



Treatment of high-strength phenolic wastewater by a new two-step method

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Abstract

Treatment of high-strength phenolic wastewater by a novel two-step method was investigated in the present study. The two-step treatment method consisted of chemical coagulation of the wastewater by metal chloride followed by further phenol reduction by resin adsorption. The present combined treatment was found to be highly efficient in removing the phenol concentration from the aqueous solution and was proved capable of lowering the initial phenol concentration from over 10,000 mg/l to below direct discharge level (1 mg/l). In the experimental tests, appropriate conditions were identified for optimum treatment operation. Theoretical investigations were also performed for batch equilibrium adsorption and column adsorption of phenol by macroporous resin. The empirical Freundlich isotherm was found to represent well the equilibrium phenol adsorption. The column model with appropriately identified model parameters could accurately predict the breakthrough times. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: High-strength phenolic wastewater; Metal chlorides; Chemical precipitation; Adsorption isotherm; Column adsorption model

1. Introduction

Phenol and phenolic derivatives are the organic chemicals that appears very frequently in the wastewater from almost all heavy chemical, petrochemical and oil refining industries. Because of their toxicity to human and marine life, increasingly stringent restrictions have been imposed on the concentrations of these compounds in the wastewater for safe discharge [1]. In Taiwan, for instance, the phenol concentration in the industrial wastewater for safe discharge has been reduced from 2 to 1 mg/l due primarily to health consideration. Hence, treatment of industrial wastewater containing phenolic compounds is a necessity.

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Traditionally, activated sludge process has been the most widely used method to deal with phenolic wastewater because of its simplicity and relatively low cost [2]. However, the microorganisms in an activated sludge system, even well acclimated, can only deal with chemical wastewater containing relatively low concentration of phenolic compounds, usually less than 100 mg/l due to low biodegradability and inhibitory effects of these compounds [3]. Unfortunately, the chemical wastewaters from many heavy chemical and petrochemical industries contain phenolic compounds exceeding this concentration level. Hence, treatment of high concentration phenolic wastewaters by chemical or physical alternatives is crucial in these industries.

There are various chemical or physical methods for dealing with industrial wastewaters containing phenol over hundreds of mg/l. They included, for example, extraction by liquid membrane [4–7], adsorption by activated carbon or activated carbon fiber [8,9], macroporous resin [10–13] and organoclays [14,15], wet air oxidation [1,16–20], chemical decomposition by Fenton's reagent [1], ozonation [31] and electrochemical method [22]. In a number of wastewaters from petrochemical or heavy chemical industries, the phenol concentration could reach as high as tens of thousand mg/l level. Among the methods mentioned above, wet air oxidation (WAO) or its catalytic variation (catalytic WAO) is one that can handle this high-strength phenolic wastewaters [1,16–21]. But as reported in the previous investigations [1,16–21], the WAO method has several drawbacks. This method is capable of rapidly decomposing the phenolic compounds in the wastewater and the phenolic decomposition is invariably accompanied by a generation of many small molecule organic compounds [1,16–21]. These small molecule organic compounds can not be effectively removed in the WAO process and a significant amount of chemical oxygen demand (COD) remains in the WAO effluent. Therefore, the WAO process is effective in destroying the phenolic compounds, but not in removing the wastewater COD. Furthermore, because of its operating high temperatures and high pressures, the WAO method has relatively high capital investment and operating costs. To remedy these disadvantages, effective treatment alternative operating under atmospheric conditions would be necessary.

The objective of this work is to present a new two-step method for dealing with phenolic wastewater containing phenol over tens of thousand mg/l. The present method consists of first step chemical precipitation of phenol by metal chloride. In this step, the metal chloride converts phenol under alkaline conditions to metal phenolate that precipitates out of the aqueous solution due to its very low solubility and the phenolate is thus recovered for reuse. The efficiency of this chemical precipitation, when properly operated and with the right kind of metal chloride, can far exceed 90%. The remaining wastewater containing considerably reduced amount of phenol is then treated using adsorption resin which is able to further lower the phenol concentration to below the discharge level of 1 mg/l. The previous investigations of the phenol adsorption by resin [10–13] focused primarily on the practical aspects only. In the present work, several theoretical aspects of resin adsorption of phenol were examined using the observed data. Again, the phenol is recovered in this adsorption step when the adsorption resin is regenerated. The present two-step method was found to be highly efficient, as would be elaborated later, enabling essentially total phenol recovery from the wastewater for reuse.

