

WATER MEDIUMS PURIFICATION FROM PHENOL BY POLYMERIC SORBENT

**A.M. MAHARRAMOV, R.M. ALOSMA NOV,
K.N. ORUJOVA, A.A. AZIZOV**
Baku State University
AZ 1048, Z. Khalilov 23, Baku, Azerbaijan
e-mail: r_alosmanov@rambler.ru

For phenol sorption from aqueous solutions P, N-containing sorbent obtained on the base of phosphochlorinated PB has been used. Experiments were carried out in dependence of sorbent concentration, contact time and phenol concentration. Equilibrium sorption characteristics have been investigated by Langmuir and Freundlich Models and it was established that at initial phenol concentration up to 346.0 mg/l sorption obeys Freundlich equation, and under higher initial phenol concentration – Langmuir equation. For analysis of experimental kinetic data pseudo-first and pseudo-second-order models have been applied. It was confirmed that under lower initial concentration sorption kinetics is described well by pseudo-first-order model, but under higher concentration by pseudo-second-order model.

Keywords: Sorption; Phenol; P, N-containing sorbent; Isotherm; Kinetic

Phenol and its derivatives are raw materials or solvents in the chemical and also petrochemical processes and occur in wastewater of a number of industries such as oil refineries, petrochemical units, paper, textile, synthetic rubber and pharmaceutical enterprises [1,2]. Almost all phenolic compounds are highly toxic at the concentrations upon their discharge into the receiving effluents. They can exert negative effects on biological processes in water and are considered to be of priority among carcinogenic pollutants.

The presence of phenolic compounds even at low concentrations can be an obstacle to the reuse of water because of unpleasant odour. Thus, the removal of phenols from such industries and wastewater streams is considered to be necessary before discharging to the environment and becomes a major environmental problem [3-5].

Various physico-chemical and biological methods have been applied to remove phenolic compounds as well as toxic organic pollutants from wastewater. Among these techniques the use of organic and inorganic natural sorbents for sorptional removal differs by its efficacy. A variety of sorbents include clays [6,7], activated carbon [1] and polymeric products (resins, polymers) [3,8].

By the comparative studies [9] a high sorption ability of activated carbon due to its vast surface area and affinity for many organic chemicals was determined. However, activated carbon is costly regenerated (high temperature and/or steam is needed) and has a high extent of granulation and also tends to

sorb most organic chemicals indiscriminately, making it difficult to selectively recover certain organic chemicals for reuse.

These deficiencies caused a growing interest in developing alternative sorbents. Polymeric sorbents can be considered as an alternative to activated carbon due to their wide variations in functionality, surface area, porosity and fine regeneration by various solvents. For this aim industrial and synthesized (in laboratory conditions) sorbents can be used. In these works analysis of equilibrium and kinetic characteristics of sorption process was realized which allows to evaluate the efficacy of using sorbent. It was found that the indicated characteristics are caused by series of factors, one of which being a type of sorbent. Thus, offering of each new sorbent presupposes an analysis of the indicated characteristics, which also allows to clear up the peculiarities of sorption mechanism.

This study focuses on investigation of sorption characteristics of the sorbent on the basis of polybutadiene (PB) towards phenol in equilibrium and kinetic aspects. Sorption equilibrium was presented by Langmuir and Freundlich models and for kinetic data analysis pseudo-first-order and pseudo-second-order kinetic models were used.

Experimental

For obtaining of sorbent the initial polymer, i.e. PB, was treated by reaction of oxidative chlorophosphorylation with PCl_3 in the presence of oxygen with following aminolysis of the obtained modificate by diethylamine. Detailed synthesis describing is presented in earlier published works [10,11].

Structure of phosphochlorinated PB was studied by NMR- ^1H , ^{13}C , ^{31}P [12] and product of aminolysis by IR-spectroscopy. It was established that sorbent included such functionally-active groups as $-\text{P}(\text{O})(\text{OH})[\text{NH}(\text{C}_2\text{H}_5)_2]^+\text{Cl}^-$; $-\text{OP}(\text{O})(\text{OH})[\text{NH}(\text{C}_2\text{H}_5)_2]^+\text{Cl}^-$; $-\text{P}(\text{O})(\text{OH})_2$; $-\text{OP}(\text{O})(\text{OH})_2$ type.

