ADSORPTION OF PHENOL AND P-CHLOROPHENOL FROM AQUEOUS SOLUTIONS ON POLYMER ADSORBENT

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ABSTRACT

In the present study, a commercial Amberlite XAD-4 resin was investigated for its ability to remove phenol and p-chlorophenol in aqueous solution. The adsorption dynamics obeyed the pseudo-second order rate equation and the adsorption rate constant of phenol was a little greater than that of p-chlorophenol. The adsorption isotherms can be correlated to Freundlich isotherm. The adsorption capacity for p-chlorophenol was larger than that for phenol at the same temperature and equilibrium concentration.

INTRODUCTION

Phenol and its derivatives are important organic intermediates, which are widely used for the manufacture of pesticide, paper, textile, synthetic rubber and plastic [1]. Due to their dramatically negative environmental impacts, once discharged into the receiving water system with industrial waste streams, the efficient removal technologies have increasingly become a significant environmental concern [2]. Many methods such as catalytic oxidation, membrane separation, and adsorption have been developed to deal with the wastewater containing phenolic compounds, and among which, adsorption by different adsorbents is shown effective [3]. In recent years, polymeric resins have attracted increasing attention as an alternative to activated carbon in industrial effluent treatment mainly due to their favorable physico-chemical stability, large adsorption capacity, good selectivity, and structural diversity [4].

The objective of this study was to investigate the adsorption potential of the commercial porous polystyrene resin (Amberlite XAD-4) for the removal of phenol and p-chlorophenol from aqueous solutions.

MATERIALS and METHODS

Adsorption experiments

The adsorption experiments were performed at 25°C, pH=6-7, using 200 mg adsorbent added at 100 mL solution of phenol and respectively p-chlorophenol with different initial concentrations of 0.8 to 1.8 mmol L^{-1}. All experiments were performed at a shaking speed of 150 rpm for 24 h to ensure the equilibrium of the adsorption process.

The concentration of phenol and p-chlorophenol was performed by spectrophotometric analysis using a Varian, Carry 300 instrument. The absorbance values were measured according to the maximum UV-absorption, at the wavelength of 270 nm for phenol and 280 nm for p-chlorophenol.

The removal efficiency (%) of phenol and p-chlorophenol was evaluated using the following formula:

$$E = \frac{C_o - C_e}{C_o} 100 \quad (1)$$

where, C_0 and Ce are the concentration of phenol and p-chlorophenol (mmol/L) in the solution at time equal 0 (initial) and equilibrium, respectively. The adsorption amount (Q) was calculated according to Eq. (2):

$$Q = \frac{V(C_o - C_e)}{m} \quad (2)$$

where, V is the solution volume (L), Ce is the concentration of phenol and p-chlorophenol (mmol/L) in the solution at equilibrium, and m is the amount of absorbent (g).

Adsoption kinetics

The experimental data was fitted to two different kinetic equations: pseudo-first order (Lagergren) and pseudo-second order equation.

The pseudo-first order rate equation of Lagergren [5] is generally described by the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where, k_1 is the pseudo-first-order rate constant. After integration [6], by applying the conditions, $q_t=0$ at t=0 and at t = t, $q_t=q_t$, Eq. (3) becomes:

$$\ln(q_e - q) = \ln q_e - k_1 \cdot t \quad (4)$$

where, q_e is the amount of phenol and respectively p-chlorophenol adsorbed at equilibrium in mmol/g. A straight line of ln(qe −q) versus t suggests the applicability of this kinetic model. The values of k_1 and $q_{e\ calc.}$ were calculated from the slope of the plots of log $(q_e - q_t)$ versus t for different concentrations of phenol and p-chlorophenol.

The pseudo-second order kinetic model [7] is expressed as follows:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where, k_2 is the pseudo-second order rate constant. By plotting, t/q versus t is a linear relationship. Values of k_2 and q_e were calculated from the intercept and slope of the plots of t/q versus t. The results of k_2 and correlation coefficients (R^2) were shown in Table 1.

Adsorption isotherms

Langmuir and Freundlich models have been widely used to describe adsorption isotherms in wastewater treatment applications [5]. The Langmuir isotherm (Eq.6), assumes uniform and constant binding of the sorbate on the surface of the adsorbent, which is usually described by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mmol/g), q_m is the maximum adsorption capacity (mmol/g), C_e is the equilibrium concentration of the solute in the bulk solution (mmol/L) and K_L is the Langmuir sorption constant (L/mmol).

