Removal of 5-Amino-2-chlorotoluene-4-sulfonic and Chlorhydric Acids From Wastewater by Weakly Basic Resin: Equilibrium and Kinetics[1]

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Objective   To study the adsorption of 5-Amino-2-chlorotoluene-4-sulfonic (CLT) and chlorhydric (HCl) acids from wastewater by weakly basic resin.   **Methods**   The kinetics and isotherm were studied. Thermodynamic parameters for the adsorption of acids were calculated and discussed.   **Results**   The adsorption of CLT and HCl acids followed Langmuir isotherm and the first-order kinetics model.   **Conclusion**   The adsorptive affinity of the two acids on D301R is in the order of CLT acid > HCl acid. CLT and HCl acids can be separated.

Key words: 5-Amino-2-chlorotoluene-4-sulfonic acid; Chlorhydric acid; Adsorption; Weakly basic resin

INTRODUCTION

5-Amino-2-chlorotoluene-4-sulfonic (CLT) acid is an important structural unit for a variety of synthetic dyes and pigments. Wastewater originating from CLT acid manufacture contains a large amount of CLT acid, less chlorhydric (HCl) acid, *etc*. In view of their influence on human and animal life as well as water environment, it is essential to remove them before discharge of wastewater into water bodies. Removal of CLT and HCl acids from effluent is one of the challenging problems in the field of environmental chemistry, because of the difficulty in treating such wastewater by conventional chemical and biological treatment methods[1-6]. Furthermore, most of these methods remain specific for pollutant removal, rather than removing other inorganic and organic pollutants. Thus, specific methods are not very useful in treating wastewater containing other pollutants. Removal of acids using ion-exchange resins by adsorption and exchange is an efficient and economic process, as it can generally remove all types of pollutant from wastewater and the effluent treatment is convenient because of its simple design and easy operations[7]. By using a good and efficient weakly basic anion exchange resin in the adsorption process, it is possible to remove, in addition to CLT acid, a large number of other organic and inorganic pollutants.

In the present study, the possibility of using a weakly basic resin D301R is considered to recover CLT and HCl acids from industrial wastewater, since the weakly basic resin has good selectivity and large capacity, and is easy for regeneration[4]. Adsorption equilibrium and kinetic have been explored.

MATERIALS AND METHODS

Reagents and Resins

CLT and HCl acids were procured from Tianjin Chemical Company (China). The adsorbent D301R, a commercially available weakly basic resin was from Nankai University Chemical Plant. Double-distilled water was used for the preparation of solutions. All reagents used in the present study were of analytical grade.

Analysis

The pH of solution was measured with the Elico LI 127 pH meter. The concentrations of CLT and HCl acids in each solution were determined by high performance liquid chromatography (Shimadzu). The adsorbed phase concentration was calculated according to the equation.

$$q=(c_0-c)m'/w \qquad (1)$$

Adsorption Experiments

Adsorption was determined by batch method, which is simple and easy to perform and permits convenient evaluation of parameters that influence the adsorption process. A fix amount of the resin (5 g) was added to 30 mL solution of varying concentrations taken in stoppered glass vessel, which was placed in the thermostat shaking assembly. The solutions were stirred continuously at a constant temperature for over 6 h to achieve equilibration. The pH of acid solution was adjusted by adding NaOH or HCl solution. The experiments were repeated several times, and average values were reported. Kinetic studies of adsorption were also carried out at a definite original concentration wherein the extent of adsorption was investigated as a function of time.

RESULTS

Effect of Contact Time

To determine the equilibration time for the maximum uptake of acids, their adsorption at a fixed concentration on D301R resins was studied as function of contact time, and the results of R resin adsorption are shown in Fig. 1.

The rate of uptake of CLT and HCI acids was rapid at the beginning and 60% of their ultimate adsorption was completed within 2 h. The time required for equilibrium adsorption was 7 h (Fig. 1).

