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The effect of ion exchange resin form on the removal of phenol from water

Özge Sandıkçı, Ayşegül Parmaksız, Arzu Kocaoğlu, Özgür Arar*, Ümran Yüksel
Ege University, Faculty of Science, Department of Chemistry, 35100, Izmir Turkey

Abstract

The removal of phenol from aqueous solutions by strongly basic anion exchange resin (Relite 2 AS) has been investigated. The effect of resin amount, pH of solution, temperature and initial phenol concentration on phenol removal was observed. Obtained results showed that the resin form has an important effect on phenol removal. In OH-form, pH has slight influence on phenol removal but when the resin was converted to Cl-form and solution pH was increased to 11, percent removal of phenol increased. Removal of phenol was 97% in Cl-form and 57 % in OH-form of resin. The Freundlich model describes the phenol removal onto the two different forms. On the other hand, pseudo-second order kinetic fit well with experimental results. Kinetic of resin in Cl-form is faster than in OH-form. The 97% of phenol removed from solution in Cl-form in 60 minutes. Thermodynamic parameters (ΔG, ΔH and ΔS) for the sorption of phenol were determined using the Gibbs-Helmholtz equation. The obtained results indicated that, sorption of phenol onto such form of resin is exothermic.

Keywords: adsorption, ion exchange, kinetic, phenol, Relite 2AS, waste waterİ

İyon değiştirici reçine formunun sulardan fenol giderilmesindeki etkisi

Öz

Bu çalışmada, kuvvetli bazik anyon değiştirici reçine (Relite 2AS) ile sulu çözeltilerden fenol giderilmesi incelenmiştir. Fenol giderilmesine; reçine miktarı, çözelti pH`I, sıcaklık ve fenol derişiminin etkisi saptanmıştır. Elde edilen sonuçlar, iyon değiştirici reçine formunun fenol giderilmesinde önemli bir etkiye sahip olduğunu göstermiştir. Hidroksit formundaki reçine ile yapılan çalışmalarda fenol giderilmesine çözelti pH`sinin önemli bir etkisi yok iken, klörür formundaki reçine kullanıldığında ve çözelti pH`si 11` e ayarlandığında fenol giderim yüzdesinin arttığı saptanmıştır. Hidroksit formundaki reçine kullanıldığında fenol giderilmesinin % 57; klorür formundaki reçine kullanıldığında ise % 90 civarında olduğu görülmüştür. Denge çalışmalarında elde edilen sonuçlar Freundlich izoterm modeline uygunluk göstermiştir. Kinetik çalışmalarda elde edilen sonuçlar yalancı ikinci mertebe kinetik modeline uygunluk göstermiştir. Klorür formundaki reçinenin fenol giderim kinetiğinin hidroksit formundaki reçinenin kinetiğinden daha hazlı olduğu saptanmıştır. Klorür formundaki reçine ile 60 dakikada fenolün % 97`si giderilmiştir. Fenol sorpsiyonu için termodinamik parametreler (ΔG, ΔH ve ΔS) Gibbs-Helmholtz denklemi kullanılarak belirlenmiştir. Elde edilen sonuçlar; fenol sorpsiyonunun her iki reçine formu için de ekzotermik olduğunu göstermiştir.

Anahtar kelimeler: adsorpsiyon, iyon değişimi, kinetik, fenol, Relite 2AS, atık su

* Corresponding author
e-mail: ozgur.arar@ege.edu.tr , ozgurarar@gmail.com

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Introduction

Phenol and its derivatives which exist in wastewater of many chemical plants are pollutants to living organism. The environmental and health risks of phenol have been well documented [1,2]. Phenolic compounds have low permissible limit (1 μg/L) according to the recommendation of the World Health Organization [3]. Therefore, it must be effectively removed from water. The adsorption [4-5], photochemical oxidation [6, 7], solvent extraction [8,9], membrane processes [10,11]; ion exchange [1, 12-16], etc. have been widely used for removal of phenols from water/wastewaters. In previous studies, non-functional or mostly OH^- form of the ion exchange resin was used. It is well known that resin form affects the removal performance of resin. In this work, strongly basic anion exchange resin (Relite 2AS) was tested for its suitability on phenol removal at Cl and OH form. The sorption capacity, pH dependency as well as adsorption isotherms were successfully applied for both resin forms. The other important discovery of this paper is the kinetics of the resin forms. In this work kinetic of the resin for both forms was investigated and successfully applied to kinetic models.