2. Materials and methods

In the first step of the present treatment process, stock solution was prepared with a phenol concentration of 50,000 mg/l. The metal chlorides chosen included barium, calcium, copper, ferrous and ferric chlorides. All chlorides were GR grade and obtained from Aldrich (Milwaukee, Wisconsin, USA). 0.5 N solutions for all chlorides were prepared. The test runs were conducted in a 250 ml Erlenmeyer flask. 100 ml of stock phenol solution was placed in the flask and the pH of the solution was adjusted to a desired value between 9 and 13 due to the fact that chemical precipitation occurs only under alkaline conditions. After adding 0.5 mol/l of chloride, the flasks were sealed and placed in a constant temperature shaker set at 100 rpm. Sufficient time (approximately 4 h for all runs) was allowed for the chemical reaction to complete. After completion of chemical reaction, metal phenolate rapidly settled out of the solution due to its low solubility. Sample was taken from the clear solution for phenol measurement. The phenol concentration in the aqueous solution was determined by a Hewlett Packard GC (Model 5890, Hewlett Packard Instrument Co., Colorado, USA) equipped with a FID detector and a GP80/100 Carboxpack capillary column. The above experimental procedure was applied to barium, calcium, copper, ferrous and ferric chlorides.

The macroreticular adsorption resin employed in the second step was the Amberlite XAD-4 resin, as obtained from Rohm and Haas, Inc. (Philadelphia, Pennsylvania, USA). This resin was a sulfonated styrene/divinyl-benzene polymer. Table 1 shows some physical properties of the Amberlite resin, as provided by the manufacturer. For pretreatment, the Amberlite resin was washed alternately several times with hexane and deionized water and dried at 60 °C in an electric oven for over 24 h. It was then placed in a desiccator for cooling. As noted earlier [10–13], the Amberlite resin was effective for phenol adsorption from aqueous solution. But the previous investigations provided little information for basic understanding of the phenol adsorption process. In the present study, experimental tests were conducted to gather data of phenol adsorption by the Amberlite resin in batch and column processes so that the adsorption isotherm and the column adsorption performance can be evaluated and established.

To determine the equilibrium phenol adsorption capacity of the Amberlite resin, a 250 ml Erlenmeyer flask was placed in a constant temperature bath for temperature control. 250 ml of the stock solution were put in the flask and 0.5 g of pretreated Amberlite resin was added. The flask was sealed. The speed of the constant temperature shaker was set at 100 cycles/min

Table 1
Physical properties of amberlite XAD-4 resin

Item	Amberlite XAD-4
BET surface area (m ² /g)	800 (dry)
Specific gravity	1.03
Porosity (ml/ml)	0.5
Particle size (mesh)	0.3–1.2
Operating pH range	0–14
Maximum operating temperature (°C)	180

and the temperature was maintained at 30 ± 0.5 °C or any desired temperature. After a test run was started, flasks were taken out periodically and the aqueous phenol concentrations determined by the HP GC for various adsorption times. It usually took approximately, 10 h for the adsorption to reach equilibrium. However, the batch equilibrium tests were run for over 15 h to ensure a adsorption equilibrium. Each of the equilibrium batch runs was repeated once to ensure the accuracy of the obtained equilibrium adsorption capacity data. In the majority of the test runs, the two equilibrium adsorption capacities differed by no more than 3% and the average was accepted. In very few cases, where the difference between the two equilibrium adsorption capacities exceeded 3%, an identical third run was made and the two closer data points were used.

The experimental apparatus for column adsorption test is shown in Fig. 1. The adsorption column was a pyrex glass tube of 1.88 cm ID and 12 cm high. It was equipped with a water jacket for temperature control. The adsorption column was packed with 10 g of the Amberlite resin to an adsorption bed volume of 20.5 cm^3 . In each test run, the stock solution containing 1000–7000 mg/l phenol was fed using a feed pump to the top of the adsorption column and its flow rate was regulated by a precision flow meter. After a test run was started, the exiting aqueous solution was sampled periodically and the phenol concentration determined.

