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# Preliminary Study on the Application of Temperature Swing Adsorption in Aqueous Phase for Pesticide Removal

B Aumeier<sup>1</sup>, H Q A Dang<sup>1,2</sup> and M Wessling<sup>1,3</sup>

1 Chair of Chemical Process Engineering, Aachener Verfahrenstechnik, RWTH Aachen University, Forckenbeckstr. 51, 52074 Aachen, Germany

2 Department of Mechanical and Process Engineering, The Sirindhorn International Thai – German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok, 1518 Pracharat 1 Road, Wongsawang, Bangsue district, 10800 Bangkok, Thailand

3 DWI – Leibniz Institute for Interactive Materials, Forckenbeckstr. 50, 52074 Aachen, Germany

E-mail: anh.h-cpe2014@tggs-bangkok.org

**Abstract.** Temperature swing adsorption (TSA) is a well-established process for gas purification. In this work, the feasibility of TSA in aqueous phase was studied. This concept could enable *in situ* adsorbent regeneration and thus fostering sustainable decentralized adsorption processes applied to water treatment. The adsorption processes with the use of granular activated carbon (GAC) have been widely applied to remove the residual amounts of pesticides in water treatment. Amitrole was chosen as a typical pesticide in this study, GAC was selected as the main adsorbent for amitrole removal. Adsorption isotherm experiments were conducted at different temperatures of 20°C, 57°C and 94°C to identify the most appropriate sorptive – sorbent system for dynamic adsorption and TSA research. Once the isotherm experiments were accomplished, breakthrough curve experiments were subsequently investigated. Finally, TSA process was conducted with the activated carbon regeneration at the elevated temperature of 125°C. Consequently, initial obtained results proved the feasibility of the proposed TSA technique for pesticide removal in aqueous phase.

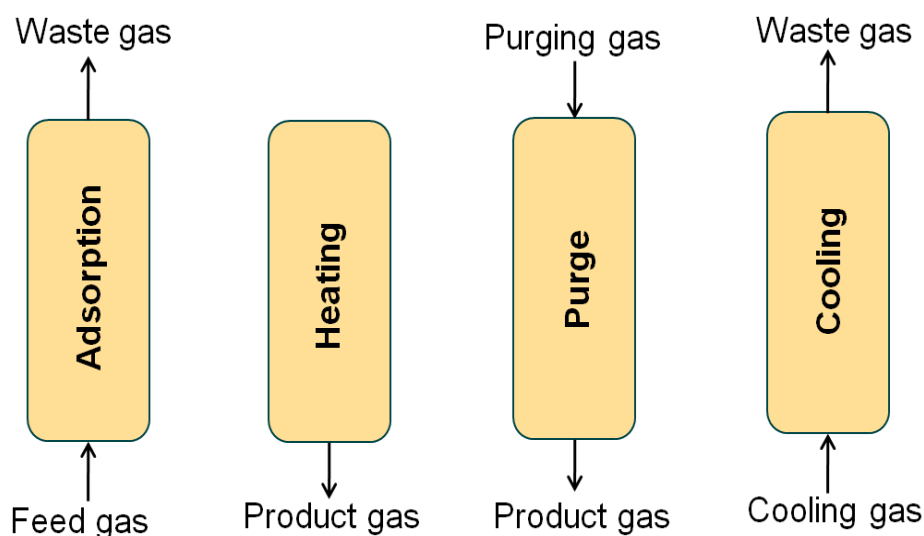
## 1. Introduction

Since the middle of the twentieth century, because of the rapid rise as well as the dynamic transition of different agricultural societies around the world, significant amount of pesticides were consumed. In recent years, because of the application of amitrole for industrial agriculture, negative environmental problems as well as human health issues have been detected. It has been well-known that heterocyclic organic compound of amitrole (3-amino-1,2,4-triazole) is a systemic and toxic reagent, which can also cause several environmental effects and health problems such as skin rash, vomiting, diarrhea, nosebleeds [1]. The applications of physicochemical processes, such as the adsorption by activated carbon is a positive and promising way to approach and mitigate the problem of pesticides.

Adsorption techniques have a long history and widespread applications on various aspects of human life, especially in different industrial production and treatment activities. It is also widely applied in the field of drinking and wastewater treatment. Practically, different hazardous materials such as colour forming reagents and synthetic organic chemicals (SOCs) can be completely removed by adsorption [2].



In gas phase adsorption, the state-of-the-art of *in situ* regeneration of adsorbents is primarily represented by pressure swing adsorption (PSA), where the chemical substances are removed from the adsorbent under reduced pressure or vacuum [3]. In addition, temperature swing adsorption (TSA) has also been applied for gas phase adsorption, especially for CO<sub>2</sub> capture and storage [4]. As shown in figure 1, typical 4-step of TSA operational procedure for gaseous phase normally includes the adsorption at low temperature, heating up, purging gas and finally the cooling process. Regarding to the thermodynamic characteristics, in gaseous phases the adsorption processes always appear to be exothermic – meaning better adsorption at lower temperature and exergonic, where reactions are spontaneous. In most cases, the sorption processes in gaseous phases are likely to occur at lower temperatures than higher temperatures [5]. As a result, it has been observed that higher adsorption capacities were obtained at lower adsorption temperatures in case of gaseous adsorption [6].