Materials and Methods

Strong base anion exchange resin; Relite 2AS was supplied by Resindion S.r.l. (A subsidiary of Mitsubishi Chemical Corp.) Italy. The characteristics of the resin are summarized in Table 1. The analytical grade phenol (Merck) was used for preparation of solution. The pH of the solutions was adjusted with NaOH (Merck) or HCl (Merck).

Table 1: Physical and Chemical Properties of Relite 2AS.

Functional group	Quaternary ammonium Type 2
Matrix	Porous copolymer styrene DVB
Functional group	Dimethyl ethanolamine
Total exchange capacity (eq/l)	1.4 min
Water retention (%)	39 -45
Chemical stability	Stable in the whole pH range
Thermal stability :	40 °C max (OH^-); 60 °C max (Cl^-)

Determination of phenol The concentrations of the phenol was determined by double beam UV/VIS spectrophotometer (PG Instruments, T80+ model) with a fixed (2nm) spectral bandwidth at 270 or 287 (at pH 11) nm using 1 cm quartz cells.

Results and Discussion

Effect of Resin amount on phenol removal

For batch-experiment 25 mL of phenol solution was contacted with various amount of resin (0.05-0.25 g), after 24 h of incubation, resin was removed from solution then phenol in the solution was analyzed and obtained results depicted in Figure 1. As can be seen from Figure 1, removal of phenol increased with an increase in resin amount. This is because of increment of available sorption sites for phenol and hence the removal of phenol increased [17].

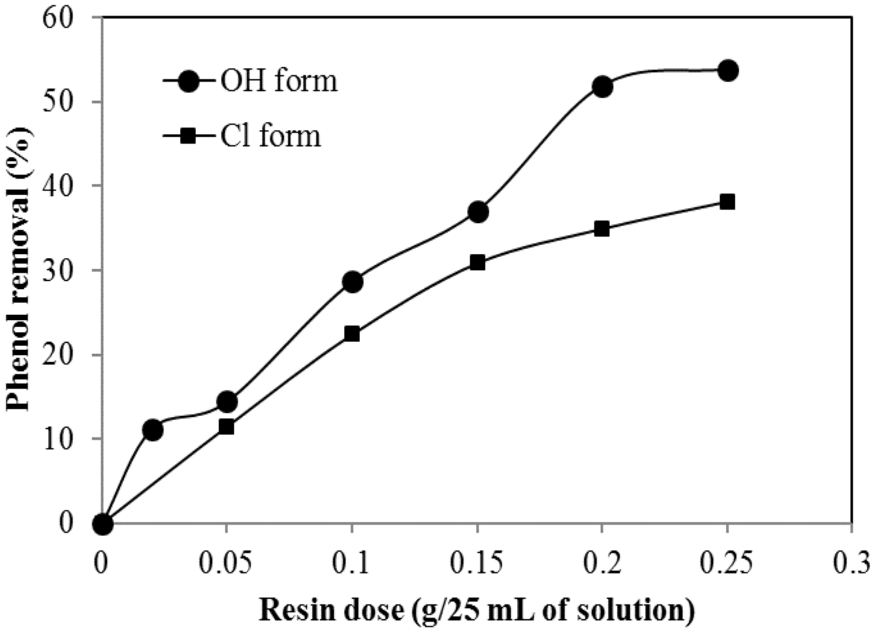

Figure 1: Effect of resin dose on the removal of phenol (Phenol concentration:5 mg/L, pH:6, Volume of solution 25 mL).

Increasing the resin amount above 0.2 g brings not much removal rate; therefore, the optimum resin amount in further experiments was set at 0.2 g for both form of resin. Figure 1 also shows that; removal rate of phenol is higher at OH-form. This can be because of the swelling effect. In OH-form; resin swells more and this leads to increase the pore size thus phenol may diffuse more inside resin and this is why the removal rate of phenol high at OH-form.

Effect of pH

In this set of experiment; initial pH of phenol solution varied from 6 to 11 by using NaOH or HCl then 25 mL of solution contacted with 0.2 g of resin. Obtained results demonstrated in Figure 2. When the OH-form of resin was used; pH of solution did not affected the removal rate, while Cl-form was used and pH was increased to 11 removal of phenol increased. The removal of phenol by resins may be ascribed to two mechanisms; adsorption and ion-exchange. When the strong base anion exchange resins in the OH-form was used; phenol are removed primarily by exchanging for OH^- ions [18].

