



Adsorption of hydrazoic acid from aqueous solution by macroreticular resin

Sheng H. Lin*, Cheng P. Huang

Department of Chemical Engineering, Yuan Ze University, Chungli 320, Taiwan, ROC

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Abstract

Sodium azide is a key component in the automobile air bag. When dissolved in aqueous solution, it reacts rapidly with water to form hydrazoic acid which is a highly toxic chemical and is strongly regulated by government. In the present study, adsorption of hydrazoic acid from aqueous solution by macroreticular resin is investigated. This method can provide a convenient means for dealing with the toxic hydrazoic acid. Experimental tests of batch equilibrium adsorption and continuous column adsorption of hydrazoic acid were conducted and the test results were employed to establish adsorption isotherm and to evaluate the column adsorption efficiency. The test results revealed that the multilayer adsorption isotherms, like the modified Langmuir or Jossens model, are needed to adequately describe the hydrazoic acid adsorption equilibrium between the liquid and solid (resin) phases. In the column adsorption process, a theoretical model was adopted for representing the hydrazoic acid change in the aqueous solution exiting the column and the verified theoretical model significantly facilitates prediction of adsorption breakthroughs and column design. Regeneration of exhausted resin was investigated. Solution of 10% (w/w) NaCl was found to be a very efficient regenerant. © 2001 Published by Elsevier Science B.V.

Keywords: Sodium azide; Hydrazoic acid; Macroreticular resin; Adsorption isotherm; Theoretical model

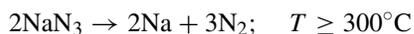
1. Introduction

Air bag is currently a necessary item in new motor vehicles for protection of human life. In a motor vehicle, air bag is designed to give the maximum protection in an accident of the driver and the passenger in the front seat. This safety device was first introduced in the late 1980. Since, then there has been considerable popularity in incorporating this safety device into all new motor vehicles. In the air bag, sodium azide is the key component. Due to

* Corresponding author. Fax: +886-3-455-9373.
E-mail address: ceshlin@saturn.yzu.edu.tw (S.H. Lin).

increasing demand for this product in recent years, annual production of sodium azide has far exceeded 5 million kg [1,2] and this demand is expected to continue for the foreseeable future.

There are three chemical compounds in an air bag, sodium azide (NaN_3), potassium nitrate (KNO_3) and silicon dioxide (SiO_2). When the motor vehicle is hit or suffers from severe deceleration, a rapid chemical reaction (or mild detonation) is triggered by an electric device and the air bag is inflated in a matter of millisecond [3]. The chemical reactions involved in the gas generation include [4]:



It is apparent from the above reactions that sodium azide is the primary nitrogen generator, potassium nitrate, as an oxidant, serves as a secondary nitrogen generator and silicon dioxide converts sodium and potassium oxides into inert alkaline silicate (a stable glass-like substance) during the chemical reactions. Depending on the supplier, the air bags installed on the driver and passenger sides contain approximately 100 and 200 g of sodium azide [2]. According to the above chemical reactions, the air bags on the driver and passenger sides are estimated to contain approximated 55 and 110 l of nitrogen at a pressure of 1 atm.

The great majority of air bags built into the motor vehicle are not used during the life of the automobiles. Hence, they are piling up in the junkyard where they are not commonly recycled. Due to its toxicity, sodium azide is becoming a big environmental concern because of its toxicity. As a biocide, sodium azide has an order of toxicity comparable to cyanide [5]. The US EPA relative risk comparison values of NaN_3 and NaCN are 0.15 and 1.5 mg/l in water [2], respectively, implying an order of magnitude of greater toxicity for the former. In air, the maximum allowable workplace concentrations for NaN_3 and KCN are 0.2 and 5 mg/m³, respectively [4]. Hence removal of NaN_3 from the aqueous solution or air environment is becoming mandatory.

