Equilibrium Studies on Phenol Removal from Industrial Wastewater Through Polymeric Resins

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The efficient removal of phenol from industrial wastewaters has increasingly become a significant environmental concern due to its high toxicity even at low concentrations. In this research work, phenol removal from aqueous solution was evaluated by using Amberlyst A26, a strong-base anion exchange resin, and Amberlite IRA-67, a weak-base anion exchange resin. The influence of phenol concentration in the feedstream was investigated as well as the effect of recirculation time. In addition, equilibrium data fitted to the Langmuir, Freundlich and Temkin isotherms showed that the best correlation is given by Langmuir isotherm for both resins (R^2 = 0.99). Experimental results revealed that phenol uptake is a spontaneous process for Amberlyst A26 ($\Delta G°$ = -1.55 kJ mol^{-1}), whereas it is not spontaneous for Amberlite IRA-67 ($\Delta G°$ = 3.06 kJ mol^{-1}). Finally, Amberlyst A26 was confirmed to be considerably more efficient than Amberlite IRA-67 for the potential removal of phenol from industrial effluents.

1. Introduction

Phenols exist in wastewaters from olive mill, oil refineries, plastics, leather, paint, pharmaceutical and steel industries (Carmona et al., 2006) as well as in domestic effluents and vegetation decay (Gupta et al., 2004). Considering the great prevalence of phenolic compounds in different wastewaters along with their toxicity to living beings even at low concentrations, and within the framework of the actual environment regulations, these compounds must be removed before discharge of wastewater into water bodies (Jain et al., 2004).

Different methods have been proposed to eliminate phenolic compounds from polluted waters, including chemical oxidation, chemical coagulation, extraction with solvents, membrane technology, adsorption and ion exchange (IE) [Carmona et al., 2006; Kujawski et al., 2004; Víctor-Ortega et al., 2014). In the past two decades, polymeric adsorbents have become a promising choice for efficient removal of aromatic pollutants. These polymeric resins present several advantages, especially those about regeneration, which can be accomplished by simple, non-destructive means, such as solvent washing, thus providing the potential for solute recovery (Caetano et al., 2009).

In this scenario, adsorption on selective resins has been investigated for the removal of phenols from aqueous solutions, either through molecular adsorption or IE mechanisms. Caetano et al. (2009) tested the removal of phenol through IE mechanism on polymeric resins followed by desorption with methanol/water mixtures. Zhu et al. (2011) tested the adsorption of phenol on N-butylimidazolium functionalized strongly basic anion exchange resin and the results showed that at acidic pH the dominant mechanism was molecular adsorption whereas at alkaline pH phenol was removed through IE mechanism. Bertin et al. (2011) examined the direct adsorption of olive mill wastewater (OMW) phenols on XAD7 and XAD16 resins followed by desorption with different solvents. The results were very encouraging, exhibiting high adsorption percentages, with 95% of the adsorbed phenols being desorbed with acidified ethanol. Ku et al. investigated phenol removal from aqueous solutions by using Purolite A-510 resin in the chloride form and found that phenol removal increased steadily with increasing pH (Ku et al., 2004). Nevertheless, they consider that the uptake of phenol compounds occurs only on the active sites of the resin by either molecular adsorption or IE. Thus, the same resin sites are considered to be accessible for both modes of uptake and so the ratio of the solute uptake through molecular adsorption and IE depends on the solution pH. The presence of OH$^-$ ions in solution would involve multicomponent exchange namely between hydroxyl, phenolate and the anion initially in the resin. Significant

dissociation of phenol occurs at a pH higher than its pKa (9.83), allowing its uptake by IE, which is an economic, effective and useful technique to remove pollutant ions from wastewaters and replace them by non-contaminant ions released from the ion exchanger (Carmona et al., 2006).

In the present work, a strong-base anion exchange resin (Amberlyst A26) and a weak-base anion exchange (Amberlite IRA-67) were evaluated to remove phenol from aqueous solution. The effect of the phenol concentration in the feedstream was investigated in the range 1-200 mg L^{-1} as well as the influence of recirculation time. On the other hand, the equilibrium behaviour of this pollutant has been described by Langmuir, Freundlich and Temkin isotherms. Additionally, the suitability of the proposed IE resins has been investigated through thermodynamic parameters.