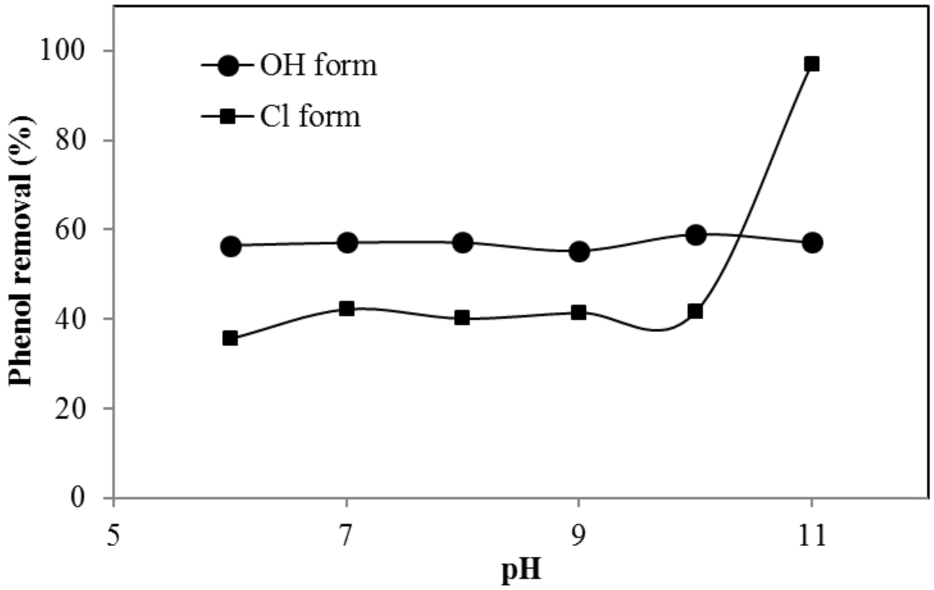

Figure 2: Effect of solution pH on the removal of phenol (Phenol concentration:5 mg/L, volume of solution: 25 mL, resin amount: 0.2 g).

The ion exchange reaction between ion exchange resin and phenolate ions is shown in Eq.1

$$\overline{R-OH} + PhO^- \leftrightarrow \overline{R-PhO} + OH^- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

Phenol (PhOH) act like weak acids in aqueous solution and its pKa is 9.9. If the pH of solution is lower than its pKa value, the molecular form of phenol is the predominant in solutions, whereas the ionic species, PhO^-, predominates in alkaline solutions (pH >10) [19]. In our case (in OH form); pH of the solution did not change the removal rate of phenol and this can be explained as follow: at high pH; concentration of OH^- is greater than phenol (about 18.9 times higher at pH 11). According Le Chatelier's principle when the OH^- concentration was increased the equilibrium shifts to left hand side so removal rate of phenol did not increase (See Equation 1). The effect of pH on removal of phenol by resin in Cl-form is complex. The removal mechanisms are largely adsorption, as shown in Eq.2, [18,14] and ion exchange (Eq.3) [14]

$$\overline{R-Cl} + PhO^{-} \rightarrow \overline{(R-ClPhO^{-})}_{adsorption} \;\ldots\ldots.\; (2)$$

$$\overline{R-Cl} + PhO^{-} \rightarrow \overline{R-PhO} + Cl^{-} \;\ldots\; (3)$$

Equilibrium adsorption isotherm

The sorption capacity of resin for phenol has been evaluated by using Langmuir and Freundlich isotherm models.

The linear form of the Langmuir equation can be represented as Eq. 4 [20]

$$\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \;\ldots\ldots.(4)$$

The maximum adsorption capacity Q_0 represents the monolayer coverage of sorbent with sorbate and b represents the enthalpy of adsorption.

Freundlich isotherm

A Freundlich adsorption isotherm equation can be written as Eq. 5 [20]

$$logQ_e = \log K_f + \frac{1}{n}\log C_e \;\ldots\ldots\ldots\ldots\ldots\ldots\; (5)$$

The sorption isotherm curves are depicted in Figure 3 and 4; isotherm constants and the correlation coefficients calculated parameters are shown in Table 2.