Adsorption Isotherm

To assess the efficiency of D301R resin in removing CLT and HCl acids, equilibrium adsorption of the two acids was studied as a function of concentration on D301R resin at different temperatures, and the adsorption isotherms obtained are shown in Figs. 3 and 4. A comparison of adsorption capacity at 25℃ and 35℃ (Figs. 2A and 2B) showed that the adsorption increased with increased
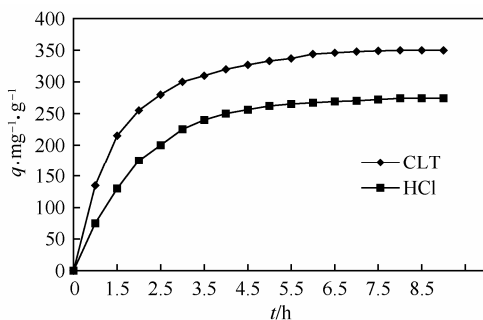

FIG. 1. Effect of contact time for the uptake of CLT and HCl acids on D301R resin adsorption (initial concentration=3%, adsorbent=5 g, temperature=25℃, pH≤2).

temperature, indicating that the process was apparently endothermic. Similar results have been reported by other workers[8-9]. This would result in more adsorption at a higher temperature.

Langmuir model $\quad 1/q_e=1/q_{max}+1/(q_{max}bc_e)$ $\quad$ (2)
Freundlich model $\qquad q_e=kc_e^{1/n}$ $\qquad$ (3)

Both acids exhibited isotherms of type I as previously described[10]. Such isotherms were characterized by strong adsorbate-adsorbent interactions. The 2-parameter Langmuir and Freundlich models were fitted to the adsorption data of each solute using the regression method, and the parameters of both adsorption models are listed in Tables 1 and 2, respectively. The values of the parameter q_{max} in the Langmuir model could roughly reflect the order of adsorption affinity between the two acids.

The monolayer capacity (q_{max}) of the D301R resin for the acids was comparable to the maximum adsorption obtained from adsorption isotherms. As b values could reflect the equilibrium constant for the adsorption process, they could also reflect the affinity of the resin for acids. In view of the values of R^2 listed in Tables 1 and 2, the Langmuir model exhibited a little better fit to the adsorption data than the Freundlich model.
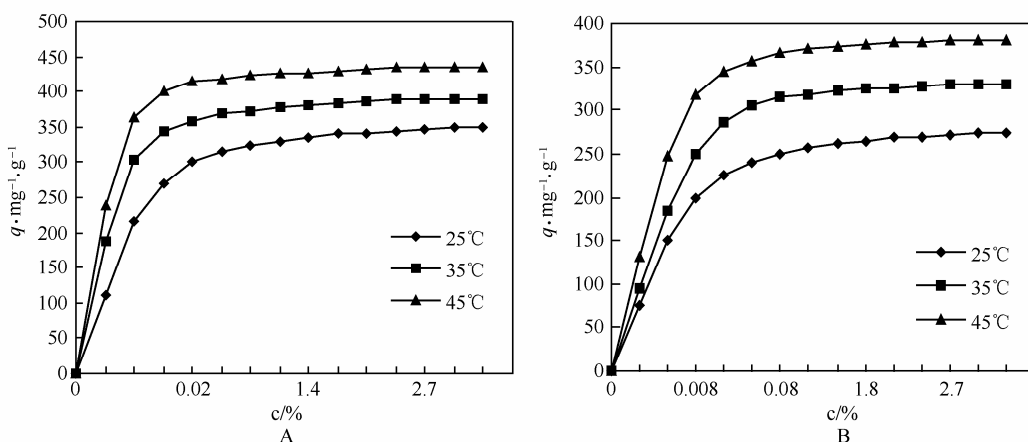

FIG. 2. Adsorption isotherms of CLT (A) and HCl (B) acids on D301R (adsorbent=5 g, pH≤2).

