CHAPTER I
INTRODUCTION

1.1 Introduction/ Background of Research/Significance

At present, water pollution is critical problem of Thailand which mainly results of discharging wastewater from industry. Most industrial wastewater are composed of numerous substances such as organics, inorganics, heavy metals, including unknown. Once releases without adequate treatment, they could severely damage the environment.

Adsorption is one advanced method to remove such pollutants effectively and simultaneously. Commonly, it is applied as tertiary or advanced treatment process to keep water quality at standard regulation requirement. For advanced industrial and municipal water treatment application, the fixed bed adsorption system is most widely used. To design fixed bed adsorption system, its breakthrough curve, more specially the breakthrough time under operating conditions of interest is a key parameter.

Generally, to calculate the breakthrough curve of the fixed bed adsorber, adsorption equilibrium and kinetic data of the specific adsorbate-adsorbent system are required. Additional, we must generally solve the mass balance equation and rate equation of mass transfer in the particle of the adsorbent simultaneously. Especially multicomponent adsorption, it is much more complicated than single component.

Furthermore, in applying carbon adsorption for treating and wastewater, one often confronts the difficulty that the identities and concentrations of the organic substances to be removed by adsorption are unknown. On the other hand, for adsorption modeling and calculations, equilibrium and kinetic data of the specific adsorbate-adsorbent system are required. Without such equilibrium and kinetic data, applications. of any adsorption models or theories as a basis for design calculations become impossible.

The common approach used to overcome this difficulty is to group all the contaminants present together and to characterize their presence by a single surrogate quantity such as BOD (biological oxygen demand) or TOC (total organic carbon). The BOD representation is incomplete in the sense that it only includes biogradable substances, does not distinguish the differences in adsorption affinity among the various substances. Whatever merit or validity these representation methods may have in characterizing or describing the presence of the organic substances, their use in designing adsorption systems is questionable

The presence of a variety of substances with different adsorption affinity in an aqueous solution to be treated by adsorption implies that one must consider the competitive interactions among the various substances in predicting the dynamics of the adsorption process. Proper characterization of the solution must reveal this difference in adsorption affinity quantitatively.

Thus, it is very important and interesting to study a new approximate method representing the characteristics of adsorption equilibrium of unknown multi-solute wastewater involving a new design procedure for predicting its breakthrough curve .

The main purpose of the present investigation is to study a simple practical method to predict the breakthrough curve which is used for designing fixed bed adsorption column. The adopted method was first proposed by Okazaki et. al. in 1989 for the prediction of the breakthrough curve of a packed bed adsorber used for the treatment of unknown multi-solute water, assuming instantaneous adsorption equilibrium between the water and the adsorbent, without reliance on expensive time-consuming column tests. In this work, Activated carbon fibers (ACFs) are used as adsorbent. Since the mass transfer rate in the case of ACF is very fast, instantaneous adsorption equilibrium may be assumed between the solution and the adsorbent (Sakoda , 1991). The total concentration of pollutants in the wastewater is given in terms of a comprehensive concentration index, namely, Total Organic Carbon (TOC) concentration index, and they obtained an approximate breakthrough curve using only the information from simple jar tests.

1.2 Objectives of the present study

1. To study a new approximate method to predict adsorber breakthrough curve for unknown multi-component wastewater system

2. To verify the availability and suitability this method

3. To adopt this new method for estimate the size of an packed bed adsorber using the obtained breakthrough curve from industrial wastewater adsorption treatment

1.3 Scopes of study

1. To study a new approximate method by which to predict adsorber breakthrough curve using activated carbon as adsorbent. The total concentration of pollutants in the wastewater is given in terms of a comprehensive concentration index, namely, Total Organic Carbon (TOC).

2. To study and verify availability and limitation by comparison between the predicted and experimental characteristic breakthrough curve and their break time in case of

2.1 Synthetic wastewater (dissolved organic solution) :- single ,binary, tertiary system

2.2 Unknown component and Factory wastewater

3. To estimate the size of an packed bed adsorber for industrial wastewater treatment using this approximated breakthrough curve

1.4 Literature review

The present work aim to study a new approximate method representing the characteristics of adsorption equilibrium of unknown multi-solute wastewater and applying this approximation, the procedure for predicting the breakthrough curve of such wastewaters is presented by further assuming instantaneous adsorption equilibrium between the water and the adsorbent which activated carbon fibers are used as adsorbent. Therefore, this literature review will emphasize these related topics.