**Figure 1.** Sequence of a temperature swing adsorption cycle in the gas phase

However, the performance of an adsorption process in aqueous phase is different. Theoretically, it depends on the nature of sorptive – sorbent, solvent – sorbent and solvent – sorptive interactions. Generally, in aqueous phase lower sorption capacities has been recognized at lower temperatures and *vice-versa*. On the contrary, in several occasions the adsorption processes can behave differently. Specific cases of amitrole and diuron removal at different temperatures can be regarded as typical examples. Significant liquid amount of diuron was better-adsorbed and removed by granular activated carbon (GAC) at the elevated temperatures, meaning an overall endothermic process. In contrast, at similar conditions the adsorption efficiency was decreased in case of amitrole [7-8].

The aim of this study is to investigate a temperature swing adsorption (TSA) in aqueous phase for amitrole adsorbed to activated carbon and foresee the future applications of TSA, especially the benefits of *in situ* regeneration of adsorbents during water treatment processes.

## 2. Methodology for TSA experiments in aqueous phase

To analyse the feasibility of TSA in aqueous sorptive solutions, three important types of experiment were conducted: adsorption isotherm analysis, breakthrough curve study and subsequently the adsorption – desorption cycles for TSA research. In case of adsorption isotherm analysis, Norit® GAC 830W was utilized as the main carbon adsorbent and it was supplied by Cabot GmbH (Germany). The original GAC (particle size: 0.6 – 2.36 mm) was applied for adsorption isotherms, while the milled GAC (particle size: 0.4 – 0.8 mm) were applied for breakthrough curve investigation. Adsorption experiments were investigated in form of batch mode until the equilibrium was reached, with the concentration of GAC were varied from 400 to 4000 mg/L and the original amitrole solution was prepared up to 20 mg/L. Temperature conditions of adsorption were set at 20°C, 57°C and 94°C. The

performance of amitrole adsorption and removal were represented by the adsorption capacity ( $q_e$ ) with the unit of mg/g. Furthermore, Freundlich equation was applied to describe the adsorption results.

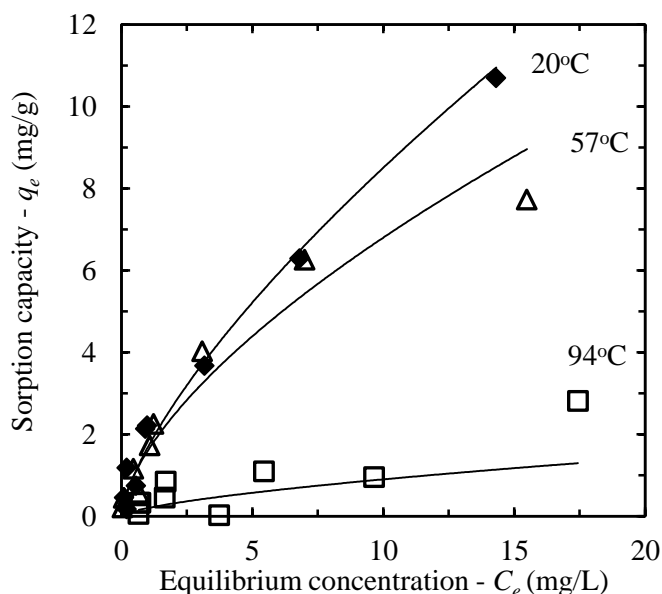
Once the amitrole isotherm data were obtained, dynamic adsorption and breakthrough curve experiments were subsequently carried out using the stainless steel column containing approximately 4.0 g GAC. The height of carbon bed ( $H$ ) was determined at 8.0 cm and the inner diameter ( $D_i$ ) was 1.0 cm. Hence, total bed volume of the stainless steel column was 6.28 cm<sup>3</sup>. Moreover, two perforated plates with mesh widths of 0.25 mm were utilized to hold the adsorbent inside the column. Amitrole solution was fed into the column in up-flow mode by a peristaltic pump. The breakthrough condition was defined as  $C_t/C_F = 0.7$  in this study.

The most important experiments in this research project were the adsorption – desorption of a TSA system. In general, the adsorption was conducted similarly to the previous dynamic adsorption investigation, while the *in situ* regeneration was performed at elevated temperature of 125°C, with the application of an autoclave (CV-EL 18, CertoClav Sterilizer GmbH, Austria).

UV-VIS spectrophotometer (Varian Cary 50 at  $\lambda = 202$  nm) was utilized for amitrole quantification during the research.