TABLE 1

Langmuir Parameters of D301R Resin

Solute	25℃			35℃			45℃		
	q_{max} (mg g^{-1})	b (g mg^{-1})	R^2	q_{max} (mg g^{-1})	b (g mg^{-1})	R^2	q_{max} (mg g^{-1})	b (g mg^{-1})	R^2
CLT Acid	344.83	483.33	0.9990	384.62	866.66	0.9988	434.78	1150	0.9990
HCl	263.16	422.22	0.9989	322.58	442.86	0.9992	384.62	519.99	0.9994

TABLE 2

Freundlich Parameters of D301R Resin

Solute	25℃			35℃			45℃		
	k (mg g^{-1})	$1/n$	R^2	k (mg g^{-1})	$1/n$	R^2	k (mg g^{-1})	$1/n$	R^2
CLT Acid	337.4	0.0330	0.8760	383.2	0.0167	0.9198	430.4	0.0109	0.8949
HCl	262.2	0.0410	0.8920	296.7	0.0334	0.7950	373.7	0.0229	0.8476

The free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) in adsorption process were calculated using the following equations[11]:

Clapeyron-Clausius equation

$$\ln c_e = -\ln(k_0) + \frac{\Delta H}{RT} \qquad (4)$$

Gibbs equation

$$\Delta G = -RT \int_0^X q \frac{dX}{X} \qquad (5)$$

Gibbs-Helmholtz equation

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (6)$$

The ΔH values in Table 3 are obtained from Figs. 3A and 3B. The ΔG and ΔS values are summarized in Tables 4 and 5.

$y = 20643x - 69.319$
$R^2 = 0.9999$
$y = 11271x - 40.864$
$R^2 = 0.9997$
$y = 11029x - 40.498$
$R^2 = 0.9999$

◆ qe=270 mg/g
■ qe=250 mg/g
▲ qe=240 mg/g

$y = 23328x - 78068$
$R^2 = 0.9992$
$y = 22498x - 76.475$
$R^2 = 0.9997$
$y = 15931x - 57.017$
$R^2 = 0.9992$

◆ qe=300 mg/g
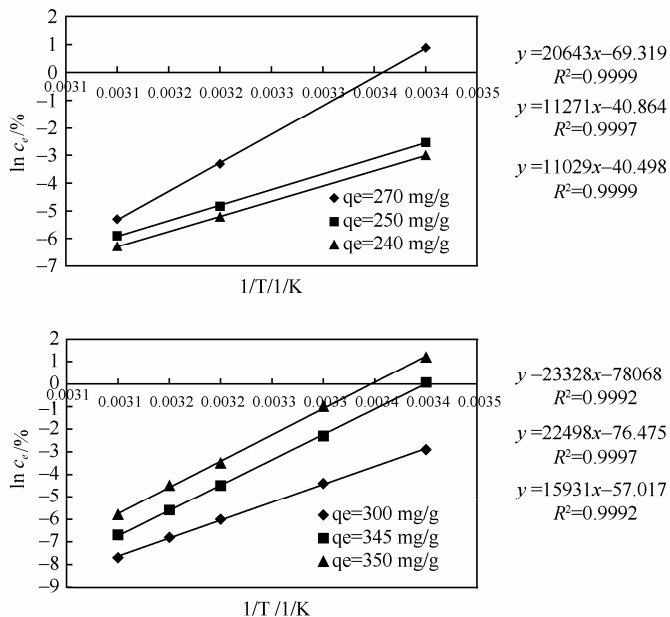■ qe=345 mg/g
▲ qe=350 mg/g

FIG. 3. Typical Clapeyron-Clausius plot for adsorption of CLT (A) and HCl (B) acids on D301R resin.