Activated carbons widely used for purification and separation in many fields are common in pelletized, granular , powdered or molded form. Recent development of activated carbon in fiber form is increasing applications of activated carbons in various areas due to its unique characteristics. Activated carbon fibers (ACFs) have unique characteristics compared with granular or powder activated carbons. Thin-fiber shape clearly assures fast intraparticle adsorption kinetics compared with pelletized or granular activated carbons commonly employed in gas phase and aqueous phase adsorption.

In the past , there were numerous fundamental studies adsorption using ACF as adsorbent. For instance,

Kunitaro Kawazoe and Toshio Osawa (1982) studied wastewater treatment by activated carbon fiber. For the purpose of establishing design procedure of wastewater treatment processes by using a new type of adsorbent, Activated Carbon Fiber, a series of adsorption experiments were performed for removing dissolved organic matters which are present in municipal wastewater by four different activated carbon fibers. Breakthrough measurement in a shallow bed of activated carbon fiber showed that it gives better performance in removing organic matters than a granular activated carbon commercially adopted at present. especially at higher space velocity. However, it is desirable to use activated carbon fiber with the considerably large micropores which are available for adsorption. And then, it was found that the activated carbon fiber can be used repeatedly through thermal regeneration. The regeneration loss will be about 5%.

Sheng H. Lin and Feng M. Hsu (1995) studied liquid phase adsorption of organic compounds by granular activated carbon (GAC) and activated carbon fibers. Acetone, isopropyl alcohol (IPA), phenol and tetrahydrofuran (THF) were employed as the model compounds for the present study. The adsorption characteristics of GAC and ACF were found to differ rather significantly. In terms of the adsrorption capacity of organic compounds, the time to reach equilibrium adsorption, and the time for complete desorption, ACFs have been observed to be considerably better than GAC.

Motoyuki Suzuki (1994) presented about fundamentals and applications of activated carbon fiber. This paper said that fibrous adsorbents have the advantages of fast adsorption rate and ease of handling when compared with granular adsorbents and powders adsorbents. The state of the art in activated carbon fiber(ACF) development in Japanese industry and emerging applications are reviewed. Fundamental works related to ACFs are briefly introduced. For designing ACF beds for adsorption in both gas phase and aqueous phase, axial dispersion in the bed becomes an important factor in determining breakthrough behavior of the bed. A method for determining the axial dispersion coefficient in fiber beds based on properties is introduced.

Akiyoshi Sakoda, Kunitaro Kawazoe and Motoyuki Suzuki (1987) studied adsorption of tri- and tetra- chloroethylene, the contaminants of groundwater, from aqueous solutions. It was found that, having larger volume of micropores, the adsorption capacities of ACFs are larger than those of granular activated carbons (GACs) widely used in this field. Also the adsorption rate on ACF is far more rapid in comparison with GAC adsorption because of much shorter diffusion path.

Akiyoshi Sakoda, Motoyuki Suzuki, Ryuichi Hirai and Kunitaro Kawazoe (1991) has reported about trihalomethane adsorption on activated carbon fibers. Adsorption isotherms of three trihalomethanes (THMs) involving $CHCl_3$, $CHBrCl_2$ and $CHBr_2Cl$ on ACFs were measured. Adsorption capacities of the ACFs for these THMs were found to be comparable with or slightly larger than those of granular activated carbons (GACs) which have been widely used for trihalomethane control in drinking water. Also , the breakthrough curve prediction was successfully carried out using a mathematical model on the basis of the assumption that the adsorption equilibrium is instantaneously established when a THM solution contacts the ACF. In practice, THM removal from drinking water was investigated at water work using bench-scale ACF adsorption columns. The volume of water treated at a space velocity (SV) of about 100 h^{-1} was approx. 40 $l(g\text{-}ACF)^{-1}$.

Y. Miyake and Motoyuki Suzuki (1993) showed that ACFs have enough capacity for removing trichloroethylene (TCE) at low concentrations contained in the off-gas from the stripping column treatment of contaminated groundwater treatment system . In their column tests, the observed breakthrough curve can be predicted by a constant pattern assumption in the adsorption zone based on the Freundlich isotherm and dominant axial dispersion kinetics.