In present investigation sorbents with the particle range of 0.4–0.43 mm were used

Standard solutions were prepared by dissolving 2g of “analytical reagent” grade phenol in 1l of distilled water ($\rho=1.034$ g/l; $\text{pK}_a=9.89$).

The test solutions were prepared by diluting of standard solutions to the desired concentration.

100 ml of phenol solutions of various initial phenol concentration are placed into 250 ml reaction flasks and a fixed sorbent amount is added to each of them. All sorption experiments were carried out using batch equilibrium tests. The suspension containing sorbent and phenol solutions were agitated on a mechanical shaker for 12 h (at 293 K). Then, the contents of the bottle were filtered and residue was analyzed for residual concentration of phenol.

Kinetic experiments were carried out using of known amount of sorbent and at different initial phenol concentrations. After fixed time intervals the

corresponding aliquots were analyzed to determine phenol concentration and registered.

Each experiment was performed twice under identical conditions and average values were used for future calculations.

The concentration of residual phenol in the adsorption media was determined spectrophotometrically. The absorbance of the coloured complex of phenol and 4-aminoantipyrine was read at 500 nm [13].

Results and discussion

Sorption of phenol onto sorbent was investigated as a function of concentration of sorbent and initial phenol concentration. The results are given as the units of sorbed phenol quantity per gram of sorbent at any time and at equilibrium, q and q_{eq} (mg/g), respectively, as well as unsorbed phenol concentration in solution at any time and at equilibrium, C and C_{eq} (mg/l), respectively, as

$$q_{eq} = (C_0 - C_{eq}) \cdot \frac{V}{W} \quad (1)$$

and sorption yield as

$$S_y = 100 \frac{(C_0 - C_{eq})}{C_0} \quad (2)$$

Fig.1 shows the amount of phenol removed as a function of sorbent dosage in their solution. Sorbent dosage was varied from 1 to 20 g/l. It is evident that for the quantitative removal of phenol from the solution of concentration 1.240 g/l, sorbent dosage of 1g/l is required for 82.6 % removal of phenol. The same regularities are observed for phenol solutions of different concentrations and respective yields. The further increasing of sorbent dosage up to 2 g/100 ml leads to the increase of phenols removal up to 84.3 %, the accretion being negligible. The data show that an efficient removal can be reached at the sorbents concentration 10 g/l.

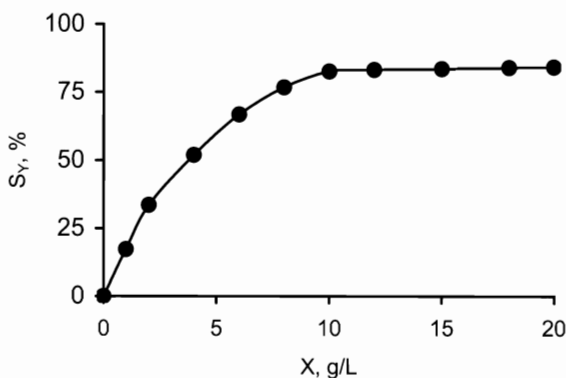


Fig. 1. Effect of sorbent dosage (X, g/l) on sorption yield (T=293 K; C₀=1.240 mg/l).

In Table 1 the effect of initial phenol concentration on the sorbed phenol quantity per gram of sorbent and sorption yield at equilibrium is shown. As seen from the Table with increasing initial phenol concentration q_e increased, too, that may be related with the increase of interaction between phenol and sorbent. At first, rate of q_{eq} increasing is fast, but at high initial concentrations of phenol it is stabilized. It means that sorbent included a limited number of active centers for sorption.

Table 1

Change of phenols amount in sorbent and sorption yield at equilibrium in dependence from initial phenol concentration

C_0 , mg/l	41.62	96.83	346.0	530.0	824.3	1018.3	1240.0	1702.0
q_{eq} , mg/g	3.82	9.12	31.99	49.16	75.50	90.81	102.40	121.88
S_Y , %	91.8	94.2	92.4	92.8	91.5	89.1	82.6	71.6

The sorption yield is high ($S_Y > 90\%$) at comparatively low initial concentrations ($C_0 < 1000$ mg/l), but as initial phenol concentration increases sorption yield gradually decreases. At lower concentrations all sorbate molecules present in sorption medium can interact with active centers, that's why sorption yields were higher. Lower values of sorption yields have been observed at higher concentrations because of saturation of sorption centers.