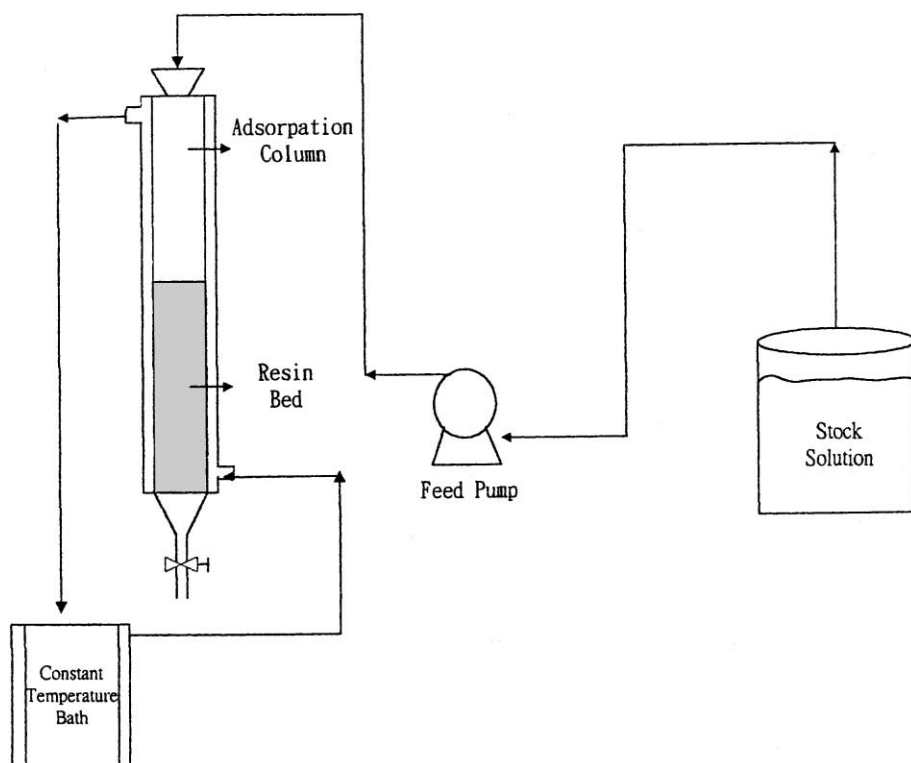
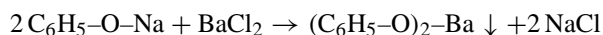
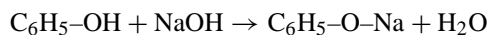


Fig. 1. Schematic of column adsorption process.

3. Results and discussion

3.1. Chemical precipitation by metal chlorides

The chemical reactions (barium chloride, for example) taking place in the aqueous solution in the precipitation stage were as follows:



In the above chemical reaction and precipitation, the important issues to be addressed included the initial pH of the aqueous solution, the kind and the amount of metal chloride needed to effect a good chemical precipitation and the effect of temperature. Fig. 2 shows the changes of phenol concentration and its removal as a function of pH for phenol precipitation using barium chloride. The phenol removal improves steadily as the pH increases and reaches a plateau at pH 13. The same pH dependence of phenol removal was observed for other metal chlorides. Hence, a pH 13 was adopted as the optimal pH condition for the present chemical precipitation. Under this pH condition, the final phenol concentration and phenol removal are listed in Table 2 for various metal chlorides. The table clearly shows that barium chloride yields the best results with over 95% phenol removal that is followed by ferric and calcium chlorides. In addition to its high phenol removal, precipitation using barium chloride was observed in the experimental tests to generate significantly denser metal phenolate sludge than metal chlorides. Hence, barium chloride is clearly the best choice for the present chemical precipitation.

According to the above chemical reactions, 1 mol of barium chloride can react with and precipitate 2 mol of phenol. The amount of phenol in 100 ml of 50,000 mg/l initial stock

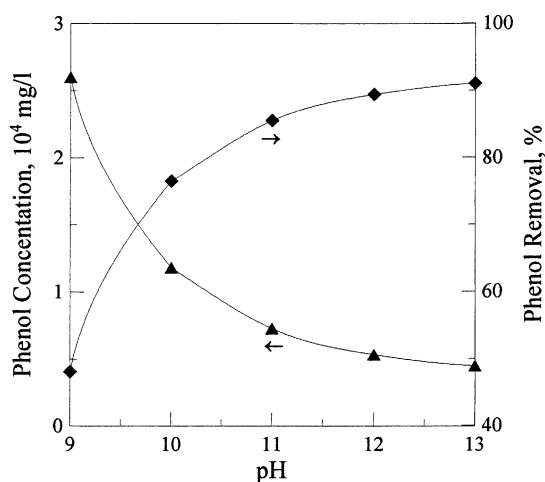


Fig. 2. Chemical precipitation of phenol by barium chloride as a function of pH with 50,000 mg/l phenol concentration.

