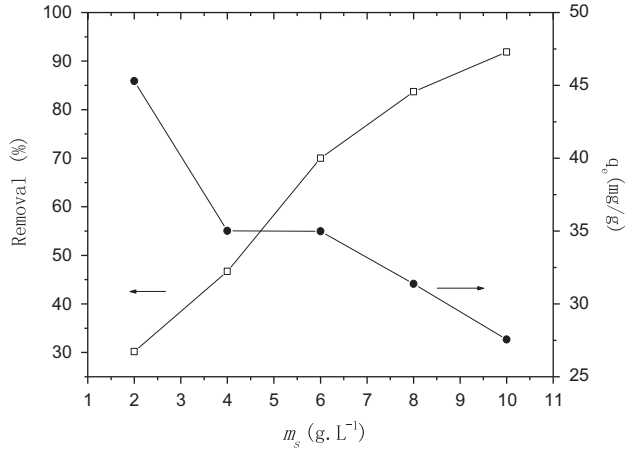


Fig. 2. The effect of adsorbent dose on the removal (%) and adsorption amount q_e ($mg\,g^{-1}$). $C_0 = 300\,mg\,L^{-1}$, pH = 6, $T = 25$℃, $t \geqslant 35$ h.

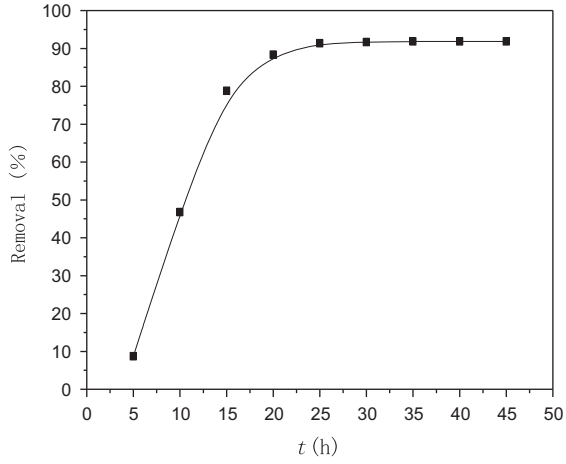
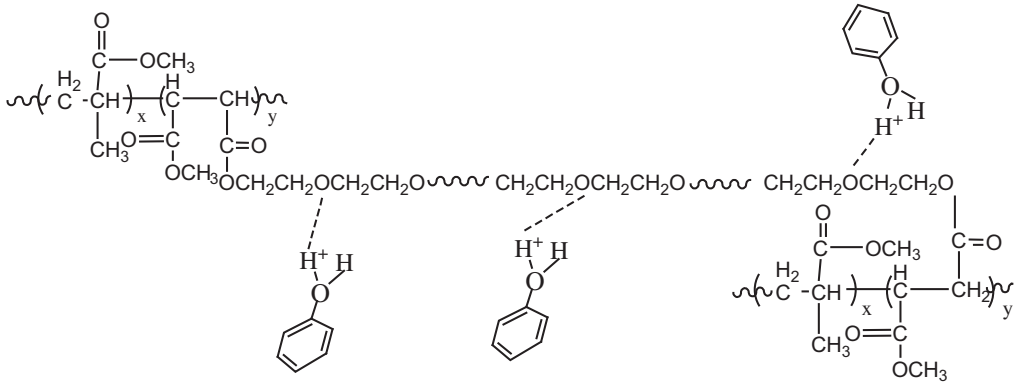


Fig. 3. The effect of adsorption time on the removal (%). $C_0 = 300\,mg\,L^{-1}$, $m_s = 10\,g\,L^{-1}$, pH = 6, $T = 25$℃.



Scheme 2. The hydrogen bonding interaction between phenol and P(MMA-MAh)-PEG33.

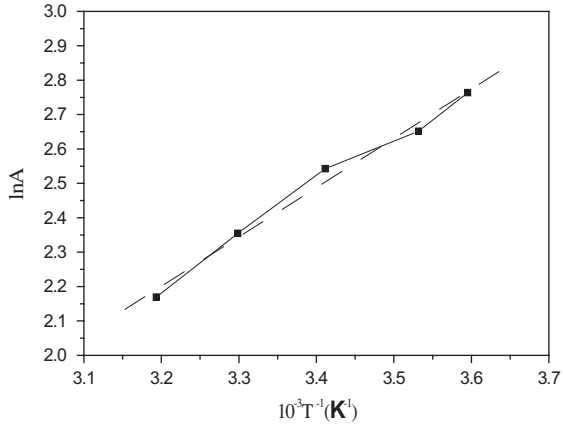


Fig. 4. The thermodynamics plots of adsorption. $C_0 = 300\,mg\,L^{-1}$, $m_s = 10\,g\,L^{-1}$, pH = 6, $t \geqslant 35h$.

up to 88.36% within 20 h. A platform was gradually formed when time was more than 25 h, indicating that the adsorption capacity of crosslinked polymer was nearly saturated. When the agitation time was 35 h, the removal reached maximum value of 91.87%.