TABLE 3

Enthalpy Change in CLT and HCl Acids on D301R Resin

Enthalpy	q_{CLT}/mg g^{-1}			q_{HCl}/mg g^{-1}		
	350	345	300	270	250	240
ΔH/kJ mol^{-1}	193.95	187.05	132.45	171.63	93.71	91.70

TABLE 4

Free Energy Change in Adsorption of CLT and HCl Acids on D301R Resin

Free Energy	Tem	q_{CLT}/mg g^{-1}			q_{HCl}/mg g^{-1}		
		350	345	300	270	250	240
	25℃	220.30	219.14	210.09	214.56	195.68	192.35
$-\Delta G$ /kJ mol^{-1}	35℃	232.45	231.07	228.67	229.23	206.23	202.69
	45℃	257.13	252.67	245.34	248.89	221.06	212.03

TABLE 5

Entropy Change in Adsorption of CLT and HCl Acids on D301R Resin

Entropy	Tem	q_{CLT}/mg g^{-1}			q_{HCl}/mg g^{-1}		
		350	345	300	270	250	240
	25℃	1390	1363	1149	1296	971	953
ΔS /J mol^{-1} K^{-1}	35℃	1384	1367	1172	1301	974	956
	45℃	1418	1383	1188	1322	989	955

Dynamic Modeling

The kinetic of adsorption is important since it controls the efficiency of the process. Various kinetics models have been used by different workers where the adsorption has been treated as first-order, pseudo-first-order, and pseudo-second-order process[11-12]. Different systems conform to different models.

The second-order kinetic rate equation can be described by the following equation:

$$dq_t/dt=k_2(q_e-q_t)^2 \qquad (7)$$

It can be rewritten as follows:

$$dq_t/(q_e-q_t)^2=k_2dt \qquad (8)$$

Integrating equation (8) for the boundary conditions $t=0$ to $t=t$ and qt=0 to $q_t=q_t$, gives:

$$1/(q_e-q_t)-1/q_e=k_2t \qquad (9)$$

which is an integrated rate law for a second-order reaction (Fig. 4), equation (9) can be rearranged to obtain:

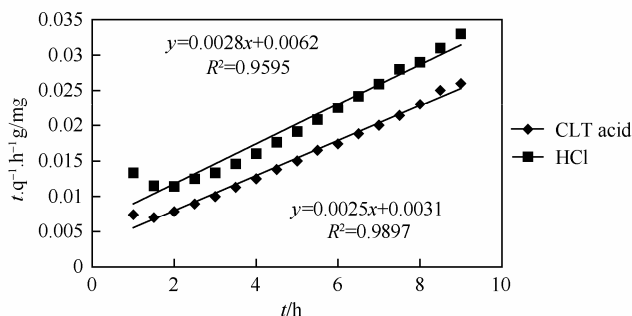$$t/q_t=1/k_2q_e+t/q_e \qquad (10)$$

FIG. 4. Second-order kinetic plot for the adsorption of acids on D301R resin at 45℃.

The t/q_e was calculated from the kinetic data of Fig. 1 and plotted against the time in Fig. 4.

The first-order sorption described by equation (11) is known as Lagergres rate equation[11]. The Lagergres rate equation (Fig. 5) is most widely used for the adsorption of a solute from a liquid solution.

$$\log(q_e-q)=\log(q_e)-k_{ads}t/2.303 \qquad (11)$$

The log (q_e-q) was calculated from the kinetic data in Fig. 1 and plotted against the time in Fig. 5. The plots were linear with correlation coefficients ranging from 0.998 to 0.999, indicating that

Lagergres rate equation was applicable to the acid adsorption on D301R resin and that the adsorption process was the first-order process. The first-order rate constants calculated from the plots (Fig. 5) were found to be 0.576 and 0.699 for CLT and HCl acids, respectively.