Table 2
Phenol removal for various metal chlorides^a

Metal	Final phenol concentration (mg/l)	Phenol removal (%)
Ba ²⁺	2387	95.2
Ca ²⁺	8424	83.2
Cu ²⁺	14831	70.3
Fe ²⁺	14940	70.1
Fe ³⁺	5697	88.6

^a Initial conditions: phenol concentration 50,000 mg/l, metal ion concentration 0.5 mol/l, pH 13.

solution was 0.0266 mol. This translated to 53.2 ml of 0.5 mol/l barium chloride solution required on the stoichiometric basis. In Fig. 3, the effect of the volumetric amount of barium chloride on the final phenol concentration and its removal is demonstrated. It is of interest to note that for barium chloride below the stoichiometric amount (53.2 ml), the final phenol concentration of the aqueous solution after chemical precipitation was approximately at 2400 mg/l. However, at or above the stoichiometric amount, the final phenol concentration was lowered to approximately, 1300 mg/l. The changes in the final phenol concentration at the stoichiometric point is quite significant. However, in terms of the percent phenol removal, the improvement went from about 95 to 97.5%. The much less impressive improvement in the phenol removal is obviously due to high initial phenol concentration (50,000 mg/l). The improvement in the final phenol concentration from 2400 to 1300 mg/l will lead to a much reduced adsorption load of the macroreticular resin. Hence, the amount of barium chloride added for chemical precipitation must be kept at or slightly above the stoichiometric point for optimum process performance.

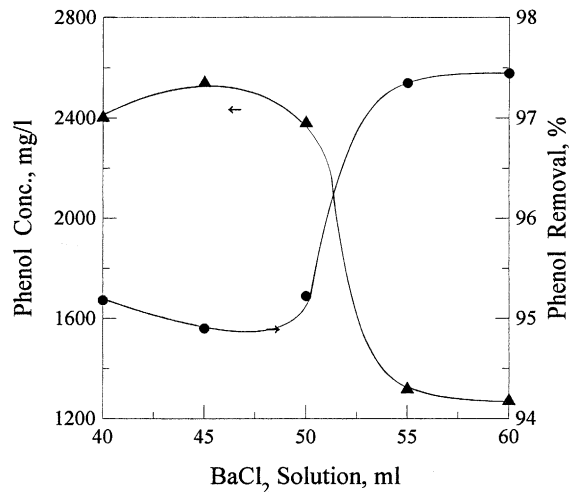


Fig. 3. Chemical precipitation of phenol as a function of the amount of barium chloride with initial 50,000 mg/l initial 50,000 mg/l phenol concentration and pH 13.

The last operating parameter explored in the chemical precipitation tests was the temperature. Four test runs were conducted by adding 50 ml of 0.5 mol/l barium chloride to 100 ml of 50,000 mg/l phenol solution within the temperature range between 20 and 65 °C with a 15 °C increment. The average phenol removal for all runs found to be $95.1 \pm 0.4\%$. Hence, the temperature effect on the chemical precipitation is negligible.

3.2. Equilibrium and column adsorption of phenol

Two general adsorption isotherms that can be used to describe the equilibrium adsorption relation are the well-known monolayer Langmuir and empirical Freundlich model [23] which are represented by

$$q_e = \frac{abC_e}{1 + bC_e} \quad (1)$$

$$q_e = KC_e^{1/n} \quad (2)$$

where q_e and C_e are the equilibrium phenol adsorption capacity of the resin and the equilibrium phenol concentration in the aqueous solution, respectively, and a , b , K and n are the isotherm parameters. Fig. 4 demonstrates the isotherm model fits to the observed data (solid symbols). The results reveals that the Freundlich isotherm represents the observed data significantly better the Langmuir isotherm, The isotherm parameters obtained from the model fit are: $K = 0.6184$ and $n = 0.6806$.