In the aqueous solution, sodium azide readily reacts with water molecule to form hydrazoic acid [6], a weak acid whose heavy metal salts are used as detonators.



According to Betterton and Robinson [1], hydrazoic acid has a very low Henry's constant ($K_H = 12 \text{ mol/atm}$ at 25°C) and hence it is a volatile compound. Due to its toxicity, the threshold limit value of HN_3 is only at 0.29 mg/m³ [5]. In the literature, there is relatively very little work done on the disposal of sodium azide in aqueous solution or air environment. Hoigne et al. [7], Pryor et al. [8] and Betterton and Craig [2] considered various reaction and kinetic aspects of ozonation of hydrazoic acid in aqueous solution. These investigators had shown that ozonation can effectively convert hydrazoic acid in aqueous solution into various nitrogenous compounds, including N_2 , NO_2^- , NO_3^- and NO_x . However, due to its volatility as mentioned earlier, hydrazoic acid formed in the aqueous solution can be easily stripped out of water by the ozone gas mixture during the ozonation process. Such

an air stripping can cause some complication to ozonation treatment. In the present work, adsorption of hydrazoic acid in aqueous solution by macroreticular resin was considered as a potential alternative. Experiments were conducted to examine various facets of the aqueous equilibrium and column adsorption of hydrazoic acid. Theoretical models were adopted for describing both equilibrium adsorption and column adsorption processes and these models were experimentally verified using the observed data.

2. Experimental studies

The macroreticular resin employed in this study was the Dowex SAR, as obtained from Dow Chemical Company (Midland, MI, USA). It was a stable polymer of styrene/divinylbenzene. According to the manufacturer, the Cl-type, strong base anion SAR resin had an average diameter of 0.3–1.2 mm (over 90%), a cation exchange capacity (CEC) of 1.4 meq/ml wet resin and a density of 1.11. For pretreatment, the resin was washed alternately several times with acetone and deionized water to remove all impurities on its surfaces. It was then rinsed with hexane a few times. Finally, it was dried at 60°C in an electric oven for over 24 h and put in a desiccator for cooling.

The stock hydrazoic acid solution was prepared gravimetrically using NaN_3 obtained from Fluka Chemical Co. (microelectronic grade). The hydrazoic acid concentrations of the stock solution and all samples during the experimental tests were measured using an ultraviolet spectrophotometer (GBC UV-VIS 916, GBC Scientific Equipment Private Ltd., Melbourne, Australia). The UV spectra of all samples had a strong absorption at 222 nm on the GBC spectrophotometer.

To determine the equilibrium adsorption capacity of hydrazoic acid by the Dowex SAR resin, a 500 ml Erlenmeyer flask was placed in a constant temperature bath for temperature control. About 250 ml of the stock solution were put in the flask and 0.5 g of pretreated Dowex resin was added. The flask was sealed. The speed of the constant temperature shaker was set at 100 cycle/mm and the temperature was maintained at $25 \pm 0.25^\circ\text{C}$. After a test run was started, flasks were taken out periodically and the hydrazoic acid concentrations of aqueous solution determined by the GBC UV-VIS for various adsorption times. It usually took approximately 2 h for the adsorption to reach equilibrium. However, the batch equilibrium tests were run for over 6 h to insure a adsorption equilibrium. Each of the equilibrium batch runs was repeated at least once to insure the accuracy of the obtained data.

The experimental apparatus for column adsorption test is shown in Fig. 1. The adsorption column was a pyrex glass tube of 1.6 cm i.d. and 20 cm high. It was equipped with a water jacket for temperature control. The adsorption column was randomly packed with 10 g of the pretreated Dowex resin. In each test run, the stock solution containing no more than 1000 mg/l hydrazoic acid 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 hydrazoic acid concentration determined. The column adsorption tests were conducted for various feed flow rates of 10, 20 and 30 ml/min and inlet hydrazoic acid concentrations of 400, 600 and 800 mg/l.

