Adsorption properties of 4-Phenylphenol in aqueous solution with adsorption resins chemically modified

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The hypercrosslinked adsorption resins modified with atrazine (named KCZ-1), o-Phthalic anhydride(named KCZ-2), trimellitic anhydride(named FJ-1) and 2-Imidazolidone hemihydrate(named FJ-2) respectively were successfully prepared by the crosslinking and chemical modification reaction and characterized by IR and BET. The structural characterization results indicated that the resins possessed predominant micropores/mesopores, moderate specific surface area. The adsorption capacity of 4-Phenylphenol onto the four resins was very large due to hydrogen bond interaction between 4-Phenylphenol and modified group on the resins. Adsorption behaviors of 4-Phenylphenol onto the KCZ-1, KCZ-2, FJ-1 and FJ-2 resins were studied by isotherm adsorption and adsorption kinetics experiments. Moreover, the adsorption thermodynamics and adsorption kinetics are also calculated to study adsorption mechanism of the adsorption of 4-Phenylphenol on adsorption resins. The isotherms were correlated by the Langmuir and Freundlich equations and the Langmuir equation was shown to be the most suitable. The enthalpy change ΔH is positive, and Gibb's free energy change ΔG and entropy change ΔS were calculated to be negative. The efficiency of dynamic adsorption on FJ-1 resin is better than that on other resins. When temperature was 333K, nearly 75% regeneration efficiency for the adsorbent was achieved at the flow rate of 0.5BV/h.

Key words: Resin, 4-Phenylphenol, Adsorption, Adsorption isotherms, Dynamic adsorption, Desorption.

INTRODUCTION

4-Phenylphenol($C_{12}H_{10}O$), also known 4-Hydroxybiphenyl, an important phenol chemical and widely used as fungicide and preservative agent in agriculture and industry, slightly soluble in water, soluble in methanol, acetone, benzene and organic solvents. 4-Phenylphenol has other bactericidal and is widely used in households, industry, and hospitals to disinfect surfaces, in addition to being utilized as a preservative in cosmetics, plastics, lame retardants antisepsis and sterilizing of fruit and vegetable, etc.[1-3]. However, 4-Phenylphenol is a toxic organic pollutant in the industrial waste water, which will be harmful to human being and animals even at low concentrations [4,5]. Therefore, remediation of aromatic compounds containing waste water is an imminent and important issue for environmental protection.

In recent years, a wide range of physical and chemical technologies including photocatalytic oxidation, membrane separation, electrochemical oxidation, solvent extraction, ion exchange and adsorption are employed for aromatic compounds removal from aqueous solution [6-8], among which the adsorption-based process is probably the most favorable treatment option due to its efficacy, practicality and economic feasibility [9]. Several of

materials have been used as adsorbents, including polymeric resins [10], activated carbon and so on [11]. Although activated carbons exhibit an excellent adsorption capacity 4-Hydroxybiphenyl removal from waste water, the used activated carbon adsorbents are difficult to regenerate and quite expensive to dispose. Therefore, it is necessary to look for alternative adsorbents that are equally effective and easier to regenerate and dispose. Recently, a new kind of hypercrosslinked polymeric adsorbent was found to be very effective for removing aromatic compounds from aqueous solution [12,13]. Since the 1970s, hypercrosslinked resins are recognized as one kind of efficient polymeric adsorbents for adsorptive removal of aromatic compounds from aqueous solution [14,15]. The hypercrosslinked resins owe their high adsorption potential due to their unique synthesis method. In general, they are synthesized from linear polystyrene-divinylbenzene polymer (PS) or low crosslinked PS by adding bi-functional cross-linking reagants such monochloromethylether, 1,4-bis(chloromethyl) benzene, and FriedelCrafts catalysts including anhydrous zinc chloride, iron (III) chloride, aluminum (III) chloride and stannic (IV) chloride are employed in the synthesis procedure. They can also be prepared from macroporous low cross-linked chloromethylated PS its self-fielder-Crafts reaction [16]. After the

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corresponding reactions. the obtained hypercrosslinked PS networks consist of an intensive bridging of strongly solvated PS chains with conformationally rigid links, leading to a major shift of their pore diameter distribution from predominately mesopores to mesopores-micropores bimodal distribution, and hence results in a sharp increase of the Brunauer–Emmet–Teller (BET) surface area and pore volume [17, 18]. Because of these significant changes, the hypercrosslinked resin displays very large adsorption capacities towards non-polar and weakly polar aromatic compounds in aqueous solution. In order to increase their adsorption capacities towards polar aromatic compounds, the resins are often modified by introducing polar units into the copolymers, using polar compounds as the crosslinking reagent and addition of polar compounds in the Friedel-Crafts reaction [19, 20]. The previous studies indicated that the chemically modified hypercrosslinked resins exhibited improved adsorption properties toward polar aromatic compounds by introducing certain specific functional groups on their surface [21].