Before studying phenol sorption equilibrium it was necessary to determine equilibrium contact time required for phenol (the time required for reaching equilibrium after contact with sorbent). The preliminary tests showed that phenol sorption is fast at the initial stages and becomes slower near the equilibrium. Fig.2 presents the plot of phenol sorption yield versus contact time for sorbent at initial phenol concentrations 96.83, 530.0 and 1240.0 mg/l, respectively, at 293 K with contact time of 240min. Sorbent concentration in all experiments was 10 mg/l. As seen from Fig.2, the rate of phenol removal is very rapid during initial 60 minutes and decreases thereafter.

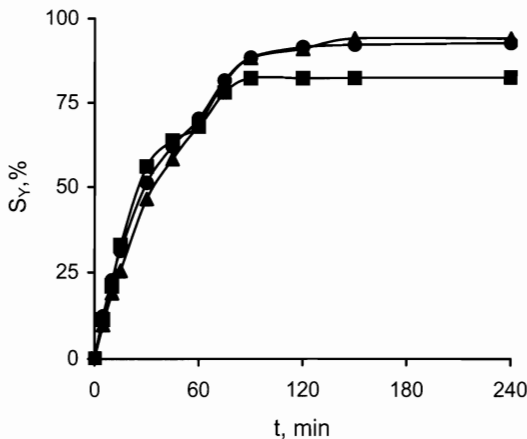


Fig.2. Effect of contact time (t, min) on sorption yield for different initial phenol concentrations: ▲-96.83; ■-530.0; ●-1240.0 mg/l (T=293 K; X=10 g/l).

It is revealed that there were no considerable changes in phenol removal after 120 min of contact time for different initial concentrations.

Fig.3 presents the plot between the equilibrium phenol values in solution and in sorbents, i.e. sorption isotherms.

As seen from Fig.3, equilibrium in system “sorbent-phenol solution” is reached for equilibrium phenol concentration in solution 483.2 mg/l and 121.88 mg/l in sorbent.

At first sight, this isotherm belongs to L2 type of isotherm in accordance with isotherm classification by Gules described in [14]. However, by more detailed describing of local sites of isotherm deviation from the common pattern of L-isotherms on its initial site (up to q_{eq} 26.1mg/g) can be observed. Therefore, isotherm has a stepwise character. It is known [14] that sorption isotherm stages show either orientation change on the surface or formation of polymolecular layers. The second assertion does not find its confirmation with regard to limiting phenol solubility in water, that equals 86.95g/l in accordance with literature [15].

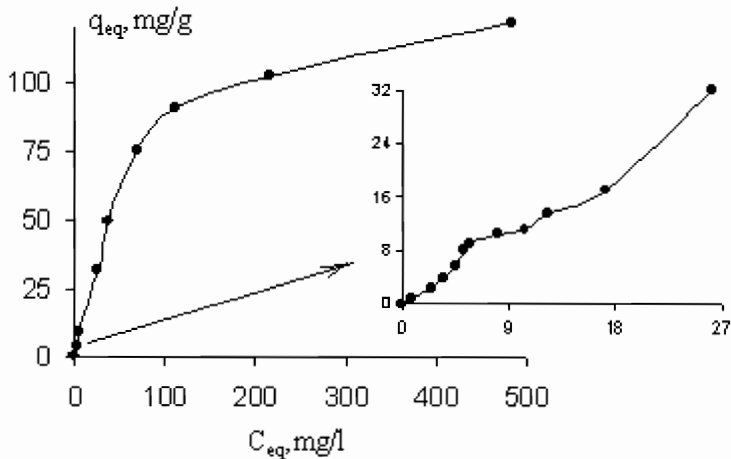


Fig.3. Isotherm of phenol sorption from water by polymeric sorbent ($T=293K$; $X=10g/l$)

Thus, the obtained isotherm can be divided into 3 sites. Intervals of equilibrium phenol concentration in solution are 0-5.63(I); 5.63-26.1(II); 26.1-483.2(III) mg/l respectively. As seen from isotherm character, Sites I and II obey S1 type of isotherm, and the third site corresponds to L2 type of isotherm.

In all probability, with increasing phenol concentration in water the character of sorbate orientation on the surface changes.