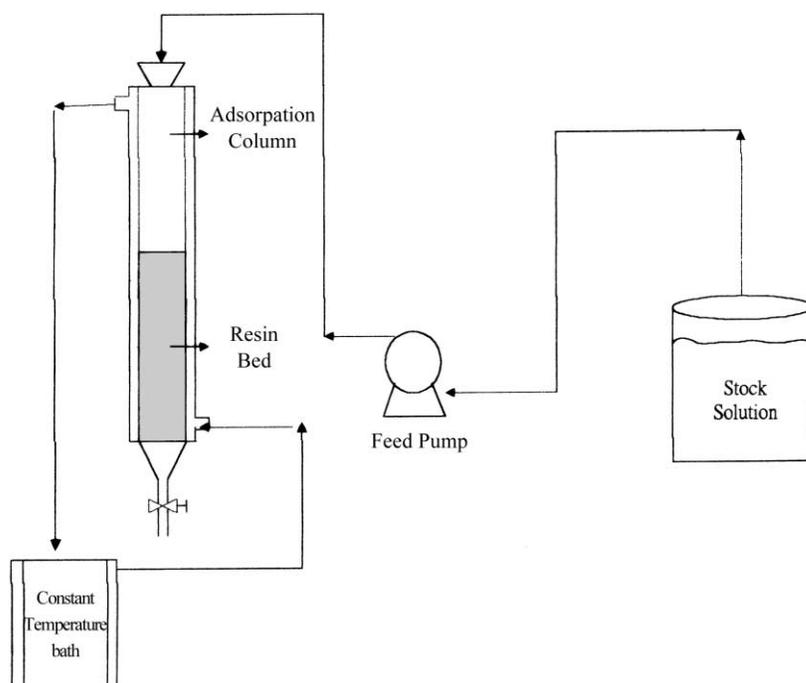


Fig. 1. Column adsorption equipment.

3. Results and discussion

3.1. Equilibrium adsorption of hydrazoic acid

Fig. 1 demonstrates the amount of hydrazoic acid adsorbed by the Dowex resin (Q) as a function of adsorption time (t). The transient amount of hydrazoic acid adsorption Q increases with an increase in the initial hydrazoic acid concentration. This is due to the increased concentration gradient of hydrazoic acid across the liquid–solid interface at higher initial hydrazoic acid concentration that facilitates overall mass transfer of hydrazoic acid from the liquid phase to the solid (resin) phase. The increase in the initial hydrazoic acid concentration also significantly shortens the time to reach adsorption equilibrium in this figure. The adsorption equilibrium was achieved in <2 h. However, for assurance of complete adsorption equilibrium, 6 h was adopted for all equilibrium test runs, shown in Fig. 2.

Various adsorption isotherms proposed [9,10] can be adopted for describing the present equilibrium hydrazoic acid adsorption by the Dowex resin. The monolayer Langmuir and empirical Freundlich isotherms are the most commonly used. These two isotherms are, respectively, represented by

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

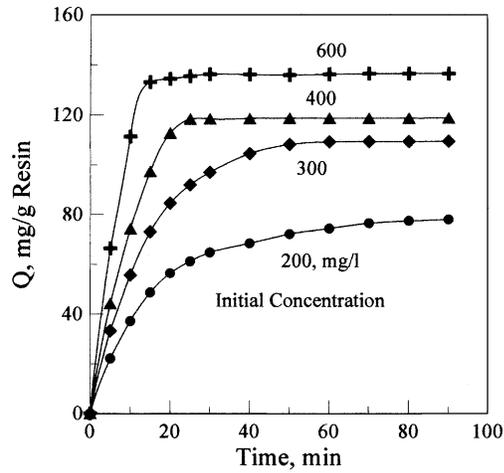


Fig. 2. The amount of hydrazoic acid adsorbed per unit weight of Dowex resin as a function of time with 0.5 g of resin and at 25°C.