In this paper, the hypercrosslinked adsorption resins modified with atrazine (named KCZ-1), o-Phthalic anhydride(named KCZ-2), trimellitic anhydride(named FJ-1) and 2-Imidazolidone hemihydrate(named FJ-2)respectively, were successfully prepared by the cross-linking and chemical modification reaction. The adsorption properties and adsorption mechanism of 4-Hydroxybiphenyl onto the KCZ-1, KCZ-2 and FJ-1, FJ-2 resins were studied by isotherm adsorption, dynamic adsorption and desorption.

EXPERIMENTAL

Materials

Analytical methods

Styrene-divinylbenzene copolymer was purchased from Nanjing Maike Fei Co. LTD. Amino sulfonic acid and Trimellitic anhydride was purchased from Element Mall. nitrobenzene, anhydrous aluminum chloride and hydrochloric acid were analytical grade, which were purchased from Shanghai Chemical Reagent. Ethanol, nitrobenzene, anhydrous aluminum chloride and hydrochloric acid were analytical

grade, which were purchased from Shanghai Chemical Reagent.

DF-101S collector-type thermostat heating magnetic stirrer(Zhengzhou Great Wall Branch Co,Henan,China.); Pore surface area analyzer Micromeritics,ASAP2010,USA); High Performance Liquid Chromatography (HPLC,ULTIMATE 3000, Thermo-Fisher, USA); Infrared spectrometer (IR, Bruker company Vertex 80 Switzerland).

The synthesis of adsorption resins

Fifteen of chloromethylcated grams styrenedivinylbenzene copolymer (CLPs) were dried at 333K in vacuum for 12 h, and then fully swollen in nitrobenzene at room temperature for 12h. After that, the mixture of the CLPs and nitrobenzene is heated to 353K while stirring, six grams atrazine and seven point five grams aluminum chloride were added to respectively the reaction system above and then the reaction was kept at this temperature for 8 h under a moderate stirring. The atrazine modified mechanical hypercrosslinked resin was obtained accordingly. After the reaction, the solid particles from the reaction mixture were filtrated. the atrazine modified hypercrosslinked resin was firstly rinsed by 1% hydrochloric acid (in ethanol) to remove unreacted nitrobenzene, followed by 10% sodium hydroxide solution, 5% hydrochloric acid and deionized water until neutral pH. Finally, the resin was extracted by ethanol for 8 h and dried under vacuum at 323 K for 8 h. Atrazine is replaced by o-Phthalic anhydride, trimellitic anhydride and 2-Imidazolidone hemihydrate respectively under the same conditions in order to obtain a series of hypercrosslinked adsorption resins (named KCZ-1, KCZ-2, FJ-1 and FJ-2) respectively. Synthetic process was shown in fig.1.

Characterization of adsorption resins

The pore structure of the resins such as specific surface area, microporous area, micropore volume and average pore radius were measured by BET(Bruaaures. S-Emmett H-Teller) method. The concentration of 4-Phenylphenol in aqueous solution was analyzed by HPLC. The IR spectra of the resin were determined by FT-IR spectrometer.

$$\begin{array}{c} -\text{CH-CH}_2\text{-CH-}\\ -\text{CH-CH}_2\text{-CH-}\\$$

Fig.1. The synthetic procedure of modified resin

The Fourier transforms infrared spectroscopy (FT-IR) of adsorption resins were collected with a pellet of powdered potassium bromide and resin on a Vertex 80 infrared spectroscopy (FT-IR) of adsorption resins were collected with a pellet of powdered potassium bromide and resin on a Vertex 80 infrared spectrometer. Results were shown in Fig.2: The results show that the functional groups have been successfully modified. Surface property of resins was shown in Table 1.