2. Materials and methods

2.1 Materials

For the IE experiments, model solutions were prepared by dissolving reagent-grade phenol (provided by Panreac) in double distilled water. On the other hand, regeneration solutions were prepared by dissolving reagent-grade NaOH (supplied by Panreac) in double distilled water.

In this research work, two anion exchange resins were used: Amberlyst A26 strong base anion exchange resin and Amberlite IRA-67 weak base anion exchange resin. Typical physical and chemical characteristics of these resins are described in Table 1.

Table 1. Physico-chemical properties of the resins.

Properties	Amberlyst A26	Amberlite IRA-67
Type	Strong-base anion	Weak-base anion
Matrix	styrene-divinylbenzene	Tertiary amine
Ionic form as shipped	OH^{-}	OH^{-}
Particle size, mm	0.56-0.70	0.50-0.75
Effective pH range	0-14	0-7
Total exchange capacity, eq L^{-1}	0.80	1.60
Shipping weight, g L^{-1}	675	700

2.2. Ion exchange equipment

The IE column employed in this study was made of an acrylic tube (540 mm height x 46 mm internal diameter), provided with a mobile upper retaining grid which could be fixed in the column to adjust it as a fixed bed or a semi-fluidized bed.

2.3. Equilibrium experiments

The uptake of phenol was carried out by performing recirculation mode experiments in order to evaluate the effect of both the recirculation time and feedstream concentration. The effect of the initial concentration of phenol was examined in the range 1-200 mg L^{-1}.

On the other hand, adsorption isotherm studies were carried out with different initial phenol concentrations ranging from 1mg L^{-1} to 200 mg L^{-1} at constant resin dosage (7 g L^{-1} for both anionic resins). Resulting data were fitted according to the following isotherm models: Langmuir, Freundlich and Temkin.

In the solid phase it was assumed that two mechanisms for the uptake of phenol into the resin beads take place, one by IE and another by molecular adsorption (Carmona et al., 2006).

The corresponding parameters for phenol/OH^{-} equilibrium uptake were obtained by means of experiments in recirculation mode. Model solutions of phenol were put in contact with each IE resin until equilibrium was achieved. The flask containing the feed solution was stirred continuously during the whole experiment. The flow rate and temperature were fixed at 10 L h^{-1} and 298 K, respectively.

The removal efficiency was determined by computing the percentage sorption using the formulae in Eq. (1):

% Phenol sorption = $\frac{Co - Ce}{Co}$ x 100 $\qquad\qquad$ (1)

where C_o and C_e refers to the initial and equilibrium phenol concentration (mg L^{-1}), respectively.

2.4. Procedures

Total phenols and phenol derivatives were analysed by reaction with a derivative thiazol, giving a purple azo dye which was determined photometrically using a Helios Gamma UV–visible spectrophotometer (Thermo Fisher Scientific) at 475 nm (Standard German methods ISO 8466-1 and DIN 38402 A51) (Greenberg et al., 1992).

Both IE resins were initially washed several times with double distilled water, following the advice of resins manufacturers, in order to get proper swelling prior to adsorption experiments. In this work, fixed-bed operation was chosen. After each operational cycle, the strong-base and weak-base anion exchange resins were regenerated by using NaOH (4 %) and NaOH (2%) aqueous solutions, respectively. Subsequently, both resins were washed with double distilled water to remove the excess of base.

The analysis of the adsorption isotherms and kinetic models was performed using the Excel program.