$$Q_e = kC_e^{1/n} \quad (2)$$

where Q_e and C_e are the equilibrium hydrazoic acid adsorption capacity of the resin and the equilibrium hydrazoic acid concentration in the aqueous solution, respectively, and a , b , k and n are the isotherm parameters. The above isotherms were fit to the experimental data in Fig. 3 by following the standard methods for determining the isotherm parameters [9,10]. It is apparent that the two-parameter monolayer Langmuir and empirical Freundlich isotherms do not appear to be adequate for describing the equilibrium adsorption process.

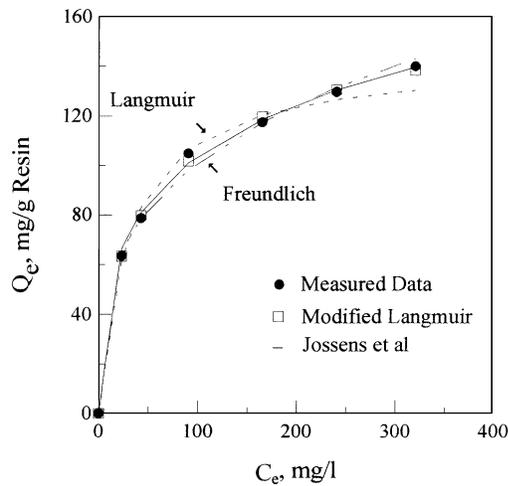


Fig. 3. Comparison of the model fit of various isotherms to the observed isotherm data at 25°C.

Table 1
Parameters of multilayer adsorption isotherms

Modified Langmuir			Jossens et al.		
a_0	b_0	m	H	k_1	p
210.2	0.072	1.752	0.894	0.045	18.48

More complex isotherms hence are needed. The three-parameter generalized Langmuir isotherm and that of Jossens et al. [11] are adopted in the present study. The generalized Langmuir isotherm is in fact a modified version combining Eqs. (1) and (2) and is represented by

$$Q_e = \frac{a_0 b_0 C_e^{1/m}}{1 + b_0 C_e^{1/m}} \quad (3)$$

and the isotherm of Jossens et al. [11], which was developed from thermodynamics of adsorption of solute on a heterogeneous surface, can be represented by

$$C_e = \frac{Q_e}{H} \exp(k_1 Q_e^p) \quad (4)$$

where a_0 , b_0 , m , H , k_1 and p in Eqs. (3) and (4) are the isotherm parameters.

They were estimated using a nonlinear least-square curve-fitting method [12] by fitting the isotherms to the observed data. Fig. 3 compares the model fit of Eqs. (1)–(4) with the measured data. Apparently, the generalized Langmuir isotherm and that of Jossens et al. represents the experimental data very well and are significantly better than the two-parameter isotherms. The isotherm parameters of the model fit are listed in Table 1.

3.2. Column adsorption model and test results

A theoretical model was adopted in the present study for describing the change in the hydrazoic acid concentration at the column exit. In the adsorption column, the entering aqueous solution flows through the stationary bed of Dowex resin and a portion of hydrazoic acid in the aqueous solution is retained within the resin bed while the other passes through. Denote that the fraction of hydrazoic acid 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

$$-\frac{dA}{dt} \propto AP \quad (5)$$

or

$$-\frac{dA}{dt} = kAP \quad (6)$$

It is noted in the above equation that $P = 1 - A$. In fact, Eq. (6) is similar to the logistic function that was originally developed by biologists and microbiologists [13] for describing

the phenomena of biological growth and decay. Eq. (6), although nonlinear, can be integrated with an initial condition of $A = A_a$ at $t = t_a$