The kinetic data were further used to learn about the slow step occurring in the present adsorption system. The applicability of the following Banghams equation (Fig. 6) to present adsorption studies was tested[12]:
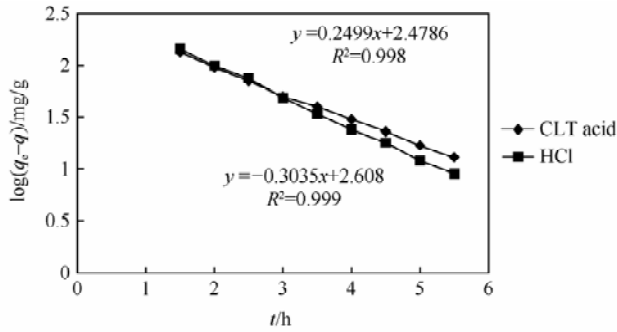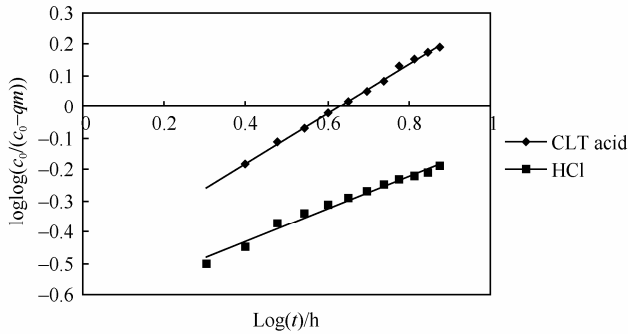
FIG. 5. Lagergres plot for acids on D301R resin.

FIG. 6. Banghams plot for acids on D301R resin.

$$\log\log(c_0/(c_0-qm))=\log(k_0m/2.303V)+\alpha\log(t) \quad (12)$$

As such loglog $(c_0/(c_0-qm))$ values were plotted against log (t) in Fig. 6, the linearity of these plots confirmed the applicability of Banghams equation, indicating that the adsorption of acids was pore diffusion controlled.

DISCUSSION

The effect of temperature can be explained on the basis of hydrogen bonding. In aqueous solutions of acids, there exists extensive hydrogen bonding between the acid molecules and water, resulting in appreciable solubility. These hydrogen bonds get broken at higher temperatures, leading to less soluble acids, and therefore exhibit a higher tendency to go to the resin surface and are then adsorbed rather than remaining in the solution.

The ΔH values are positive. As the adsorption process is pore diffusion controlled, an increase in molecular diffusion occurs at a higher temperature, leading to endothermic enthalpy of adsorption. Furthermore, negative ΔG values indicate the spontaneous process while positive ΔS values indicate the affinity of the adsorption for acids.

The experimental values for CLT and HCl acids are not in significant agreement with the plot of the second-order kinetic rate equation, suggesting that the second-order kinetic rate equation does not appear to be able to characterize the adsorbent-adsorbate system in this case.

The higher rate constant for HCl acid may be due to its smaller size, which would facilitate its approach through pores to adsorbent surface.

CONCLUSION

D301R resin is shown to be effective for the adsorption of acids from aqueous solution. The uptake of acids on D301R is substantial and found to be 350 mg/g and 274 mg/g for CLT and HCl acids, respectively. For the adsorption of CLT and HCl acids on D301R, the second-order kinetic rate equation, though being unable to provide the best fit model, could display the first-order chemical reaction kinetics, which provides the best correlation of data. For the systems, the Langmuir isotherm model could give a reasonably good fit to the isotherm data, rather than the Freundlich equation. The detailed adsorption studies on D301R indicate that the adsorption process is endothermic and pore diffusion controlled.

The breakthrough curves will be studied to realize separation of CLT and HCl acids from waste water in column process, and the regeneration method of saturated resin with different concentration of NaOH, which can be used as a adsorption agent,

will be discussed.

NOMENCLATURE

b equilibrium constant, g mg^{-1}
c final concentration in liquid phase, %
c_e equilibrium concentration in liquid, %
c_0 initial concentration in liquid phase, %
k empirical Freundlich constant
k_0 constant
m concentration of resin, g L^{-1}
m' weight of solution, mg
n empirical Freundlich constant
q_{max} saturation capacity, mg g^{-1}
q adsorbed phase concentration, mg g^{-1}
q_e equilibrium concentration in solid phase, mg g^{-1}
R gas constant, J mol^{-1}k^{-1}
T temperature, k
t time, h
V volume of solution, mL
w weight of resin, g
X equilibrium molar ratio of adsorbate in liquid phase

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