It is known that equilibrium data can be analyzed by using commonly known sorption isotherms, which provide the basis for the design of sorption systems [3-5]. The most widely used isotherm equation for modeling the sorption data is the Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number of identical sites and is given by equation (3).

$$q_{eq} = \frac{q_{max} K C_{eq}}{1 + K C_{eq}} \quad (3)$$

where K is the adsorption equilibrium constant including the affinity for binding sites (l/mg) and q_{max} is the maximum amount of phenol per unit weight of sorbent to form a complete monolayer on the surface (mg/g). The equation represents a practical limiting sorption capacity when the surface is fully covered with phenol. q_{max} and K can be determined from the linear plot of C_{eq}/q_{eq} versus C_{eq} [1].

The Freundlich model is an empirical equation based on sorption on a heterogeneous surface. It is given as:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (4)$$

where K_F and n are the Freundlich constants that indicate relative capacity and adsorption intensity, respectively. The Freundlich equation can be linearized by taking logarithms and its constants can be determined [1].

The isotherm constants and correlation coefficients by linearized isotherms of Langmuir and Freundlich were estimated and tabulated in Table 2.

Table 2

Isotherms constants for phenol sorption on sorbent at different concentration intervals

Concentration intervals		Langmuir Model			Freundlich Model		
C_0 , mg/l	C_{eq} , mg/l	q_{max} , mg/g	K , l/mg	R^2	K_F , (mg/g)·(l/mg) ^{1/n}	1/n	R^2
0-96.83	0-5.63	-	-	-	1.006	1.1847	0.9681
96.83-346.0	5.63-26.1	131.58	0.010	0.1732	1.955	0.8017	0.9109
346.0-1702.0	26.1-483.2	140.85	0.014	0.9957	9.977	0.4315	0.8758

As seen from Table 2 at the comparatively low initial concentrations (Sites I and II) the Freundlich Model exhibited a slightly better fit to the sorption data than the Langmuir Model. At these sites sorption mainly takes place on the energetically heterogeneous surface and interaction force between sorbate molecules is larger than interaction force between the solute and sorbent. In this case phenol molecules tend to place on the sorbent surface in the form of chains and clusters. Their such kind of disposition is promoted by high solvent sorption, phenols monofunctionality and enough polarity of sorbents surface. But with increasing of concentration (Site III) the Langmuir Model is more suitable. Apparently, in this Site phenol molecules have another, namely a parallel, orientation.

Kinetic models are used to examine the rate of the adsorption process and potential rate-controlling step, i.e. mass transfer or chemical reaction. The capability of pseudo-first-order and pseudo-second-order kinetic models were examined in this study.

The pseudo-first-order equation of Lagergren is generally expressed as follows [2]:

$$\frac{dq}{dt} = k_1 (q_{eq} - q) \quad (5)$$

where k_1 is the rate constant of pseudo-first-order sorption (min^{-1}).

Integrating this equation for boundary conditions: $t=0$ to t and $q=0$ to q_{eq} gives

$$\log(q_{eq} - q) = \log(q_{eq}) - \frac{k_1}{2.303} t \quad (6)$$

A plot of $\log(q_{eq} - q)$ against of t should gives a linear relationship with the slope of $K_1/2.303$ and intercept of $(\log q_{eq})$.

The pseudo-second-order kinetic rate equation is expressed as:

$$\frac{dq}{dt} = k_2 (q_{eq} - q)^2 \quad (7)$$

where k_2 is the rate constant of pseudo-second-order sorption ($\text{g mg}^{-1} \text{min}^{-1}$).

For the same boundary conditions, the integrated form of equation (7) becomes

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \quad (8)$$

The second-order rate constant can be determined from the intercept of the linearized pseudo-second-order rate equation.

The plots of equations (6) and (8) are shown in Fig.4 and 5. Values of corresponding parameters for the models are presented in Table 3.