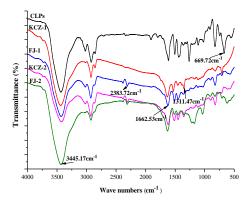


Fig. 2. IR spectra of resins and CLPS

Table. 1. Surface property of resins

Propertie	KCZ-1	KCZ-2	FJ-1	FJ-2
Specific surface area (m²/g)	743.9	761.0	804.7	768.5
Average pore radius (nm)	2.58	1.10	3.69	1.33
Microporous area (m^2/g)	455.2	393.8	689.5	581
Microporous volume (mL/g)	61.02	40.42	24.96	2.60

Adsorption isothermal experiment

Adsorption equilibrium data were determined by contacting about 0.1000 g of resin with 100 ml of 4-Phenylphenol aqueous solution. The nitial concentration of 4-Phenylphenol, C₀(mg/l), was set to be about 100, 200, 300, 400, 500 mg/l. Then the conical flasks having a series of different concentrations were shaken in a temperature oscillator for twenty four hours to reach equilibrium at speed of 110 rpm and temperature (288, 303, 313 and 288K*). After the adsorption equilibrium, 1.5ml equilibrium solution was withdrawn with the injector and the equilibrium concentration of 4-Phenylphenol, Ce(mg/l), was determined by HPLC. The equilibrium adsorption capacity of 4-Phenylphenol on the resin, Qe (mg/g), was calculated according to the following formula:

$$Qe = (C_0 - Ce)V/W$$
 (1)

Where Ce is the equilibrium concentration of the adsorbate (mg/L), Qe is the equilibrium adsorption capacity (mg/g). C_0 is the initial concentration (mg/L), V is the solution volume (L), W is resins weight (g).

Dynamic adsorption and desorption

1BV(1BV=10mL, BV is the volume of resin bed) wet resins were packed in the glass column(16mm of diameter) to assembly a resin column at 288K. The initial concentration of 4-Phenylphenol was 400mg/L and passed through the resin column at a flow rate. The residual concentration of 4-Phenylphenol in the effluent from the resin column, C1 (mg/L), was recorded until it almost reached the initial concentration. The effluents from the column were quantitatively. The concentrations 4-Phenylphenol compounds were determined by

using HPLC. After the dynamic adsorption, ethanol (v/v) passed through the resin column for the desorption process, the effects of desorption temperature and desorption velocity on the desorption properties of the resin were investigated.

RESULTS AND DISCUSSION

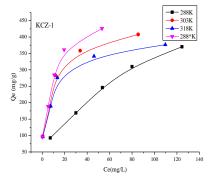
Static equilibrium adsorption isotherm

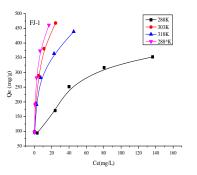
The relationship curve of equilibrium adsorption capacity of the adsorbate on the adsorbent (Qe) and solution equilibrium concentration of the adsorbate (Ce) is called the adsorption isotherm at constant temperature. As shown in Fig.3, the equilibrium adsorption capacity of 4-Pheylphenol on the KCZ-1. KCZ-2, FJ-1, FJ-2 increases with the increment of equilibrium adsorption concentration. The overall adsorption capacity of 4-Phenylphenol on the KCZ-1, KCZ-2 and FJ-1 resins were better than that on FJ-2 resin at the same temperature and concentration, this was mainly because that the specific surface area of the FJ-2 resins was less than the other resins. The adsorption capacity of 4-Phenylphenol on the KCZ-1, KCZ-2, FJ-1 and FJ-2 resins increased with increasing temperature from 288K to 303K, which shows that the adsorption process is mainly chemical adsorption. Compared with those in 303K, the adsorption capacity of 4-Phenylphenol decreased when the temperature increased to 318K, which is mainly due to the increment of temperature continuously. Although it is beneficial to the chemical adsorption, the physical adsorption force decreased obviously. adsorption increased capacity of irreversible chemical action less than decreased adsorption capacity of physical adsorption. Therefore. the adsorption capacity 4-Phenylphenol on the resins decreased. When the temperature dropped from 318K to 288K*, the adsorption capacity of 4-Phenylphenol was significantly higher than that of the adsorption capacity of 4-Phenylphenol on the resins at 288K. This also shows that the adsorption process does have a strong irreversible chemical adsorption.