3.4. Thermodynamics analysis

The thermodynamics analysis of adsorption can provide useful information concerning the evidence of spontaneity of adsorption reaction. The following equation describes the adsorption thermodynamics of phenol with the crosslinked polymer.

$$\ln A = \frac{-\Delta H}{RT} + \frac{2.303\Delta S}{R} \quad (4)$$

where A is the allocation coefficient, $A = C_s/C_e$. C_s and C_e ($mg\,L^{-1}$) are the equilibrium concentration of phenol adsorbed on adsorbent and reserved in solution, respectively. ΔH and ΔS are enthalpy change and entropy change, respectively. R denotes the gas law constant ($8.314\,J\,mol^{-1}K^{-1}$), and T is the absolute temperature (K).

In Fig. 4, the plot of ln A vs. $1/T$ was found to be linear. The negative value of ΔH calculated in Table 1 suggested the exothermic nature of the process. Usually, adsorption processes are exothermic whether adsorption occurs from chemical or physical forces. The fast-moving phenol molecule loses kinetic energy when adsorbed on the solid adsorbent, which results in the liberation of heat. The negative value of ΔS shows the decreased randomness at the solid/solution interface during the adsorption of phenol on the crosslinked polymer and also reflects the affinity between the adsorbent material and the organic molecular of phenol. According to thermodynamics formula $\Delta G = \Delta H - T\Delta S$, the negative value of ΔG suggests that the process is spontaneous.

3.5. Adsorption kinetics

Determination of the kinetic parameters and explanation of the mechanism in heterogenenous system are often complex procedures, as surface effects can be superimposed on chemical effects. The adsorption of phenol from aqueous solution to the solid phase of crosslinked polymer can be considered as the first-order reaction. So the following integrated rate expression is used to calculate the rate constant (k_{ad}) value:

$$\ln(q_e - q_t) = \ln q_e - k_{ad} \times t \quad (5)$$

where q_e and q_t are the amount of phenol adsorbed ($mg\,g^{-1}$) at equilibrium and time t, respectively, and K_{ad} is the first order rate constant.

Fig. 5 is the adsorption kinetic of phenol onto the crosslinked polymer and presents the relation of ln ($q_e - q_t$) vs. time. As shown in Fig. 5, the value of ln ($q_e - q_t$) linearly decreased with the increase in agitation time, so it concluded the adsorption of phenol with the crosslinked polymer belonged to the first-order reaction. The rate constant of adsorption at different concentration was determined from the slope of plot using a regression analysis. At 25°C, the k_{ad} value of P(MMA-MAh)-PEG_{33} at initial concentration of 50, 100, 200, and $300\,mg\,L^{-1}$ was 0.24, 0.24, 0.25, and $0.26\,h^{-1}$, respectively. The rate constant was very near with increasing initial concentration. The findings clearly indicate that phenol removal by adsorption on

Table 1
Thermodynamics model of three kinds of adsorbents and thermodynamic parameters

Adsorbent	Linear relation coefficient r	Adsorption thermodynamics equation	ΔH/ ($kJ\,mol^{-1}$)	ΔS/ ($J\,mol^{-1}\,K^{-1}$)	ΔG/ ($kJ\,mol^{-1}$)
P(MMA-MAh)-PEG_{33}	0.995	$\ln A = 1.43 \times 10^3/T - 2.37$	−11.89	−8.56	−9.34

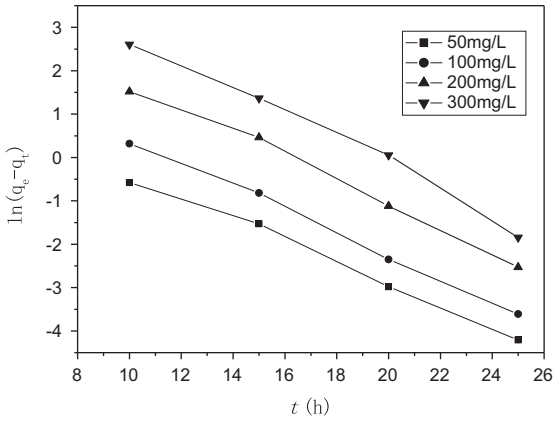


Fig. 5. $\ln(q_e\text{-}q_t)$ vs. time plots for the adsorption of phenol. $C_0 = 50$, 100, 200, 300 mg L^{-1}, $m_s = 10$ g L^{-1}, pH = 6, $T = 25$°C, $t \geqslant 35$ h.

