불균일한 활성탄 표면에서 액상 Trinitrotoluene 관한 흡착 특성

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Properties of liquid-phase trinitrotoluene adsorption on heterogeneous activated carbon surfaces

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Introduction

Environmental regulations for the removal of trinitrotoluene (TNT) from wastewater have steadily become more stringent. This study focuses on the adsorption equilibrium, kinetics and column dynamics of TNT on heterogeneous activated carbon. Adsorption equilibrium data in terms of temperature and Ph were obtained and were correlated by Sips equation. In addition, the adsorption energy distribution functions which describe heterogeneous characteristics of porous solid sorbents, were calculated by using the generalized nonlinear regularization method (GENEREG). Adsorption breakthrough curves were studied in a column adsorber under various operating conditions such as temperature, pH, concentration, flow rate, and column length. An adsorption model was formulated by employing the surface diffusion model inside activated carbon particles. The model equation was solved numerically by an orthogonal collocation method. The model successfully simulates the adsorption breakthrough curves.

Experimental

The adsorbent used in this study was activated carbon supplied by Dongyang Co. (Korea). For the equilibrium isotherm experiment, the adsorbent was sieved to give the fraction of 14/30 mesh particle size. All particles were boiled in distilled water for 12 h, dried at 373.15 K thermostatic oven, and kept on a desiccator. Equilibrium data were obtained by introducing a given amount of activated carbon into an aqueous solution of TNT with a known concentration (within the range of 1.0 - 50 mg/L), shaking the adsorbates in a constant temperature incubator for 72 h enough to reach equilibrium. The adsorption capacity of TNT was determined from material balance by measuring the remaining TNT concentration in the solution. Batch experiments to obtain concentration decay curves were conducted in a carberry-type batch adsorber. Sorbent particles were loaded into four cages made of stainless-steel screen and the cages were affixed to the rotatingshaft to permit good contact with the solution. Fixed-bed adsorption experiments were carried out in an adsorber which was made of a glass column of 2.5 cm in diameter and 25 cm in length. The column was lined with a water jacket to maintain a uniform column temperature, and all the experimentswere performed under varying the temperature (298.15, 313.15, 323.15 K) and pH (3, 8). A precision FMI pump (model RHOCKE) regulated the flow rate. The solution was introduced downward into the column. To prevent channeling and to enhance a uniform flow, small glass beads were packed in both the top and bottom regions of the column.

Results and discussion

Adsorption equilibrium is the most fundamental data on an adsorption system. It is also very important in model prediction for analyzing and designing an adsorption process. Figure 1(a) shows the adsorption isotherms in terms of temperature (298.15, 313.15, 323.15 K) and pH (3, 8, 10). The adsorption capacity increased with increasing temperature which indicates chemisorption. The rate of adsorption is an important criterion for the determination between physisorption and chemisorption. The chemisorption usually requires activation energy which increases with increasing temperature. Similar results were reported by Marinovic et al. [1]. They investigated the adsorptioncapacity of activated carbon under wide temperature ranges from 283.15 K to 333.15 K. At temperatures up to 293.15 K, physical adsorption predominates while the contribution of chemisorption becomes increasingly large within temperature region from 298.15 K to 333.15 K because of the positive temperature coefficient of the rate of chemisorption [1]. On the other hand, Figure 1(b) shows the adsorption isotherms in terms of pH (3, 8, 10).As expected, the adsorption capacity increased with decreasing pH (i.e., increasing hydrogen concentration) and the isotherm data showed more concave (i.e., favorable adsorption). To compare the influence of temperature on adsorption capacity as a function of solution pH, the adsorption isotherm data at pH 3 were obtained under higher temperatures (313.15, 323.15 K). It can be seen that the adsorption capacity greatly increased at lower pH. In addition, the effect of pH on the adsorption capacity was much higher than that of temperature. This result implies that the effective separation of TNT could be achieved at lower pH and higher temperature.