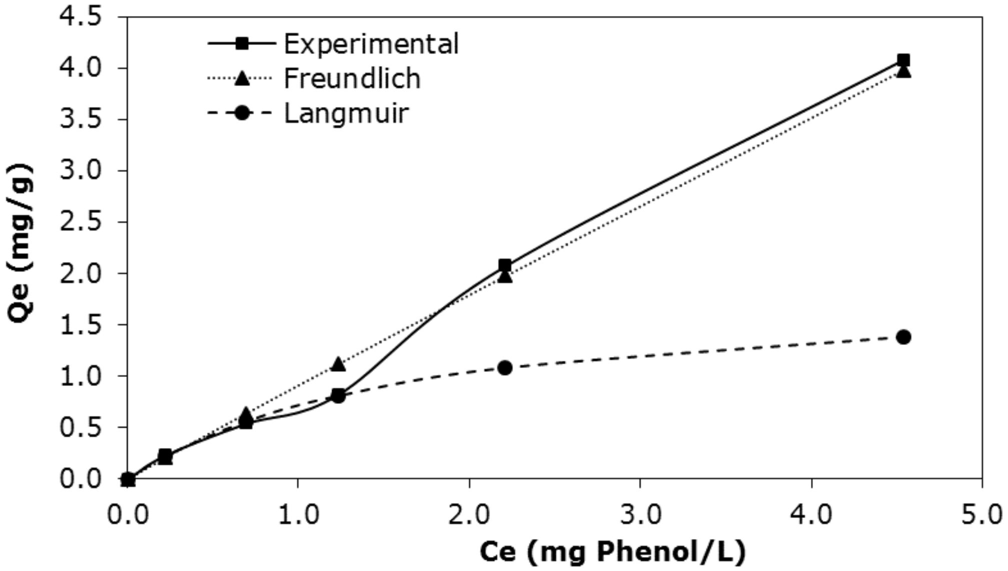

Figure 3: Equilibrium isotherms of phenol on Cl^- form of resin (Volume of solution:25 mL, pH 11, resin amount: 0.2 g).

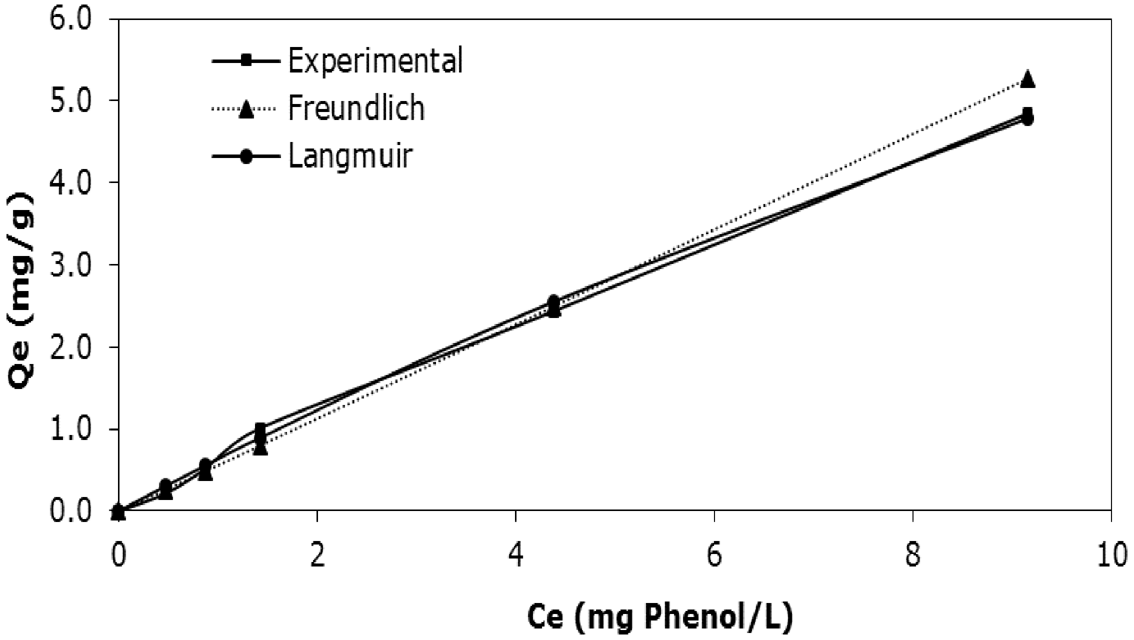

Figure 4: Equilibrium isotherms of phenol on OH^- form of resin (Volume of solution:25 mL, pH 11, resin amount: 0.2 g).