A theoretical model was adopted in the present study for describing the change in the phenol concentration at the column exit. The basic idea of this model is mathematically similar to that originally employed by biologists for describing the phenomena of biological growth and decay [24]. In the present case, the entering aqueous solution flows through the

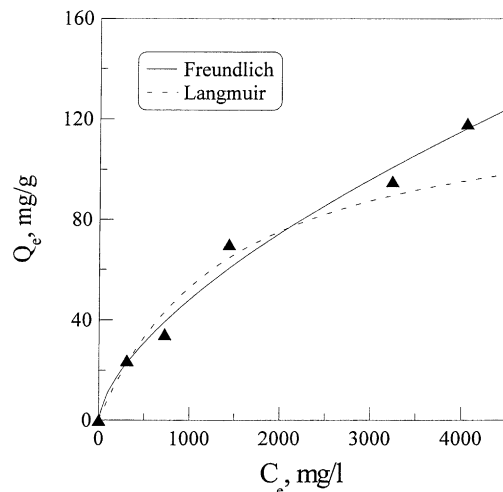


Fig. 4. Comparison of model fit of equilibrium phenol adsorption by Amberlite XAD-4 resin.

stationary bed of adsorption resin and part of phenol in the aqueous solution is adsorbed onto the resin, while the other passes through the bed. Note that the fraction of phenol being adsorbed is A and the fraction of that remaining in the aqueous solution and passing through the stationary resin bed is P . It is reasonable to assume that the rate of decrease in the adsorption fraction (A) is proportional to A and P as represented by

$$-\frac{dA}{dt} \propto AP \quad (3)$$

or

$$-\frac{dA}{dt} = kAP \quad (4)$$

Noting that $P = 1 - A$, Eq. (4) can be integrated with an initial condition of $P = P_a$ at $t = t_a$

$$\ln \left[\frac{P_a(1 - P)}{P(1 - P_a)} \right] = k(t_a - t) \quad (5)$$

For phenol removal at $P_a = 0.5$, the adsorption time (t_a) is denoted as τ and Eq. (5) becomes

$$P = \frac{1}{1 + \exp[k(\tau - t)]} \quad (6)$$

or

$$t = \tau + \frac{1}{k} \ln \left(\frac{P}{1 - P} \right) \quad (7)$$

The phenol fraction (P) that passes through the Amberlite column is equal to C/C_0 with C being the phenol concentration in the aqueous solution exiting the adsorption column at time t and C_0 the inlet concentration. According to Eq. (7), a plot of adsorption time (t) versus $\ln[C/(C_0 - C)]$ yields a straight line with the intercept and slope of the straight line equal to τ and $1/k$, respectively. Alternatively, τ can also be obtained at the adsorption time when $\ln[C/(C_0 - C)]$ is zero because of the fact that by definition, τ is the adsorption time when C is one-half of C_0 . With k and τ determined in this fashion, Eq. (7) can be used to construct the entire breakthrough curve. Since only two model parameters are involved in Eq. (7), two accurate experimental data points of C as a function of adsorption time (t) would be theoretically sufficient to establish those two parameters. However, for accurate estimation of the model parameters, a complete breakthrough curve would be recommended as necessary.

The derivation for Eq. (7) was based on the definition that 50% breakthrough of the adsorption process occurs at τ . Accordingly, the resin bed should be completely saturated at 2τ . Due to the symmetrical nature of the breakthrough curve, the amount of phenol adsorbed by the resin is one-half of the total phenol entering the adsorption column within the 2τ period. Hence, the following equation can be written

$$W_e = \frac{1}{2} C_0 F (2\tau) = C_0 F \tau \quad (8)$$

The above equation establishes the relation among the adsorption capacity of the column (W_e), inlet phenol concentration (C_0), liquid flow rate (F) and the 50% breakthrough time (τ).