The Freundlich expression is an empirical equation based on adsorption onto a heterogeneous surface. The Freundlich isotherm equation (Eq.7) is:

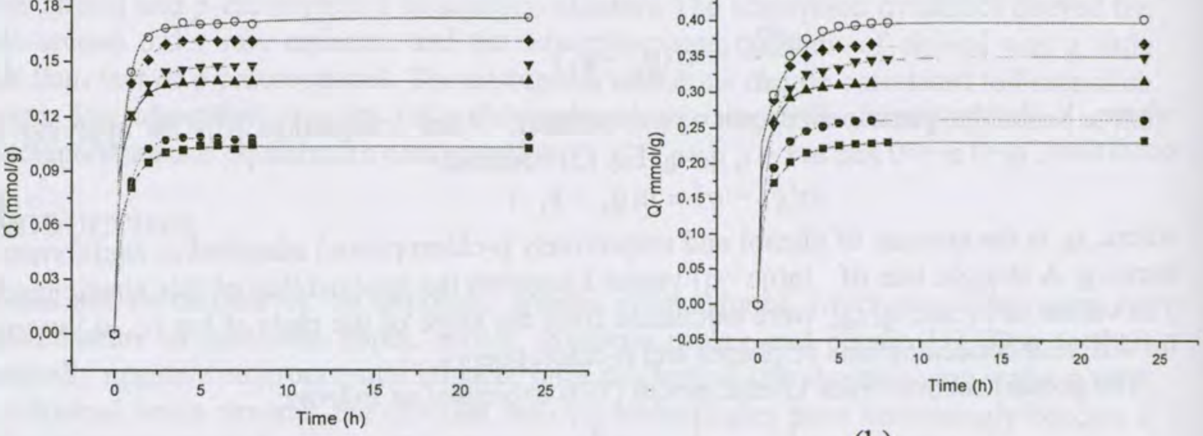
$$q_e = k_F C_e^{1/n} \tag{7}$$

where, k_F is the Freundlich sorption constant, indicating the relative adsorption capacity of the adsorbent ((mmol$^{1-(1/n)}$ L$^{1/n}$)/g)) and n is a constant, representing the intensity of adsorption.

RESULTS

Adsorption results

The results show an increase adsorption of phenol and para-chlorophenol per unit weight with increasing initial concentration and, also, the uptake of phenol and para-chlorophenol at initial stages of the contact time being somewhat fast, with reduction in uptake rate closer to equilibrium time (after 24 h). Based on the results, the contact time was fixed as 24h. As it is shown in Fig. 3, phenol and 4-CP removal increased with time attaining the maximum value at 24h and then remained constant.



(a)

(b)

Fig.3 Effect of contact time of phenol (a) and 4-CP (b) adsorption on XAD-4 at 25 °C; t_e=24h; (■)Co=0.8mmol/L, (●)Co=1.0mmol/L, (▲)Co=1.2 mmol/L, (▼)Co=1.4mmol/L, (♦)Co=1.6mmol/L, (○)Co=1.8mmol/L.

Adsorption kinetics

The pseudo-first order (Eq.4) and the pseudo-second order model (Eq.5) were applied for the experimental data to predict the adsorption kinetics.

The fitted results summarized in Table 1 reveal that the pseudo-second-order rate equation gives a perfect fitting for the adsorption because the correlative coefficients R^2 are all higher than 0.99 and the equilibrium adsorption capacities q_e predicted from the pseudo-second order rate equation are very close to the experimental ones by extrapolating the adsorption dynamic curves.

Adsorption isotherms

Langmuir and Freundlich isotherm models were chosen for evaluating the relationship between the amount of phenol and 4-CP adsorbed onto XAD-4.

The results (Table 2) indicate that the experimental data cannot be correlated to the Langmuire isotherm whereas the Freundlich isotherm is suitable for describing the adsorption since the correlation coefficients R^2 are higher than 0.9. The adsorption is a multilayer and a heterogeneous process with sites that have different energies of adsorption. The value of n varies with the heterogeneity of the adsorbent and for favorable adsorption process the value of n should be less than 10 and higher than unity [8].