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Table 2: Isotherm constants for phenol sorption on the ion exchange resin.

Resin Form	**Langmuir Isotherm Constants**			**Freundlich Isotherm Constants**		
	Q_0 (mg·g^{-1})	b (L/mg)	R^2	K_f (mg/g)	n	R^2
Cl^- form	30.58	0.03	0.82	0.91	1.2	0.99
OH^- Form	35.21	0.02	0.87	0,60	1,1	0,99

From the Figure 3-4 and the regression coefficient in Table 2, the Freundlich isotherm is more suitable than Langmuir. K_f is the Freundlich constant (mg/g) related to adsorption capacity [21] Kf value of Cl^- form is higher than OH- form. This may be because of ion exchange and adsorption reaction occurs together in Cl$^-$ form.

Kinetic of Resin

In this series of experiments 1000 mL of 5 mg L^{-1} phenol solution was contacted with optimum resin amount (8 g resin/L for Cl and OH form) with continuous shaking. The 10 mL of samples were withdrawn and analyzed. A blank experiment was also carried out to find out if the phenol concentration changed because of oxidation. In the blank experiment, the phenol concentration was constant.

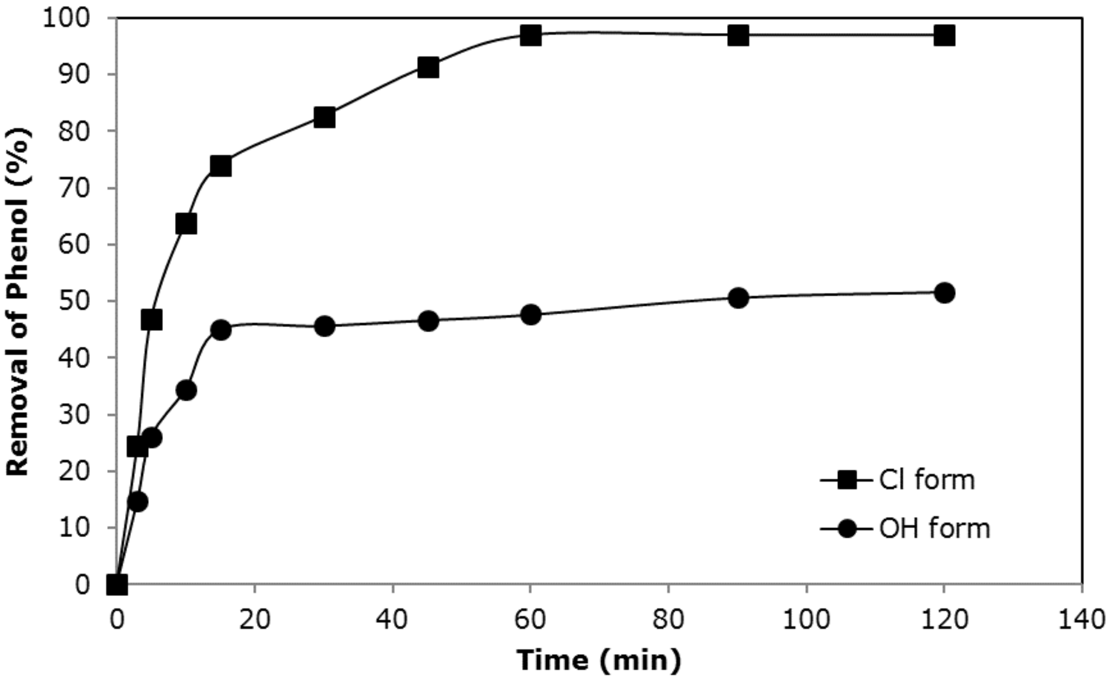

Figure 5: Removal of Phenol versus time as a function of resin form ((Volume of solution:1000 mL, pH 11, resin amount: 8 g).

Figure 5 reveals that, removal of phenol is fast. In 60 minutes 97% phenol removed by resin in Cl form. The kinetic of resin in OH form is slower that resin in Cl form. As explained in Section 3.2. pH of solution and low concentration has negatively effect on phenol removal by resin in OH form.