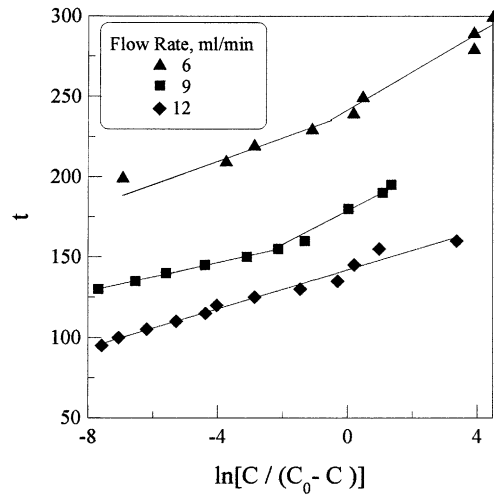


Fig. 5. Plot of t vs $\ln[C/(C_0 - C)]$ with initial 50,000 mg/l phenol concentration and pH 13.

Fig. 5 shows, a plot of adsorption time (t) versus $\ln[C/(C_0 - C)]$ for phenol adsorption in a Amberlite XAD-4 column for three flow rates. This figure reveals that only the run for 12 ml/min flow rate observes the simple linear relationship stipulated by Eq. (7). For the runs with flow rates 6 and 9 ml/min, the relation can be represented by two line segments. Hence, a set of τ and k was obtained for the run with 12 ml/min flow rate and two sets for the two other runs. The model parameters of breakthrough curves obtained from this figure are listed in Table 3 that shows reasonably good fit of the model equation to the breakthrough curve data with r^2 being larger than 0.98. The difference in the t versus $\ln[C/(C - C_0)]$ relationship shown in Fig. 5 for different flow rates is due probably to the fact that the breakthrough curves at 6 and 9 ml/min flow rate take longer to reach saturation than at 12 ml/min, and thus they become slightly unsymmetrical around 50% breakthrough point unlike the symmetric one for 12 ml/min flow rate. This implies that a non-linear relationship

Table 3
Column adsorption model parameters^a

	τ_1	$1/k_1$	τ_2	$1/k_2$	r^2
Flow rate (ml/min)					
6	238.7	2.281	241.7	11.875	0.984
9	164.2	4.403	178.9	10.555	0.992
12	142.1	6.047	–	–	0.986
Initial concentration (mg/l)					
1000	368.9	14.228	–	–	0.981
3000	217.3	6.182	–	–	0.983
5000	164.2	4.403	178.9	10.555	0.992
7000	140.9	4.678	–	–	0.985

^a Both τ and k in min.

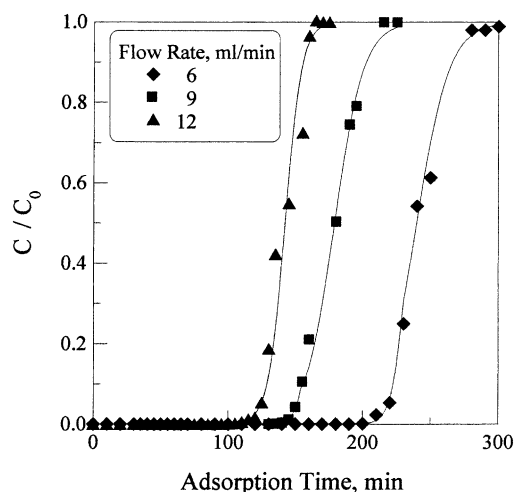


Fig. 6. Comparison of predicted and observed breakthrough curves of chemical precipitation of phenol by barium chloride for various flow rates and with initial 50,000 mg/l phenol concentration and pH 13.

between the saturation time of phenol adsorption and the liquid flow rate. The breakthrough curves (solid lines) constructed using the model parameters listed in Table 3 are compared with the observed data in Fig. 6. It is apparent that the model predictions are reasonably good. The excellent model fit at the low C/C_0 is particularly important because it allows improved prediction of the breakthrough point for safe phenol discharge. Using the model parameters listed in Table 3, the breakthrough times for 1 mg/l phenol discharge standard were calculated to be 173, 125 and 89 min, respectively, for 6, 9 and 12 ml/min flow rates. These breakthrough times are seen in Fig. 6 to be reasonable.

The lower portion of Table 3 lists the adsorption model parameters for three initial phenol concentrations of 1000, 3000, 5000 and 7000 mg/l and they were obtained in the same fashion by plotting t against $\ln[C/(C_0 - C)]$ as shown in Fig. 5. The theoretical predictions based on the model parameters listed here are shown in Fig. 7 along with the observed data. Again the model fit is quite good. Based on the model fit shown in Figs. 6 and 7, Eq. (7) can be recommended as a good means for theoretical modelling of the column adsorption process.