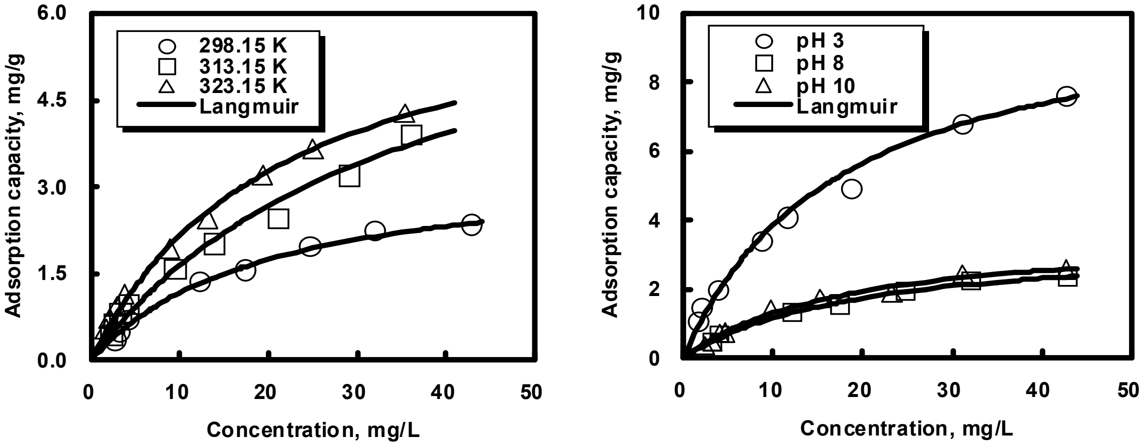

Figure 1. Adsorption isotherm of TNT in terms of temperature (left) and pH (right).

As a commercial equipment for adsorption separation, a column adsorber has been used since it gives a sharp breakthrough by means of the difference in affinity to the particle. The breakthrough curve of any species in general depends on adsorption equilibrium, interparticle mass transfer, and the hydrodynamic conditions in the column. These factors tend to make the breakthrough curves more dispersive or less sharp. Recently, Marinovic et al. [1] compared the adsorption dynamic models (models of (a) normal distribution; (b) a first order system with dead time; (c) gas adsorption kinetics) for describing the experimental results of the dynamicadsorption of TNT by activated carbon. Although the employed models are simple because of no consideration of adsorption isotherm, they have limitation for the analysis of the practical adsorption process operated under wide experimental conditions. Therefore, it is reasonable to consider adsorption equilibriumand mass transport simultaneously in simulation the adsorption behavior in the fixed-bed adsorber. The operational factors such as temperature, pH, input concentration, flow rate and column lengthare important in column designing and optimization.

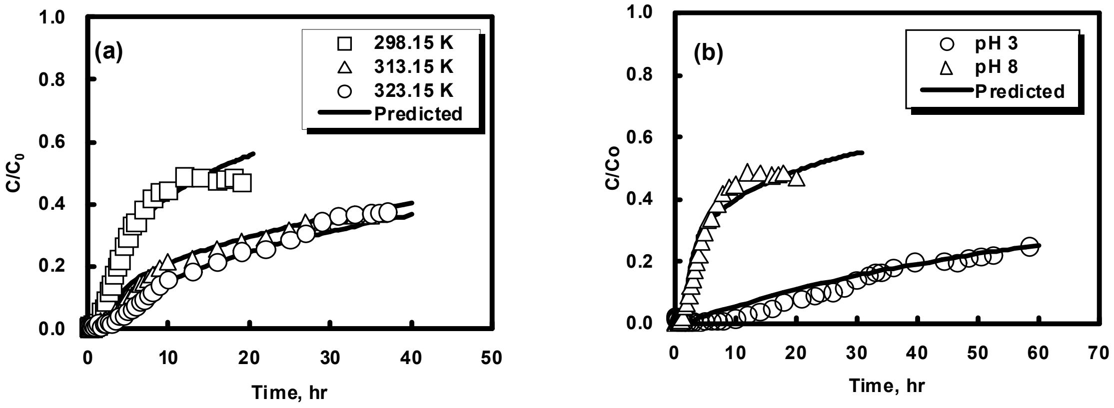

Figure 2. Adsorption breakthrough curves of TNT in terms of temperature (a) and pH (b).