In part of the various characterization method representing the characteristics of adsorption equilibrium of unknown multi-solute wastewater , developing such a characterization method including its application for predicting the breakthrough curve or designing adsorption column system has been the main focus of several investigators. For example,

Morio Okazaki , Hiroyuki Kage , Fumio Iijima and Ryozo Toei (1981) proposed a new approximate description of adsorption equilibrium of wastewater containing a number of unknown pollutants has been developed by using such a comprehensive index of concentration as TOC, BOD or COD. The description has been constructed on the basis of a new concept, " Characteristics Distribution of Langmuir Coefficient (C.D.C.)", which is to be identified by the observed differential adsorption equilibrium data. The accuracy of prediction of the integral adsorption equilibrium using this description has been demonstrated by several experiments. It was found that the adsorption equilibrium data using the new proposed conception of C.D.C. are fair success. Therefore it became possible to describe the adsorption equilibrium of wastewater containing a number of unknown solutes by the proposed method to some degree.

Morio Okazaki, Hiroyuki Kage, Makoto Kusuoka, Jun Tsubota and Ryozo Toei (1989) developed a new method to predict the breakthrough curve of a packed bed adsorber used for the treatment of unknown mutli-solute wastewater in terms of a comprehensive concentration index (such as a total organic carbon concentration index) assuming instantaneous adsorption equilibrium between the water and the adsorbent and their integral adsorption equilibrium curves was described here by a parabolic distribution curve. The suitability of the present method is examined by a comparison between the predicted and observed curves. They were found that the agreement is not so poor. However, the method is restricted to solutes having small overall mass transfer resistances, long lengths of packed bed of adsorbent and wasterwaters of low superficial velocities.

Jarmo Reunanen , Seppo Palosaari, Minoru Miyahara and Morio Okazaki (1993) studied column adsorption in multi-solute water. Adsorption equilibrium in multi-solute water is described via a multi-component Langmuir equation. of the two possible variable, one is assumed to be constant whereas the other is specific to each component. This coefficient is assumed to be a distributed variable. The relationship between the amount of adsorbent and the equilibrium concentration in the solution in experiments where different quantities of adsorbent are in contact with the same amount of liquid is called the integral adsorption equilibrium curve, and is described here by a show Gaussian distribution. The coefficients have been determined by parameter fitting to the experimental measurements. The obtained distribution was then used to calculate the breakthrough curve in a packed be adsorber. It has been found that the new distribution function when used in the simulation of the breakthrough curve, gives better results than the parabolic distribution reported earlier.

Mary Beth Calligaris and Chi Tien (1982) studied species grouping in multicomponent adsorption calculations. The validity of the assumption of species grouping, which combines several adsorbable species into a fewer number of pseudo-species in adsorption calculations, was examined by comparing the equilibrium concentrations obtained from exact calculations with those obtained with the use of the assumption. It was found that if the adsorption affinities of the individual species exhibited by their single-species isotherms are of the same order of magnitude, the use of the species grouping assumption yields acceptable results.

Kumaraswamy Jayaraj and Chi Tien (1985) suggested the characterization of adsorption affinity of unknown substances in aqueous solutions. An aqueous solutions with a large number of unknown adsorbates may be approximated by one with a fewer number of pseudospecies identified by their Freundlich constants. A procedure is proposed which calculates the pseudospecies composition from total adsorbate equilibrium concentration data obtained from batch contacting measurements. The present study assumes the validity of the IAS theory in describing multicomponent adsorption equilibrium.

Hee Moon, Heung Chul Park and Chi Tien (1991) studied adsorption of unknown substances from aqueous solutions. Moon et. al. suggested modifying the procedure proposed by Jayaraj and Tien for characterizing the adsorption affinity of solution with unknown compositions by assuming that the pseudospecies concentration may be given by a discrete distribution function and specifically the binomial function of a parameter vector. The new method yields results comparable to those of the original Jayaraj-Tien procedure although it requires much less computation. Prediction of batch and fixed-bed adsorption based on the characterization results were found to agree well with experiments.