$$\ln \left[\frac{A(1 - A_a)}{A_a(1 - A)} \right] = k(t_a - t) \quad (7)$$

Noting that $P = 1 - A$, the above equation can be rewritten as

$$\ln \left[\frac{P_a(1 - P)}{P(1 - P_a)} \right] = k(t_a - t) \quad (8)$$

By defining t_a as the adsorption time, as denoted by τ , when $P = 0.5$ (one-half of the adsorption capacity), Eq. (8) becomes

$$P = \frac{1}{1 + \exp[k(\tau - t)]} \quad (9)$$

$$t = \tau + \frac{1}{k} \ln \left(\frac{P}{1 - P} \right) \quad (10)$$

The hydrazoic acid fraction (P) that passes through the Dowex resin column is equal to C/C_0 with C being the hydrazoic acid concentration in the aqueous solution exiting the adsorption column at time t and C_0 is the inlet hydrazoic acid concentration. According to Eq. (10), 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 $\ln[C/(C_0 - C)] = 0$, because of the fact that by definition, τ the adsorption time, when C is one-half of C_0 . With k and τ determined in this fashion, Eq. (10) can be used to construct the entire breakthrough curve. Since, only two model parameters are involved in Eq. (10), 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 estimates of the model parameters, a complete breakthrough curve would be necessary.

The derivation for Eq. (10) 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 sigmoid nature of the breakthrough curve. The amount of hydrazoic acid adsorbed by the resin is one-half of the total hydrazoic acid entering the adsorption column within the 2τ period. Hence, the following equation can be written

$$W_e = \frac{1}{2} C_0 F (2\tau) = C_0 F \tau \quad (11)$$

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

Fig. 4 shows a plot of adsorption time (t) versus $\ln[C/(C_0 - C)]$ for hydrazoic acid adsorption in a Dowex SAR column for three flow rates. This figure reveals that for all flow rates, the observed data follow the linear relationship of t versus $\ln[C/(C_0 - C)]$ reasonably well. The model parameters of the breakthrough curves (τ and k) obtained from this figure are listed in Table 2 for various flow rates. The breakthrough curves constructed using the

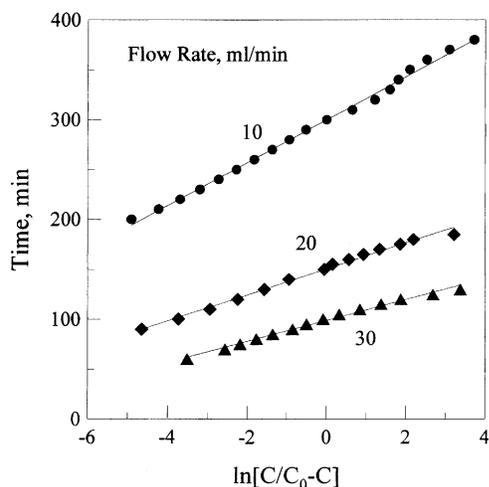


Fig. 4. Linear plot of t versus $\ln[C/(C_0 - C)]$ for various flow rates with 600 mg/l initial hydrazoic acid concentration.

model parameters listed in Table 2 (solid lines) are compared with the observed data in Fig. 5. It is apparent that the model predictions are quite good. The excellent model fit at the low C/C_0 is particularly important because it allows accurate prediction of the breakthrough point for safe hydrazoic acid discharge. Using the model parameters listed in Table 2, the breakthrough times for 0.1 mg/l exit hydrazoic acid concentration were calculated to be 117.8, 39.0 and 5.4 min, respectively, for 10, 20 and 30 ml/min flow rates for an inlet hydrazoic acid concentration of 600 mg/l. These breakthrough times are seen in Fig. 5 to be reasonable. Indeed, without Eq. (10), they will be very difficult to obtain with good accuracy from Fig. 5 because C/C_0 for this discharge hydrazoic acid level is very close to the abscissa.