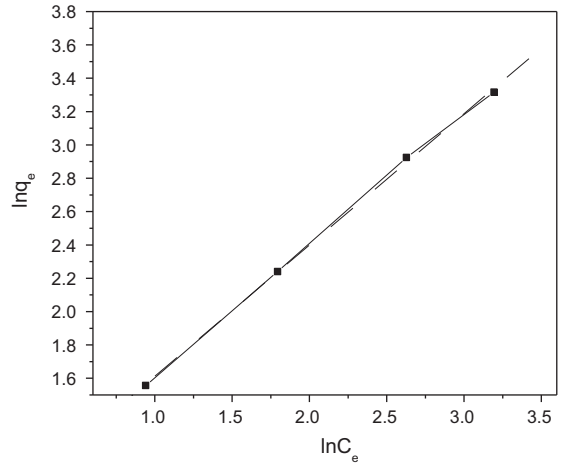


Fig. 6. Adsorption isotherm of phenol. $C_0 = 50$, 100, 200, 300 mg L^{-1}, $m_s = 10$ g L^{-1}, pH = 6, $t \geqslant 35$ h, $T = 25$°C.

crosslinked polymer was totally independent of the initial concentration.

3.6. Adsorption isotherm

The research of adsorption isotherm can provide the information of adsorption mechanism of phenol onto the crosslinked polymer. In Fig. 6, the adsorption isotherm accorded with the Freundlich equation was depicted. It was shown that the adsorption of phenol satisfied the Freundlich equation of the type.

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (6)$$

where K_F and $1/n$ are constants and considered to be relative indicators of adsorption capacity and adsorption intensity, respectively. The values of these constants were listed in Table 2. The adsorption isotherm of phenol with the crosslinked polymer was shown in Fig. 6. The isotherm ascended almost linearly within the equilibrium concentration. The value of $0.1 < 1/n < 1.0$ indicated the favorable adsorption of phenol on the crosslinked polymer.

Table 2
Adsorption coefficient K_F and adsorption constant n of Freundlich isotherm

Adsorbent	Linear relation coefficient, r	Adsorption coefficient, K_F	Adsorption constant, $1/n$
P(MMA-MAh)-PEG_{33}	0.998	2.27	0.79

4. Conclusions

In order to achieve the promising adsorption efficiency of phenol with the crosslinked polymer of P(MMA-MAh)-PEG_{33}, the optimum condition was initial phenol solution pH 6, adsorbent dose 10 g L^{-1} for the initial phenol concentration of 300 mg L^{-1} and adsorption time of 35 h at room temperature. The research results of thermodynamics and kinetic of adsorption implied the adsorption process carried out spontaneously and belonged to the first-order reaction, respectively. The adsorption isotherm demonstrated that the mechanism of adsorption was Freundlich model. The present results indicated that P(MMA-MAh)-PEG_{33} was a powerful potential alternative for replacing other adsorbents for removing phenol from aqueous solutions.

Acknowledgement

The authors gratefully acknowledge the financial support from the Open Fund (PLN1111) of State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation of Southwest Petroleum University, Youth Fund of Educational Committee of Sichuan Province (10ZB112) and the Specialized Research Fund for the Doctoral Program of Higher Education of China (20115121120005).

References

[1] N. Roostaei, F.H. Tezel, Removal of phenol from aqueous solutions by adsorption, J. Environ. Manage. 70 (2004) 157–164.
[2] G. Dursun, H. Çiçek, A.Y. Dursun, Adsorption of phenol from aqueous solution by using carbonised beet pulp, J. Hazard. Mater. 123 (2005) 175–182.