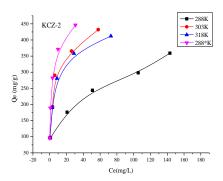
The Langmuir equations for the equilibrium adsorption can be written as:

$$Ce/Qe = 1/(K_L \times Qm) + Ce/Qm$$
 (3)

Where Qe is the equilibrium adsorption capacity (mg/g) with the equilibrium concentration Ce , Qm is the maximum monolayer adsorption capacity (mg/g) and K_L is a Langmuir constant related to adsorption energy (l/mg).







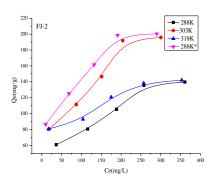


Fig.3. Equilibrium adsorption isotherms of 4-Phenylphenol on resins at different temperatures.

The Freundlich equations for the equilibrium adsorption can be written as:

$$lnQe=1/nlnCe+lnK_F$$
 (4)

Where K_F [(mg/g)(l/mg)1/n] and n are the characteristic constants and they are temperature dependent. The parameter n is usually greater than

unity. As this value becomes larger, the adsorption isotherm becomes more nonlinear as its behavior deviates further away. When the n value is less than 1, it is non preferential adsorption; when the n value is more than 1, it is preferential adsorption; when the n value is 1, it is linear adsorption.

According to the research of Zhang Y *et al*, the adsorption data can be fitted by Langmuir and Freundlich equation, and the results were shown in Table.2 and Table.3.

Table.2. Fitting result of the Langmuir isotherm equation

Resins	Т	Ce/Qe= Ce/ Qm	R^2	Qm	KL*
Kesiiis	(K)	$+1/(K_L \bullet Qm)$		QIII	
	288	Ce/Qe=0.0022 Ce +0.0699		454.5	0.0290
	303	Ce/Qe=0.0021 Ce +0.0283		476.1	0.0811
KCZ-1	318	Ce/Qe=0.0026 Ce +0.0165		384.6	0.247
	288*	Ce/Qe=0.0023 Ce +0.0045		434.8	0.526
	288	Ce/Qe=0.0032 Ce +0.0304		312.5	0.101
KCZ-2	303	Ce/Qe=0.0021 Ce +0.0181		476.2	0.163
	318	Ce/Qe=0.0023 Ce +0.0104		434.8	0.217
	288*	Ce/Qe=0.0022 Ce +0.0062		454.5	0.530
FJ-1	288	Ce/Qe=0.0031 Ce +0.0501		322.6	0.0680
	303	Ce/Qe=0.0021 Ce +0.0204		476.2	0.0922
	318	Ce/Qe=0.0022 Ce +0.0103			0.235
	288*	Ce/Qe=0.0021 Ce +0.0025		479.2	0.834
	288	Ce/Qe=0.0054 Ce +0.3079		185.2	0.0360
FJ-2	303	Ce/Qe=0.0044 Ce +0.4017		227.3	0.0100
	318	Ce/Qe=0.0066 Ce +0.1807		151.5	0.0360
	288*	Ce/Qe=0.0051Ce +0.1003	0.9726	196.1	0.0490

As shown in Table 2 and Table 3, the value of the correlation coefficient (R²) in the Langmuir isotherm model is more than 0.98 for KCZ-1, KCZ-2, FJ-1, FJ-2 resins, which suggested that the Langmuir isotherm model was more suitable to fit

the adsorption equilibrium data. The Langmuir is thermal adsorption equation is based on the homogeneous solid adsorbent surface, it is the single molecular layer adsorption. Moreover, for the FJ-1 resins, the R² in the Freundlich isotherm model and in the Langmuir isotherm model were all greater than 0.99, which suggested that the Langmuir isotherm model and Freundlich isotherm model can fit the experimental data well. In addition, for the KCZ-1, KCZ-2, FJ-1 and FJ-2 resins, the parameters n in Freundlich isotherm model at different temperatures were all greater than 1, which found the four kinds of resins are preferential adsorption for 4-Phenylphenol.