Pseudo first order and second order kinetic models were used to investigate the mechanism of sorption.

The sorption kinetics following the pseudo-first-order model is given by Eq. 6 [22].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (6)$$

If the rate of sorption is a second order mechanism, the pseudo-second order chemisorption kinetic rate equation (final form) is expressed as in Eq. 7 [23]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (7)$$

Constant k_2 is used to calculate the initial sorption rate h (mg/g min) at t →0, as shown in Eq. 8; [22,23]:

$$h = k_2 q_e{}^2 \qquad (8)$$

The calculated parameters of pseudo first and second order kinetic model were summarized in Table 3.

Table 3: The calculated parameters of pseudo first and pseudo second order kinetic model.

Kinetic model	Parameter	Cl^- form	OH^- form
Pseudo First order	k_1 (min^{-1})	0.0456	$4.66x10^{-4}$
	q_e (mg/g)	0.32	2.2877
	R^2	0.95	0.77
Pseudo Second order	k_2 (g/mg min)	2.235	0.3826
	q_e (mg/g)	0.4932	0.1921
	h (mg/gmin)	0.5437	0.0141
	R^2	0.99	0.99

On the basis of the values of the correlation coefficient (R^2), it can be concluded that the removal of phenol in both form of resin was better described with the pseudo-second-order model. The values of the calculated q_e is higher in Cl^- form.

The Infinite Solution Volume Models (ISV) and the Unreacted Core Models (UCM) were also examined for the relative kinetic performance and to investigate the sorption mechanism. The theoretical part of these model can be find in [24].

Table 4 Linear regression analysis data related to diffusion models on sorption kinetics of phenol from water resin.

Method	**Rate-controlling step**	**R^2 value**	
		Cl- Form	**OH- form**
ISV	Film diffusion	0.97	0.89
	Particle diffusion	**0.99**	**0.95**
UCM	Liquid film	0.90	0.79
	Reacted layer	**0.99**	**0.96**
	Chemical reaction	0.95	0.80

According with the infinite solution volume model (ISV), the rate is controlled by particle diffusion process. When the particle diffusion controls the kinetic; the concentration gradients exist only inside the exchanger beads [25]. According to the unreacted core model (UCM), the reacted layer is the rate-determining step in both form of resin (See Table 4). In this case; reacted layer forms during reaction and reacted layer resistance is unaffected by changes in liquid velocity [26].

Thermodynamic study

In order to investigate the effect of temperature on phenol sorption by resin; 25 mL of phenol solution (5.0 mg/L, pH 11) contacted with 0.2 g of resin at different temperatures (30, 40 and 50 °C). Thermodynamic parameters like change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated by using following equations [27,28]:

$$\Delta G = -RT\ln k_d \text{ …………………(9)}$$

$$\ln k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \text{ …………………….. (10)}$$

$$\Delta G = \Delta H - T\Delta S \text{ ……………………. (11)}$$

Calculated parameters are presented in Table 5. The negative value of ΔH suggests that the sorption of phenol onto ion exchange resins is an exothermic process. The negative values of ΔG indicate the spontaneous nature of the sorption process. The ΔS value is positive for OH-form resin. The positive values of ΔS for OH-form resin indicate increasing randomness at the solid/ solution interface during the sorption process [29]. On the other hand; ΔS is negative for Cl-form resin but ΔH outweighs TΔS and sorption becomes spontaneous [30].

Table 5: Thermodynamic parameters for phenol sorption

Resin form	ΔS (kJ/(mol K))	ΔH (kJ/mol)	ΔG (kJ/mol)
Cl- form	-0.03	-17.27	-8,18 (303 K) -7.88 (313 K) -7.58 (323 K)
OH- form	0.002	-6.32	-6.93 (303 K) -6.95 (313 K) -6.97 (323 K)

Conclusions

The removal of phenol from model solution by an ion exchange resin have been tested. The obtained results showed that the resin form has an important effect on phenol removal. Chloride form of resin showed better results than OH form. Adsorption equilibrium behavior of phenol by Relite 2AS resin can be described by Freundlich model. Uptake of phenol onto ion exchange resin occurs by both adsorption and ion exchange at alkaline pH (in Cl^- form). The ion exchange kinetic of Cl form is much faster than the OH form. Thermodynamic data showed that, removal of phenol by resin is exothermic and spantenous.

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