[3] A.Y. Dursun, Ç.S. Kalayci, Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto chitin, J. Hazard. Mater. 123 (2005) 151–157.
[4] A.T. Mohd Din, B.H. Hameed, A.L. Ahmad, Batch adsorption of phenol onto physiochemical-activated coconut shell, J. Hazard. Mater. 161 (2009) 1522–1529.
[5] S. Mirmohamadsadeghi, T. Kaghazchi, M. Soleimani, N. Asasian, An efficient method for clay modification and its application for phenol removal from wastewater, Appl. Clay Sci. 59–60 (2012) 8–12.
[6] T. Kawai, K. Tsutsumi, Adsorption characteristics of surfactants and phenol on modified zeolites from their aqueous solutions, Colloid Polym. Sci. 273 (1995) 787–792.
[7] S. Yapar, V. Özbudak, A. Dias, A. Lopes, Effect of adsorbent concentration to the adsorption of phenol on hexadecyl trimethyl ammonium-bentonite, J. Hazard. Mater. 121 (2005) 135–139.
[8] K. Lin, J. Pan, Y. Chen, R. Cheng, X. Xu, Study the adsorption of phenol from aqueous solution on hydroxyapatite nanopowders, J. Hazard. Mater. 161 (2009) 231–240.
[9] R.I. Yousef, B. El-Eswed, A.H. Al-Muhtaseb, Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: Kinetics, mechanism, and thermodynamics studies, Chem. Eng. J. 171 (2011) 1143–1149.
[10] Y. Huang, X.Y. Ma, G.Z. Liang, H.X. Yan, Adsorption of phenol with modified rectorite from aqueous solution, Chem. Eng. J. 141 (2008) 1–8.
[11] E. Fernandez, D. Hugi-Cleary, M.V. López-Ramón, F. Stoeckli, Adsorption of phenol from dilute and concentrated aqueous solutions by activated carbons, Langmuir 19 (2003) 9719–9723.
[12] S. Altenor, B. Carene, E. Emmanuel, J. Lambert, J.J. Ehrhardt, S. Gaspard, Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation, J. Hazard. Mater. 165 (2009) 1029–1039.
[13] L.A. Rodrigues, M.L.C.P. Silva, M.O. Alvarez-Mendes, A.R. Coutinho, G.P. Thim, Phenol removal from aqueous solution by activated carbon produced from avocado kernel seeds, Chem. Eng. J. 174 (2011) 49–57.
[14] J. Huang, X. Jin, S. Deng, Phenol adsorption on an N-methylacetamide-modified hypercrosslinked resin from aqueous solutions, Chem. Eng. J. 192 (2012) 192–200.
[15] D.S. Farrier, A.L. Hines, S.W. Wang, Adsorption of phenol and benzoic acid from dilute aqueous solution onto a macroreticular resin, J. Colloid Interface Sci. 69 (1979) 233–237.
[16] H. Li, M. Xu, Z. Shi, B. He, Isotherm analysis of phenol adsorption on polymeric adsorbents from nonaqueous solution, J. Colloid Interface Sci. 271 (2004) 47–54.
[17] X. Zeng, H. Yao, N. Ma, Y. Fan, C. Wang, R. Shi, Synthesis, characterization and adsorption performance of a novel post-crosslinked adsorbent, J. Colloid Interface Sci. 354 (2011) 353–358.
[18] T.T. Cesar, A.F. María, F.G. Carmen, A.D. Manuel, G.S. Vicente, Development of adsorbents from used tire rubber: Their use in the adsorption of organic and inorganic solutes in aqueous solution, Fuel Process Technol. 92 (2011) 206–212.
[19] I.Y. Ipek, N. Kabay, M. Yüksel, D. Yapıcı, Ü. Yüksel, Application of adsorption-ultrafiltration hybrid method for removal of phenol from water by hypercrosslinked polymer adsorbents, Desalination 306 (2012) 24–28.
[20] M. Jáckowskaa, S. Bociana, B. Gawdzikb, M. Grochowiczb, B. Buszewskia, Influence of chemical modification on the porous structure of polymeric adsorbents, Mater. Chem. Phys. 130 (2011) 644–650.
[21] P.S. Suchithra, L. Vazhayal, A.P. Mohamed, S. Ananthakumar, Mesoporous organic-inorganic hybrid aerogels through ultrasonic assisted sol-gel intercalation of silica-PEG in bentonite for effective removal of dyes, volatile organic pollutants and petroleum products from aqueous solution, Chem. Eng. J. 200–202 (2012) 589–600.
[22] Y. Huang, X. Ma, Y. Lin, X. Wang, Study on the interaction between lithium ion and polar group in GPE based on the crosslinked polymer of P(MMA-MAh)-PEG1500 with FTIR, Acta Chim. Sinica 70 (2012) 591–598.