Table. 3. Fitting result of the Freundlich isotherm equation

Resins T (K)		lnQe=1/nlnCe +lnK _F	R^2	n	KF*
	288	lnQe=04902lnCe +3.4962	0.9771	2.03	32.9
	303	lnQe=0.307lnCe +4.8028	0.9601	3.25	122
KCZ-1	318	lnQe=0.262lnCe +4.8033	0.9559	3.82	122
	288*	lnQe=0.2441lnCe +5.0610	0.9401	4.09	158
	288	lnQe=0.1592lnCe +4.5401	0.9293	6.28	93.7
KCZ-2	303	lnQe=0.2704lnCe +5.0172	0.9905	3.69	151
	318	lnQe=0.2903lnCe +5.0058	0.9779	3.44	149
	288*	lnQe=0.2792lnCe +5.3017	0.9902	3.58	200
	288	lnQe=0.3099lnCe +4.0972	0.9870	3.23	60.0
	303	lnQe=0.3399lnCe +5.1027	0.9982	2.94	164
FJ-1	318	lnQe=0.3148lnCe +5.0160	0.9906	3.18	157
	288*	lnQe=0.2939lnCe +5.3027	0.9970	3.40	201
	288	lnQe=0.4803lnCe +2.2901	0.9090	2.08	9.87
FJ-2	303	lnQe=0.4002lnCe +3.2038	0.9027	2.49	24.6
	318	lnQe=0.2008lnCe +3.7999	0.9750	4.98	44.7
	288*	lnQe=0.2592lnCe +4.0710	0.9017	3.85	58.6

Because the n value is larger, the adsorption performance is better. Moreover, the n value for KCZ-1, KCZ-2, FJ-1 is larger than that for FJ-2, indicating that the adsorption performance for 4-Phenylphenol on the KCZ-1, KCZ-2 and FJ-1 resins is better than that on the FJ-2 resins.

Adsorption thermodynamics

The enthalpy change of adsorption and the adsorption capacity are closely related, when the adsorption capacity is fixed at a constant value, the adsorption enthalpy change is known as the equivalent enthalpy change. The adsorption enthalpy change can be calculated by Clausius-Clapeyron equation:

$$lnCe = \Delta H/RT - lnK$$
 (5)

Where Ce is the equilibrium concentration of the adsorbate (mg/L). Here Ce was obtained from the fitted isotherms by the Langmuir equation at a defined qe. T is the absolute temperature (K), ΔH is the isosteric enthalpy change of adsorption (kJ/mol), R is the ideal gas constant (8.314 J/mol) and K is a constant. ΔH was determined by plotting lnCe versus 1/T and could be calculated from the slope of the fitting line.

Adsorption free energy can be calculated as:

$$\Delta G = -nRT \tag{6}$$

Where ΔG is the adsorption free energy (kJ/mol), n represents the Freundlich exponent and R is the ideal gas constant (8.314 J/mol K).

The adsorptive entropy change, $\Delta S(J/mol \cdot k)$ were calculated using the Gibbs–Helmholtz equation:

$$\Delta S = (\Delta H - \Delta)G/T \tag{7}$$

As shown in Table.4, The value of ΔH were all positive indicating an endothermic process and 4-Phenylphenol is more easily adsorbed with temperature rising. The negative values of ΔG also indicated the adsorbate tends to adsorb from the solution to the surface of the adsorbent, suggesting the adsorption of 4-Phenylphenol on the KCZ-1, KCZ-2, FJ-1 and FJ-2 resin were spontaneous. Moreover, the absolute value of the free energy of adsorption increased with the rising of temperature, indicating that the trend of adsorption is much easier and rising of temperature was beneficial to adsorption. Positive values of ΔS showed the increasing randomness of the solid-solution interface during the adsorption of 4-Phenylphenol onto four kinds of resins. These positive values of ΔS might be due to the presence of the adsorbent surface chemisorption though degrees of freedom of adsorbate drop during the adsorption of 4-Phenylphenol. These results further show that exist irreversible chemical adsorption during the adsorption of 4-Phenylphenol on four kinds of resins.

Table.4. Thermodynamic parameters of 4-Phenylphenol adsorption based on resins at different temperatures

Resins $\frac{\Delta H}{(KJ/mol)}$		ΔG	ΔG(KJ/mol)			ΔS(J/mol·k)		
		288K	303K	318K	288K	303K	318K	
KCZ-1		-4.272					199	
KCZ-2	32.7	-15.1	-9.51	-9.27	169	138	136	
FJ-1	53.6	-7.71	-7.38	-8.50	215	202	196	
FJ-2	12.8	-5.04	-6.32	-12.9	63.4	63.7	85.0	