The lower portion of Table 2 lists the model parameters of adsorption column for three initial hydrazoic acid concentrations of 400, 600 and 800 mg/l and they were obtained in

Table 2
Model parameters of the breakthrough curves

	k (1/min)	τ (min)	r^2
Flow rate (ml/min)			
10	0.048	299	0.997
20	0.077	152	0.993
30	0.092	100	0.991
Initial concentration (mg/l)			
400	0.043	216	0.989
600	0.077	152	0.993
800	0.057	113	0.989

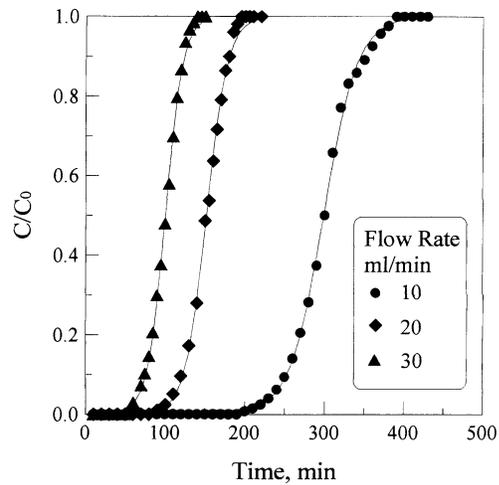


Fig. 5. Comparison of the observed and predicted breakthrough curves for various flow rates with 600 mg/l initial hydrazoic acid concentration.

the same fashion by plotting t against $\ln[C/(C_0 - C)]$ as shown in Fig. 4. The theoretical predictions based on the model parameters listed here are shown in Fig. 5 along with the observed data. Again the model fit is quite good. Based on the model fit shown in Figs. 5 and 6, Eq. (10) can be recommended as a good means for theoretical modeling of the column adsorption process.

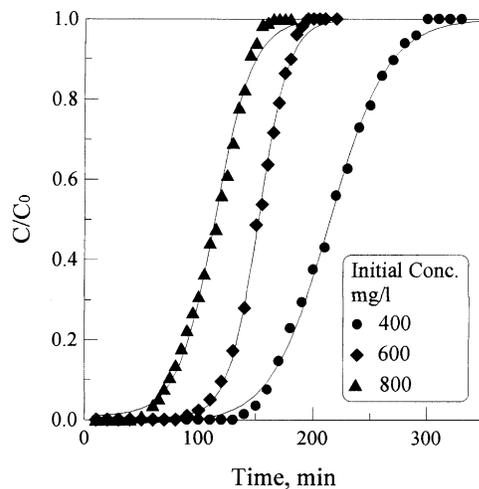


Fig. 6. Comparison of the observed and predicted breakthrough curves for various initial hydrazoic acid concentration with 20 ml/min flow rate.

3.3. Regeneration of exhausted resin

In the aqueous ion exchange process, the Cl^- ion in the Dowex resin is replaced by the hydrazoic ion (N_3^-). It was observed in the experimental tests that with a presence of the Cl^- ion in the initial aqueous solution, the equilibrium adsorption capacity of the Dowex resin (Q_e) was reduced as shown in Fig. 7. This figure indicates that the equilibrium adsorption capacity decreases rapidly as the initial Cl^- ion concentration in the aqueous solution increases. Beyond 0.2 mg/l initial Cl ion concentration, the decrease in Q_e significantly slows down and Q_e becomes nil as the Cl^- ion concentration reaches approximately 1.5 mol/l. In other words, if the Cl^- ion concentration in the aqueous solution is maintained at or greater than 1.5 mol/l, the N_3^- ion originally adsorbed by the Dowex resin will be completely driven off the resin surfaces. The Cl^- ion concentration of 1.8 mol/l is equivalent to 9.52% (w/w) NaCl concentration. This is very close to the 10% (w/w) NaCl solution recommended by the manufacturer for regeneration of the exhausted resin.