In this work, breakthrough curves were obtained under various experimental conditions and the corresponding results are shown in Figure 2 and 3 together with the predicted curves based on the proposed model. Figure 2 shows the effect of temperature and pH on the adsorption breakthrough curve at different temperatures (298.15, 313.15, 323.15 K) and pH (3, 8, 10).

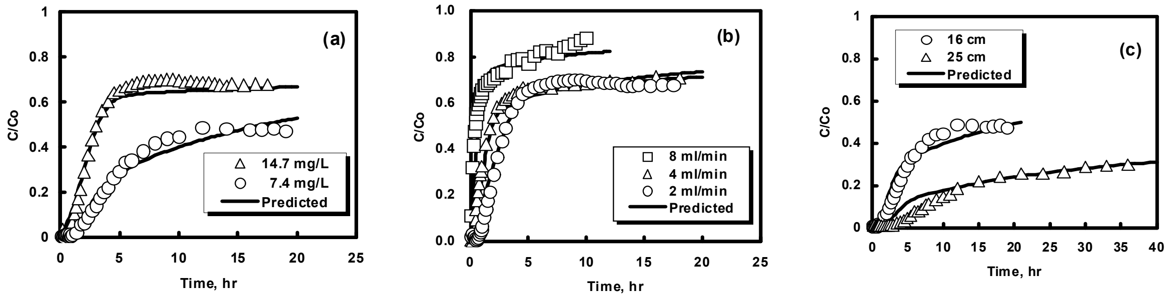

Figure 3. Adsorption breakthrough curves of TNT in terms of (a) concentration, (b) flow rate and (c) column length.

As expected from adsorption isotherms (Figure 1), the breakthrough time (i.e, adsorption amount) was higher for higher temperature and lower pH. In especial, the adsorption breakthrough curves were highly sensible to the variation of solution pH. Further studies on the effect of solution pH will be continued systematically. Figure 3 illustrates the effect of input concentration (7.4, 14.7 mg/L), flow rate (2, 4, 8 mL/min) and column length (16, 25 cm) on adsorption breakthrough curves. The breaktime for higher input concentration is earlier than that for lower input concentration. The result can be explained by the concept of the moving velocity of the mass transfer zone(MTZ)[2,3]. On the basis of the experimental and theoretical results, the proposed adsorption dynamic model can be successfully applied for the simulation of the general features of TNT in activated carbon column. Moreover, theresults obtained in this study may be useful in column design, scale-up, and optimization required for direct separation of TNT from aqueous solution.

Conclusions

As a separation method for TNT dissolved in aqueous solutions, the adsorption equilibrium, kinetics and column dynamics of TNT were investigated using granular activated carbon. Adsorption isotherm data in terms of temperature and pH were well fitted by Langmuir equation. In addition, the adsorption capacity increased with increasing temperature and decreasing pH. Contrary to our expectation, the adsorption of TNT on activated carbon seems to be near homogenous adsorption properties based on the results of the shape and intensity of adsorption energy distribution calculated by the generalized nonlinear regularization method. The formulated adsorption dynamic model, which employs the surface diffusion mechanism, successfully simulated the breakthrough curves obtained under key operating conditions such as temperature, pH, concentration, flow rate, and column length. In especial, the effect of solution pH on both adsorption capacity and breakthrough curves was considerably high. Therefore, further studies on pH effect are systematically underway to remove TNT effectively.

References

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