3. Results and discussion

3.1 Effect of initial concentration

The effect of the initial phenol concentration on the removal efficiency is plotted in Fig. 1 and Fig. 2. In this study phenol concentration was varied between 1 to 200 mg L^{-1} and the resins dosages were kept at 7.0 g L^{-1}. Results show that phenol ions removal through both resins is considerably influenced by its concentration in the feedstream. It was found that the phenol removal efficiency decreases from 99.6 % for 1 mg L^{-1} phenol in the feedstream, to 74.2 % for the highest assayed concentration (200 mg L^{-1} phenol in the feedstream) under identical IE operating conditions in terms of recirculation time and temperature for the strong-base anion exchange resin. In this case, it can be ensured that IE was the predominant process responsible of the phenols ion removal since the increase in pH in the outlet stream was directly proportional to the removal efficiency for each assayed initial concentration. This fact is due to the replacement of OH- ions with hydroxide. Hence, the decrease in the removal percentage with the phenol concentration in the feedstream could be related to saturation of the IE resin (Senthil Kumar and Gayathri, 2004).
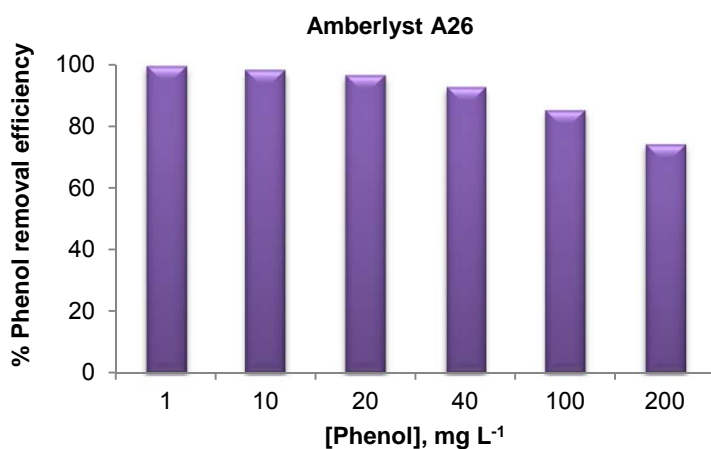

Figure 1. Effect of initial concentration ([Phenol]$_0$) on phenol uptake through Amberlyst (resin dosage = 7 g L^{-1}, recirculation time = 60 minutes and temperature = 298 K).
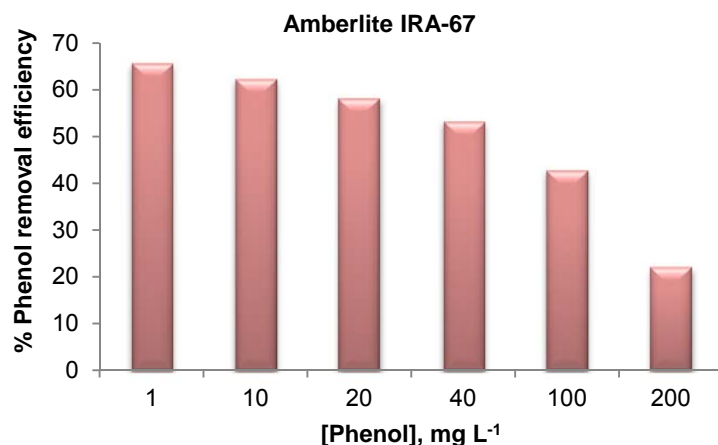
Figure 2. Effect of initial concentration ([Phenol]$_0$) on phenol uptake through Amberlite IRA-67 /resin dosage = 7 g L^{-1}, recirculation time = 60 minutes and temperature = 298 K).

On the other hand, phenol removal efficiency was found to decrease from 65.7 % for 1 mg L^{-1} phenol in the feedstream, to 22.1 % for the highest assayed concentration (200 mg L^{-1} phenol in the feedstream) under the same conditions for the weak-base anion exchange resin. In this case, the removal percentage decrease was more pronounced. The phenol removal efficiency dropped around 25% for the strong-base anion exchange resin. Otherwise, this drop was about 44 % (almost the double) for the weak-base anion exchange resin. In this case, phenols IE by Amberlite IRA-67 would be favored at low pH, since this resin is only active in the range of 0–7 (see table 1). In addition, the phenol dissociation to phenol and phenolate can be considered as a function of the total concentration of phenol and the pH of the liquid solution (pH > 8). At acidic pH (pH < 8) the phenol dissociation is low and therefore, the molecular adsorption process is the predominant one, whereas both adsorption and IE are important at alkaline pH (Carmona et al., 2006). Consequently, it can be assumed that the adsorption is the main responsible process for phenol removal through Amberlite IRA-67.