Regeneration of the Dowex resin is needed when the breakthrough point is reached or when the resin is completely saturated. Regeneration of the exhausted resin was conducted by feeding the 10% (w/w) sodium chloride solution at a 10 ml/min flow rate to the top of the adsorption column. The hydrazoic ion concentration in the exit NaCl solution was measured every 5 mm. Fig. 8 depicts the change of exit hydrazoic ion concentration as a function of time. Regeneration was essentially completed in about 25 min. The total NaCl solution required for complete regeneration was thus 250 ml. With a 17.6 ml bed volume (BV) of the present adsorption column, regeneration of the exhausted resin requires approximately 14 BV of regenerant. The adsorption/regeneration cycle was repeated four-times to see how much the adsorption capacity of the Dowex resin was affected by the process. The test results revealed that loss of equilibrium adsorption capacity is very small, <5% loss after 5 cycle and the Dowex resin is expected to last long.

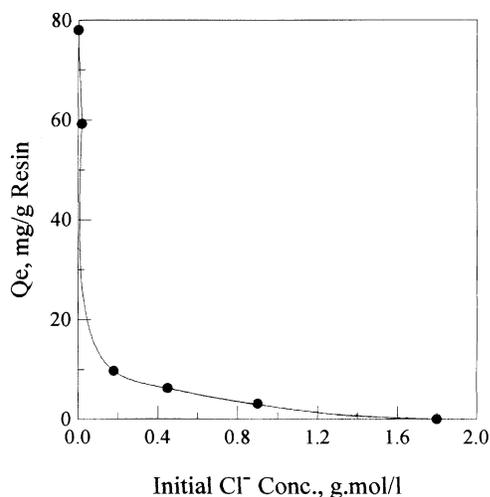


Fig. 7. Effect of the initial chloride ion concentration of the equilibrium adsorption capacity.

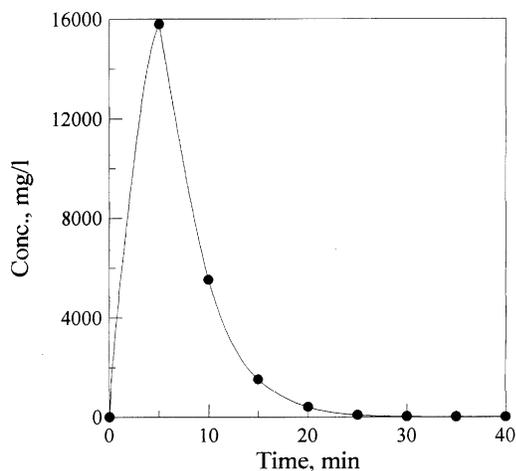


Fig. 8. Change of the hydrazoic acid concentration in the exit NaCl solution as a function of time with a 10 ml/min flow rate of 10% (w/w) NaCl.

4. Conclusions

In the present study, the Dowex SAR resin was tested in batch and continuous processes to remove hydrazoic acid from the aqueous solution. Theoretical models were adopted for representing the equilibrium and column adsorption processes. Based on the experimental and theoretical investigations, the following conclusions were drawn.

1. Test results revealed that monolayer isotherms were inadequate for describing the equilibrium adsorption of hydrazoic acid. Instead, multilayer, three-parameter modified Langmuir isotherm or that of Jossens et al. represents the equilibrium adsorption data quite well.
2. Theoretical column model based on nonlinear adsorption mechanisms was successfully developed for predicting the hydrazoic acid concentration in the exit aqueous solution. The two model parameters involved can be readily determined by a complete breakthrough curve. With properly identified parameters, the column adsorption model represents the breakthrough curves quite well. The theoretical column model offers a convenient means for accurate estimation of the breakthrough times.
3. The exhausted Dowex resin can be efficiently regenerated by 10% (w/w) sodium chloride solution. Test runs showed that approximately 14 BV of sodium chloride solution yield very good results. Repeat adsorption tests showed that the regeneration process is very efficient with negligible loss of the resin adsorption capacity.

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