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Phenols removal from industrial effluents through novel polymeric resins: Kinetics and equilibrium studies

M.D. Víctor-Ortega *, J.M. Ochando-Pulido, A. Martínez-Férez

Chemical Engineering Department, University of Granada, 18071 Granada, Spain

A B S T R A C T

The efficient removal of phenols from wastewaters has increasingly become a significant environmental concern due to its high toxicity even at low concentrations. In this research work, phenols 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 phenols concentration in the feed-stream was investigated as well as the effect of recirculation time. Equilibrium data fitted to the Langmuir, Freundlich and Temkin isotherms revealed Langmuir isotherm provided the best correlation for both resins (R^2 = 0.99). Kinetic studies performed based on pseudo-first order, pseudo-second order and intraparticle diffusion models showed that although the correlation coefficients of the second-order model were the highest (R^2 = 1) and also the SSE values were the lowest (<2%), the kinetics of phenols uptake could be also satisfactorily described by intraparticle diffusion. On the other hand, results revealed that phenols 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 phenols from industrial effluents.

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1. Introduction

Phenols are pollutants presenting high toxicity, refractoriness as well as persistence and accumulation in the environment, and thus its removal is a main environmental issue. Phenolic compounds exist in wastewaters from olive mill, oil refineries, plastics, leather, paint, pharmaceutical and steel industries [1]. Phenols are also present in domestic effluents and vegetation decay [2]. 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 [3].

Different methods have been proposed to eliminate phenolic compounds from polluted waters, including chemical oxidation [4–7], chemical coagulation [8,9], extraction with solvents [10], membrane technology [11,12] adsorption [13–16] and ion exchange (IE) [12,17–27]. In this scenario, adsorption technology is currently being applied widely for the removal of organic micropollutants from aqueous solutions. Concretely, 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 [23].

Adsorption on selective resins has also been investigated for the removal of phenols from aqueous solutions, either through molecular adsorption or IE mechanisms. Caetano et al. tested the removal of phenol through IE mechanism on polymeric resins followed by desorption with methanol/water mixtures [23]. Zhu et al. 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 [24]. Juang et al. studied the adsorption of phenol and 4-chlorophenol on XAD4, XAD7, and XAD16 [26]. Furthermore, Bertin et al. examined the direct adsorption of olive mill wastewater (OMW) phenols on XAD7 and XAD16 resins followed by desorption with different solvents [27]. 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

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* Corresponding author.
  E-mail address: mdvictor@ugr.es (M.D. Víctor-Ortega).

removal increased steadily with increasing pH [22]. 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 pK_a (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 [1]. Anasthas and Gaikar have also used the IE technique for the separation of alkylphenols from non-aqueous systems. They found that the separation is mainly governed by acid–base interactions between phenolic OH⁻ groups and the basic groups of the resin structure [28].

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 phenols from aqueous solution. The effect of the phenols 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, kinetics of experimental data have been analysed using pseudo-first order, pseudo-second order and intraparticle diffusion models. Finally, the suitability of the proposed IE resins has been investigated through thermodynamic parameters.

2. Experimental

2.1. Materials

Analytical grade reagents and chemicals with purity over 99% were used for the analytical procedures, applied at least in triplicate.

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, both provided by Sigma Aldrich. Typical physical and chemical characteristics of these resins are described in Table 1.

2.2. Ion exchange equipment

Fig. 1 shows the flow-sheet scheme of the experimental apparatus (MionTec), which consisted of a peristaltic pump (Ecoline VC-380) and a column containing IE resin. The IE column employed in this study was made of an acrylic tube (540 mm height × 46 mm
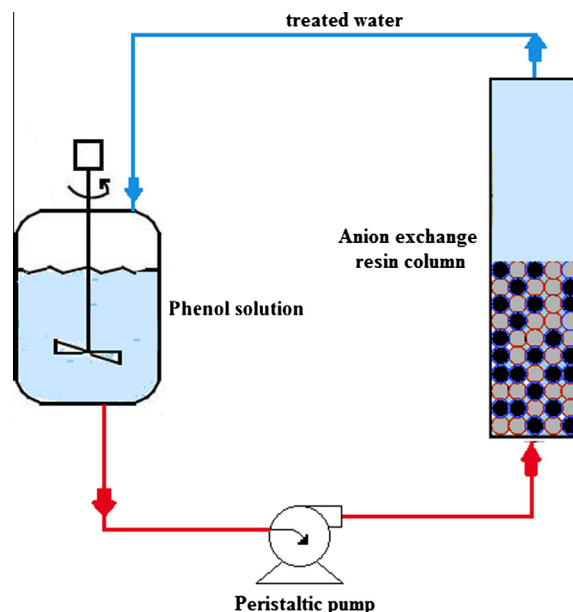

Fig. 1. Flow-sheet scheme of IE recirculation operating device for phenols removal.

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. The dead volume of this column was 0.55 L.

2.3. Equilibrium experiments

The uptake of phenols 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 phenols was examined in the range 1–200 mg L⁻¹, until equilibrium was achieved.

On the other hand, adsorption isotherm studies were carried out with different initial phenols concentrations ranging from 1 mg 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.

Furthermore, for the determination of the kinetics at different phenols initial levels, data were fitted to the following kinetic models: first-order kinetic model, second-order kinetic model and intraparticle diffusion model.

In the solid phase it was assumed that two mechanisms for the uptake of phenols into the resin beads take place, one by IE and another by molecular adsorption [1]. The following equations describe these mechanisms.

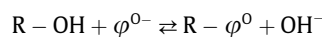(a) Exchange of phenolate anion with the counter-ion (OH) of the resin:

$$R - OH + \varphi^{O-} \rightleftarrows R - \varphi^{O} + OH^-$$

Table 1
Physicochemical 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