3.2. Equilibrium isotherms

The experimental data at equilibrium amount of adsorbed phenol on Amberyst A26 and Amberlite IRA-67 (q_e) and the concentration of phenol in the liquid phase (C_e) at a constant temperature were used to describe the optimum isotherm model. The linear forms of Langmuir, Freundlich and Temkin equations were employed to describe the equilibrium data. The performance of each form was judged through the correlation coefficients (R^2).

C_0 represents the initial phenol concentration in the inlet stream (mg of phenol L^{-1} of solution), V (m^3) is the volume of the phenol solution and m$_s$ (kg) is the corresponding resin amount.

In this work, the IE capacity of both selected resins was evaluated as a function of the pollutant concentration, by determining its loading capacity q_e (mg of pollutant / g of adsorbent) (Eq. 2):

$$q_e = (C_0 - C_e) \cdot \frac{V}{m_s} \qquad (2)$$

Langmuir isotherm model describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place (Langmuir, 1918). Thereby, the Langmuir model represents the equilibrium distribution of ions between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites, which is represented by the following equation (Eq. 3):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (3)$$

where C_e is the equilibrium concentration in the solution (mg L^{-1}), q_m and K_L are the Langmuir constants, representing the maximum IE capacity for the solid phase (resin) loading and the energy constant related to the uptake heat, respectively.

Freundlich isotherm represents the relationship between the amounts of ionic species exchanged per unit mass of resin, q_e, and the concentration of the ionic species at equilibrium, C_e (Freundlich, 1906). The Freundlich exponential equation is described as follows:

$$q_e = K_f C_e^{1/n} \qquad (4)$$

where K_f and n are the Freundlich constants, characteristic of the system, indicators of the IE capacity and intensity, respectively.

On the other hand, Temkin isotherm model was finally tested to modelize the adsorption potential of both anionic resins towards phenolic compounds. This model takes into account the effects of indirect adsorbent (resin) /adsorbate (phenol) interactions on the adsorption process (Temkin and Pyzhev, 1940). The model is given by Eq.(5), as follows:

$q_e = B \cdot \ln (A \cdot C_e)$ (5)

where A is the Temkin isotherm equilibrium binding constant (L g^{-1}) and B is the constant related to heat of sorption (J/mol).

The relevant coefficients of each model for both resins and the calculated linear fit means squares are also reported in Table 2.

The results indicate that the linear form of Langmuir model fits with utmost accuracy the experimental data for both resins, as indicated by the high value of the regression coefficient (R^2 = 0.99). Furthermore, as it can be observed in Table 2, the maximum IE capacity, q_m, was calculated as 22 mg g^{-1} for Amberlyst A26, whereas it was 7.5 mg g^{-1} for Amberlite IRA-67. This means the strong-base anion exchange resin (Amberlyst A26) has triple phenol removal capacity compared to the weak-base anion exchange resin (Amberlite IRA-67).

Caetano et al. studied phenol adsorption onto AuRix 100 (weak base anion exchange resin) and Dowex XZ (strong anion exchange resin) for initial phenol concentrations in the range 5-2000 mg L^{-1}. In this case, the maximum IE capacity (q_m) was found to be 46.2 mg g^{-1} (pH 3) and 75.8 mg g^{-1} (pH 11) for Aurix 100, whereas it was 43.5 mg g^{-1} (pH 3) and 76.8 mg g^{-1} (pH 11) for Dowex XZ. It is worthy to highlight that for the same data, the slope of the Langmuir equation decreases considerably with increasing C_e (and therefore with increasing C_e). On the other hand, q_m is indirectly proportional to the slope. This fact could explain why q_m is higher for studies from Caetano et al. (2009), since their isotherms experiments were based on higher initial phenol concentrations (5-2000 mg L^{-1} vs. 1-200 mg L^{-1}).