Dynamic adsorption

Due to the satisfactory adsorption capacity for the 4-Phenylphenol compounds on resins in our research, it is hopeful for resins to be developed as a polymeric adsorbent for the removal of organic pollutants from drinking water or the recovery of organics from waste water. It is necessary to test the dynamic adsorption and desorption. 3 kinds of resins were selected for dynamic adsorption, which had been used in the above static adsorption. The concentration of each 5 BV effluent was determined respectively. Fig.4 shows the dynamic curve for the adsorption of 4-Phenylphenol on 3 kinds of resins. From the beginning of 25 BV, the concentrations of effluent liquid for 4-Phenylphenol onto three kinds of resins was increased rapidly and the slope of adsorption breakthrough curve is larger, indicating the adsorption rate in wastewater was faster. The concentrations of effluent liquid for 4-Phenylphenol on FJ-1 resin was lowest. Therefore, the efficiency of dynamic adsorption on FJ-1 resin is better than that on other resins.

Effect of desorption temperature on dynamic desorption

After the dynamic adsorption, the ethanol were used to desorb 4-Phenylphenol from FJ-1 resin column.at the flow rate of 0.5BV/h, Fig.5 shows dynamic desorption curves of 4-Phenylphenol onto FJ-1 at different temperature. The higher the temperature is, the greater the desorption efficiency is. When desorption temperature was 333K, nearly 75% regeneration efficiency for the adsorbent was

achieved. This is mainly due to the possibility of increasing the electrostatic force between the adsorbate and the FJ-1 resin at higher temperatures. Therefore, 333K is the best desorption temperature.

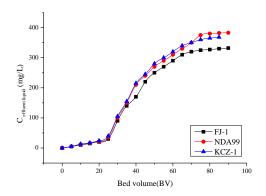


Fig. 4. Dynamic Adsorption Curves of 4-Phenylphenol in Water onto different Resins at 288K.

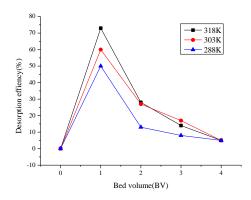


Fig.5. Dynamic Desorption Curves of methyl anthranilate onto FJ-1 at different temperature

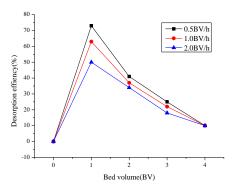


Fig.6. Dynamic Desorption Curves of methyl anthranilate onto FJ-1 at Different Flow Rate at 333K

Effect of desorption velocity on dynamic desorption

The ethanol were used to desorb 4-Phenylphenol from FJ-1 resin column.at 333k, Fig.6 shows dynamic desorption curves of 4-Phenylphenol onto FJ-1 from 0.5 BV/h to 2 BV/h. When velocity desorption is 0.5BV/h, regeneration efficiency for

the adsorbent is the largest. Therefore, 0.5BV/h is the best desorption velocity.

CONCLUSION

IR spectra of KCZ-1, KCZ-2, FJ-1and FJ-2 resins show that four kinds of hypercrosslinked adsorption resins were successfully prepared. The four resins have better adsorption properties. However, as shown in fig.3, at the same temperature and concentration, the adsorption capacity of 4-Phenylphenol on the KCZ-1, KCZ-2 and FJ-1 resins is better than FJ-2 resins, mainly due to modified functional groups and its specific surface area. As shown in Table.4, The value of ΔH was all positive indicating an endothermic process. 4-Phenylphenol is more easily adsorbed with temperature rising, ΔG shown that the adsorption of phenol on four kinds of resins was a feasible spontaneous endothermic process. ΔS showed the increasing randomness of the solid-solution interface during the adsorption of 4-Phenylphenol on resins. The Langmuir isotherm model can fit the adsorption process for the four resins well. However, Freundlich isotherm model also can fit the adsorption for the FJ-1 resins well. The efficiency of dynamic adsorption on FJ-1 resin is better than that on other resins. When temperature was 333K, nearly 75% regeneration efficiency for the adsorbent was achieved at the flow rate of 0.5BV/h.