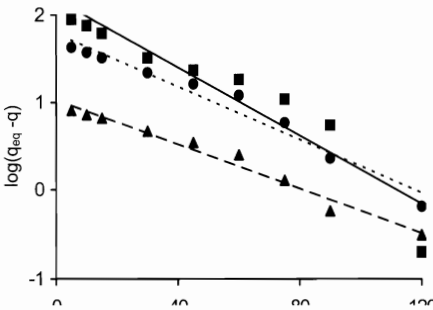


Fig.4. Pseudo-first-order sorption kinetics of phenol at different concentrations ▲-96.83; ■-530.0; ●-1240.0 mg/l (T=293 K; X=10 g/l)

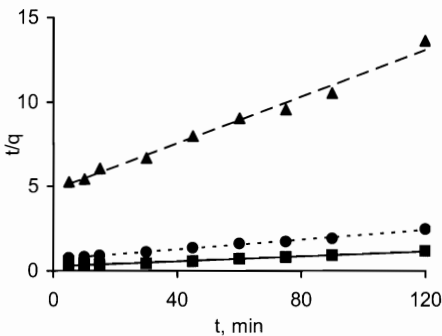


Fig.5. Pseudo-second-order sorption kinetics of phenol at different concentrations ▲-96.83; ■-530.0; ●-1240.0 mg/l (T=293 K; X=10 g/l)

Table 3**Kinetic analysis of phenol sorption by various models**

Initial concentration, C_0 , mg/l	$q_{eq,exp}$, mg/g	Pseudo-first-order			Pseudo-second-order		
		K_1	$q_{eq,cal}$	R^2	K_2	$q_{eq,cal}$	R^2
96.83	9.12	0.029	10.73	0.977	0.001	14.45	0.9866
530.00	49.16	0.035	62.22	0.964	0.0003	69.44	0.995
1240.00	102.40	0.044	150.73	0.8865	0.0002	136.99	0.9858

The results show that at initial phenol concentrations 96.83 and 530.0 mg/L the correlation coefficient obtained both for the first-order kinetic model and second-order kinetic order are high enough. The theoretical q_{eq} values found by pseudo-first-order kinetic model gave more reasonable values. Thus, at these initial concentrations pseudo-first-order model describes phenol sorption better.

At the initial phenol concentration 1240.0 mg/l correlation coefficient obtained for pseudo-second-order model is higher and theoretical values of q_{eq} are more suitable. It means that at given initial concentration value are involved new active centers into sorption process.

Thus, according to a change of the initial phenol concentration in solution, sorption nature changes too, that can be explained by participation of the active centers of different nature in sorption processes.

Conclusions

In present investigation the ability of P, N-containing sorbent on the basis of phosphochlorinated PB for sorption has been studied in equilibrium and kinetic aspects. It was found that sorption isotherm can be divided conditionally into 3 sites. The first 2 sites, corresponding to initial phenol concentrations 0-96.83 and 96.83-346.0 mg/l obey the Freundlich equation, and the third Site with phenol concentration 346.0-1702.0 mg/l – the Langmuir equation. Phenol sorption kinetics was studied by using pseudo-first and pseudo-second-order models. Under comparatively low initial phenol concentrations the results point to better correlation of obtained data for pseudo-first-order model. With increasing initial phenol concentrations the better correlation is provided by pseudo-second-order model.

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FENOLUN SULU MƏHLULLARDAN POLİMER SORBENTLƏ TƏMİZLƏNMƏSİ

**A.M. MƏHƏRRƏMOV, R.M. ALOSMANOV,
K.N. ORUCOVA, A.Ə. ƏZİZOV**

Fenolun sulu məhlullardan sorbsiyası üçün fosfoxlorlaşmış polibutadien əsasında alınmış P,N tərkibli polimer sorbent istifadə olunmuşdur. Prosesə sorbentin miqdarı, sorbsiya müddəti və fenolun qatılığının təsiri öyrənilmişdir. Sorbsiya izotermninin təcrübi nəticələri Lenqmür və Frenclix modellərilə işlənmiş və tədqiq olunan sistem üçün modellərin parametrləri hesablanmışdır. Müəyyən olunmuşdur ki, fenolun ilkin qatılığının 346.0 mq/l-ə qədər qiymətlərində sorbsiya izotermi Frenclix, yuxarı qiymətlərində isə Lenqmür tənliyinə tabe olur. Təcrübi kinetik nəticələr psevdo 1-ci və 2-ci tərtib modelləri ilə tədqiq olunmuşdur. Fenolun aşağı qatılıqlarında prosesin kinetikasının psevdo 1-ci tərtib, yuxarı qatılıqlarında isə psevdo 2-ci tərtib modellərinə tabe olması müəyyənləşdirilmişdir.