Table 2. Langmuir, Freundlich and Temkin isotherm parameters for phenol uptake by Amberlys A26 and Amberlite IRA-67 resins.

	Langmuir model			Freundlich model			Temkin model		
	K_L	q_m	R^2	K_f	n	R^2	A	B	R^2
Amberlyst A26	0.30	22	0.99	3.5	1.8	0.98	5.8	3.4	0.94
Amberlite IRA-67	0.038	7.5	0.99	0.29	1.4	0.95	0.41	1.6	0.95

* Coefficient Units: K_L (L mg^{-1}); q_m (mg g^{-1}); K_f (L mg^{-1}); A (L g^{-1}); B (J mol^{-1})

On the other hand, the linear form of the Freundlich isotherm at room temperature was employed to determine the value of K_f and n (Table 2). The R^2 values of Freundlich model were found to be lower than the R^2 value of Langmuir isotherm for the studied resins. In both cases, the value of the n coefficient is higher than 1, which highlights the favourability of the adsorption process. In this sense, the value of n was higher for Amberlyst A26 (1.8 vs 1.4), indicating that adsorption process was more favoured for this resin.

Finally, it was obtained that the value of R^2 for Temkin model (0.95) was lower than that calculated for Freundlich model (0.98) for Amberlyst A26 (Table 2). Moreover, the heat of sorption process, estimated by Temkin isotherm model, was found to be 5.8 J mol^{-1} and 0.41 J mol^{-1} for Amberlyst A 26 and Amberlite IRA-67, respectively.

3.3. Gibbs free energy

Gibbs free energy was also calculated from the standard thermodynamic equilibrium constant, K_C (L g^{-1}), which was defined as follows:

$K_C = \dfrac{qe}{Ce}$ (6)

where q_e is the amount of adsorbed phenol per unit mass of resin at equilibrium (mg g^{-1}) and C_e is the equilibrium aqueous concentration of phenol.

The standard Gibbs free energy changes ($\Delta G°$) can be calculated according to the following equation (Alzaydien, 2009):

$\Delta G° = -RT \ln K_C$ (7)

where T is the temperature (K) and R is the ideal gas constant (kJ mol^{-1}K^{-1}).

The $\Delta G°$ was found to be -1.55 kJ mol^{-1}for Amberlyst A26, indicating that the uptake process of phenol by this strong-base anion exchange resin is spontaneous at room temperature. Notwithstanding, the free energy changes in phenol-Amberlite IRA-67 system were 3.06 kJ mol^{-1}. In this case, the positive value points out that the uptake process is not spontaneous at room temperature.

4. Conclusions

The phenol uptake by weak-base anion exchange resin (Amberlite IRA-67) and strong-base anion exchange resin (Amberlite IRA-67) has been investigated on the basis of the feedstream phenol concentration effect. The aim of this study was to examine the potential of these IE resins towards the removal of phenol.

The phenol removal efficiency decreases considerably as the initial phenol concentration increases. In this sense, the phenol removal efficiency decreased from 99.6 % for 1 mg L^{-1} phenol in the feedstream, to 74.2 % for the highest assayed concentration (200 mg L^{-1}) for the strong-base anion exchange resin. In this case, it can be ensured that IE was the predominant process responsible of phenol removal.

On the other hand, phenol removal efficiency decreased from 65.7 % for 1 mg L^{-1} phenol in the feedstream, to 22.1 % for the highest assayed concentration (200 mg L^{-1}) for the weak-base anion exchange resin. In this case, the decrease was more pronounced and it can be assumed that the adsorption is the main responsible process for phenol removal through this resin. Langmuir isotherm provided the best correlation for both IE resins (R^2 = 0.99).

Finally, results demonstrated that phenol uptake onto Amberlyst A26 resin is a spontaneous process ($\Delta G°$ = -1.55 kJ mol^{-1}), whereas it is not spontaneous for the phenol-Amberlite IRA-67 system ($\Delta G°$ = 3.06 kJ mol^{-1}). Therefore, Amberlyst A26 was confirmed to be considerably more efficient than Amberlite IRA-67 for the potential removal of phenol from industrial effluents.

Acknowledgements

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