In the phenol adsorption process, the macroreticular resin would reach the breakthrough point or even become completely saturated. In these instances, regeneration of the exhausted resin will be necessary in order to recover the adsorbed phenol and reuse the resin. Several regenerants could be used, including methanol, ethanol, acetone or sodium hydroxide. In the present study, methanol was chosen. In the experimental tests, methanol was fed at a flow rate of 8 ml/min to the exhausted resin column and samples gathered from the solution exiting the column once every 5 min for phenol concentration measurement. Fig. 8 demonstrates the phenol concentration change of the exiting solution. It is noted that after two bed volumes, the phenol concentration in the exiting solution became negligible, indicating very efficient regeneration of exhausted resin by methanol. The regenerated resins were tested for phenol

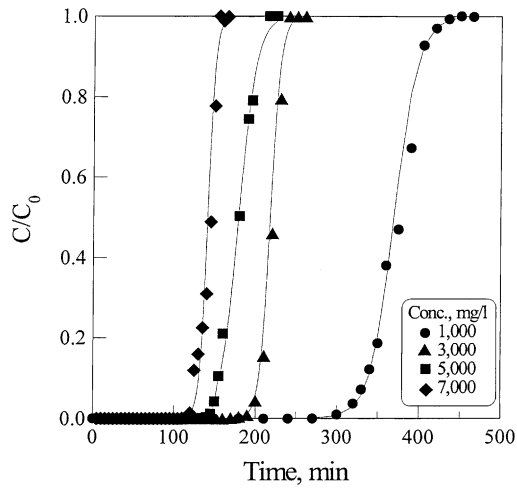


Fig. 7. Comparison of predicted and observed breakthrough curves of chemical precipitation of phenol by barium chloride for various initial phenol concentrations and with 9 ml/min flow rate and pH 13.

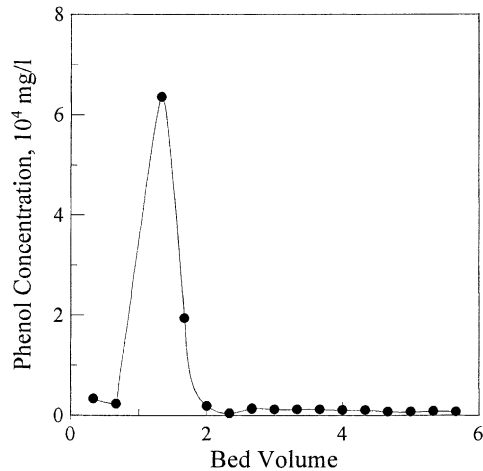


Fig. 8. Phenol concentration of aqueous solution exiting the adsorption column during the regeneration period.

adsorption again and for up to 10 repeated runs conducted in the present study, practically no loss of adsorption efficiency of regenerated adsorption resin was observed.

4. Conclusions

The high-strength phenol wastewater was treated by a novel two-step process in the present study. The two-step method consists of chemical precipitation of the high-strength

phenolic wastewater by metal chloride followed by phenol adsorption using macroreticular resin. The two-step treatment method offers an excellent means for dealing with the high-strength phenolic wastewater. Based on the results obtained from tests of individual step, the optimum operating conditions were identified. The test results revealed the following.

1. An optimum initial pH around 13 was observed for chemical precipitation for all metal chlorides. Among the chlorides tested, barium chloride is the best with a phenol removal over 95%. Under similar operating conditions, ferric chloride and calcium chloride yield good phenol removal over 80%. The test results also indicated that a stoichiometric amount is sufficient to effect a very good phenol removal.
2. Adsorption using macroreticular resin (Amberlite XAD-4) would be sufficient to further reduce the remaining phenol in the wastewater to the safe discharge level (i.e. 1 mg/l).
3. Results of batch equilibrium tests reveal that the equilibrium phenol adsorption can be well characterized by a Freundlich isotherm. A theoretical model was also developed for describing the phenol adsorption process. The adsorption model involves only two model parameters that can be conveniently determined using a complete breakthrough curve. With the model parameters established in this fashion, the theoretical predictions using the adsorption model compare very well with the experimental breakthrough data. The established adsorption model allows accurate predictions of breakthrough time.

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