The values of Freundlich constants (Tab 2), K_f and n, are 0.138 and 1.401 respectively in the case of phenol and 0.401 respectively 2.016 in the case of 4-CP with correlation coefficient (R^2) of 0.977 respectively 0.971. From the results, the adsorption pattern of phenol and 4-CP onto the polymer fit satisfactorily to Freundlich equation.

Table 1. The correlative parameters for the adsorption curves of phenol and 4-CP adsorbed onto XAD-4 according to pseudo-first order and pseudo-second order rate model.

Adsorbed	**Initial concentration**	**Pseudo-first order**		**Pseudo-second order**			
	C_o[mmol/L]	**$k_1 \cdot 10^3$ [min^{-1}]**	**R^2**	**k_2[g/mmol min]**	**R^2**	**q_e[mmol/g]**	
						Exp.	**Calc.**
Phenol	0.89	15.93	0.9734	2.3347	0.9997	0.1047	0.1037
	0.97	19.34	0.9855	1.4313	0.9998	0.1093	0.1098
	1.23	10.32	0.7991	1.7133	0.9999	0.1397	0.1402
	1.44	9.609	0.8469	1.0838	0.9999	0.1486	0.1493
	1.57	13.93	0.8453	1.5704	0.9999	0.1617	0.1622
	1.76	8.58	0.7797	0.7439	0.9999	0.1742	0.1749
P-CP	0.80	36.29	0.932	0.326	0.999	0.2331	0.2353
	0.99	25.32	0.971	0.370	0.999	0.2620	0.2642
	1.20	34.06	0.900	0.438	0.999	0.3157	0.3173
	1.42	27.69	0.951	0.211	0.999	0.3496	0.3532
	1.62	25.63	0.955	0.344	0.999	0.3684	0.3707
	1.52	27.79	0.919	0.212	0.999	0.4022	0.4059

Table 2. The correlated parameters for the adsorption isotherms of phenol and 4-CP onto the polymer according to Freundlich and Langmuire isotherm.

Adsorbed	**Freundlich**			**Langmuire**		
	n	**K_F**	**R^2**	**q_m**	**K_L**	**R^2**
Phenol	1.401	0.138	0.9777	0.471	0.416	0.8975
P-CP	2.016	0.401	0.9712	0.630	1.681	0.9736

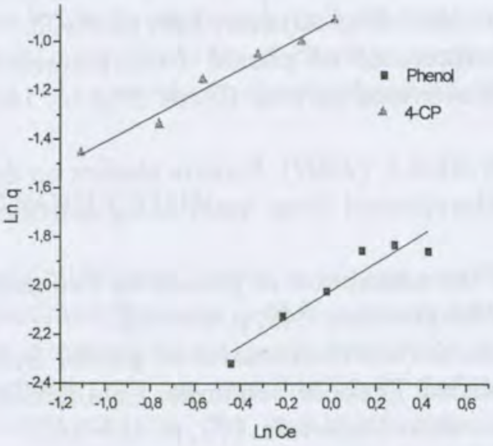


Fig.5 Freundlich isotherm model of XAD-4 for phenol and 4-CP. Temperature: 25°C; adsorption time: 24h.

Tab.3 Values of the removal efficiency (E) for phenol and 4-CP at different initial concentrations

C_0 (mmol/L)	E (%)	
	Phenol	4-CP
0.8	23.4	58.5
1.0	22.6	52.9
1.2	22.7	52.6
1.4	20.5	49.1
1.6	20.6	45.6
1.8	19.8	44.2

CONCLUSIONS

- The XAD-4 adsorbent exhibited higher adsorption capacity for 4-CP removal compared to Phenol.
- For the first 5 hours and higher initial concentrations, uptake for phenol and 4-CP is more pronounced in comparison with the lower initial concentrations.
- The kinetic adsorption model correspond to the pseudo-second order.
- The adsorption of phenol and 4-CP on the polymer is better described by the Freundlich's isotherm. This means that polymer has a heterogeneous surface with sites that have different energies of adsorption.
- The values of the removal efficiency (E) and of the Freundlich's constant (n) demonstrate the much better efficiency of the polymer for the 4-CP then for the phenol removal.
- Adsorption experiments showed that a complete phenol and 4-CP removal from aqueous solution could be realized by grafting the polymer with suitable groups.

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