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REFERENCES

- 1. N. Kolbe, J.T. Andersson, J. Agric. Food Chem, **54**, 5736 (2006).
- 2. Y. Higashi*, Y. Fujii, Journal of Analytical Chemistry, 70, 346 (2015).
- 3. M. De Boeck, B.van der Leede, K. De Vlieger, *Mutation Research*, **786–788**, 151 (2015).
- 4. M. Khalid, G. Joly, A. Renaud, P. Magnoux, *Industrial & Engineering Chemistry Research*, **43**, 5275 (2004).
- 5. G. Busca, S. Berardinelli, C. Resini, L. Arrighi, *Journal of Hazardous Materials*, **160**, 265 (2008).
- 6. B. Pourabbas, B. Jamshidi, *Chem. Eng. J*, **138**, 55 (2008).
- 7. J. Huang, X. Jin, J. Mao, *Journal of Hazardous Materials*, **217–218**, 406 (2012).

- 8. H.T. Li, M.C. Xu, Z.Q. Shi, B.L. He, *J. Colloid Interface Sci*, **271**, 47 (2004).
- 9. K. László, P. Podko'scielny, *Appl. Surf. Sci*, **252**, 5752 (2006).
- A. Li, Q. Zhang, G. Zhang, J. Chen, Z. Fei, F. Liu, Chemosphere, 47, 981 (2002).
- 11. A. Da browski, P. Podkos'cielny, Z. Hubicki, M.Barczak, *Chemosphere*, **58**, 1049 (2005).
- 12. A.L. He, J.H. Huang, C. Yan, J.B. Liu, L.B. Deng, K.L. Huang, *J. Hazard. Mater*, **180**, 634 (2010).
- 13. A.C. Pan, W. Du, W.M. Zhang, X. Zhang, Q.R. Zhang, B.J. Pan, L. Lv, Q.X. Zhang, J.L. Chen, *Environ. Sci. Technol*, **41**, 5057 (2007).
- 14. M.P. Tsyurupa, V.A. Davankov, *React. Funct. Polym*, **66**, 768 (2006).

- 15. X. Wang, R. Deng, X. Jin, Chemical Engineering Journal, 191, 195 (2012).
- 16. A.M. Li, Q.X. Zhang, G.C. Zhang, J.L. Chen, Z.H. Fei, F.Q. Liu, *Chemosphere*, **47**, 981 (2002).
- 17. V.A. Davankov, M.P. Tsyurupa, *React. Polym*, **13**, 27 (1990).
- 18. M.P. Tsyurupa, V.A. Davankov, *React. Funct. Polym*, **53**, 193 (2002).
- X.H. Yuan, X.H. Li, E.B. Zhu, J. Hu, W.C. Sheng,
 S.S. Cao, *Carbohydr. Polym*, 74, 468 (2008).
- 20. C.L. He, J.H. Huang, C. Yan, J.B. Liu, L.B. Deng, K.L. Huang, *J. Hazard. Mater*, **180**, 634 (2010).
- 21. C.G. Oh, J.H. Ahn, S.K. Ihm, Funct. Polym, **57**, 103 (2003).

АДСОРБЦИОННИ СВОЙСТВА НА 4-ФЕНИЛФЕНОЛ ВЪВ ВОДЕН РАЗТВОР С ХИМИЧЕСКИ МОДИФИЦИРАНА АДСОРБЦИОННА СМОЛА

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(Резюме)

Приготвена е адсорбираща смола от атразин (KCZ-1), о-фталов анхидрид (KCZ-2), тримелитов анхидрид (FJ-1) и 2-имодазолидон (FJ-2) чрез успешно кръстосано свързване и химическа модификация. Смолата е охарактеризирана чрез IR-спектроскопия и BET-анализ. Структурното охарактеризиране показва, че смолата има предимно микропори/мезопори и умерена специфична повърхност. Адсорбционният капацитет на 4-фенилфенол върху четирите смоли е много голям поради взаимодействието чрез водородни връзки между 4-фенилфенола и модифицираните функционални групи на смолата. Адсорбционните отнасяния на 4-фенилфенола върху KCZ-1, KCZ-2, FJ-1 and FJ-2 са изследвани чрез адсорбционните изотерми и кинетиката на адсорбция. Освен това, адсорбционната термодинамика и кинетика са използвани за изучаването на механизъма на адсорбцията. Изотермите се корелират с уравненията на Лангмюир и Фройндлих, като изотермата на Лангмюир е по-подходяща. Изменението на енталпията Δ H е положително, а изменението на свободната енергия по Гибс Δ G и на ентропията Δ S са отрицателни. Ефективността на динамичната адсорбция върху смолата FJ-1 е по-добра, отколкото на останалите. При температура 333K почти 75% от адсорбента се възстановява при дебит 0.5BV/h.