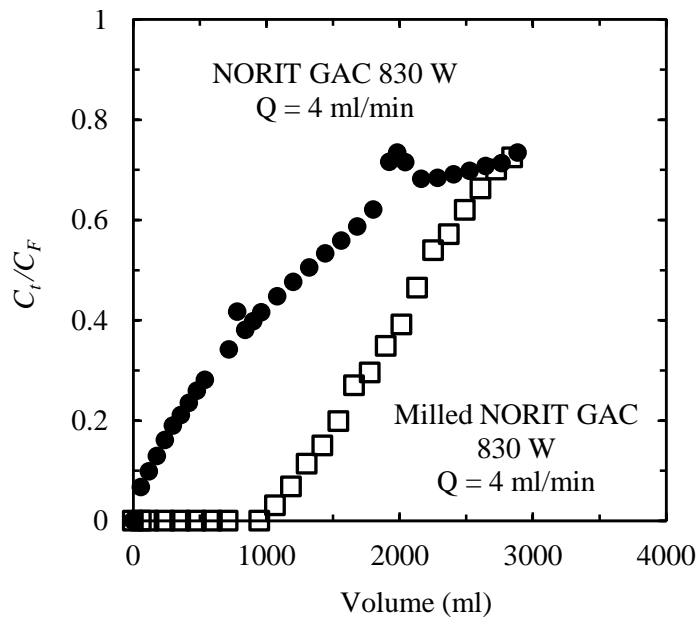
### 3. Initial results and feasibility of the research

From the adsorption isotherm results, amitrole and GAC were subsequently selected as an appropriate system for TSA research in terms of thermodynamic behaviours. Obviously, higher adsorption capacity ( $q_e$ ) of approximately 10.68 mg/g was measured at lower temperature as shown in figure 2. The adsorption of amitrole by GAC was fitted with the Freundlich equation for each temperature and it was considered as an exothermic as well as a spontaneous process.



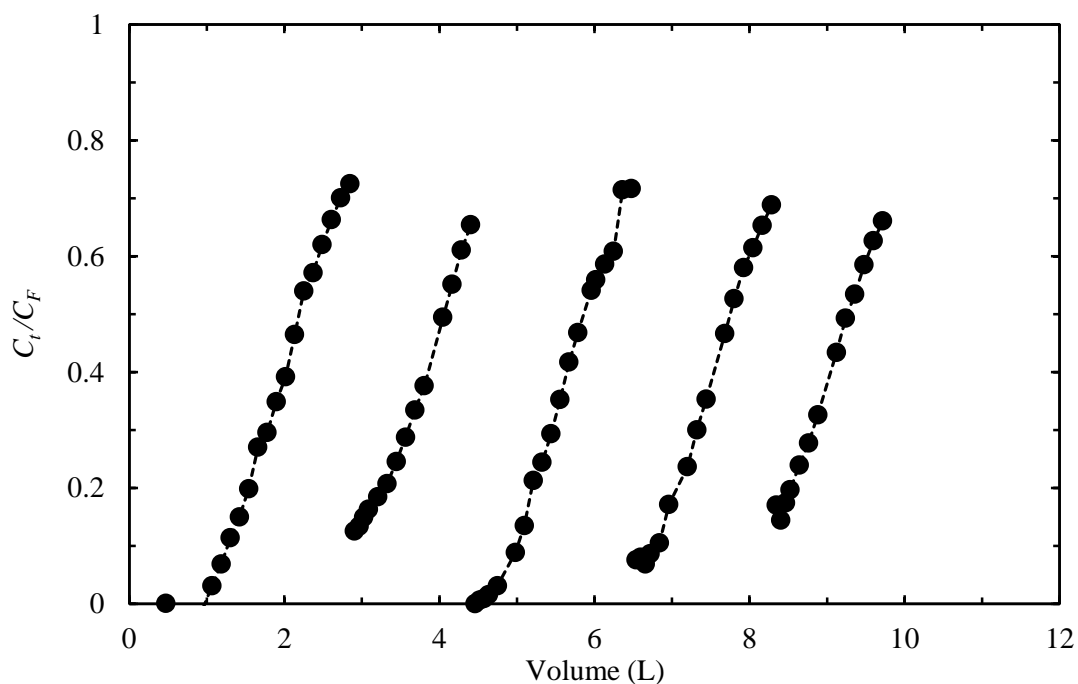
**Figure 2.** Adsorption isotherms of amitrole by 400 & 4000 mg/L NORIT GAC 830W

On the other hand, particle sizes of the adsorbents also contribute their important roles to the experimental shape of breakthrough curves. In this research, samples of the original NORIT GAC 830 W (particle size: 0.6 – 2.36 mm) as well as milled activated carbon of the same type (particle size: 0.4 – 0.8 mm) were utilized for 10 mg/L amitrole adsorption to clarify the effect of different particle sizes. The obtained data were subsequently demonstrated in figure 3. Specifically, milled samples of NORIT GAC 830 W have shorter mean diffusion length, hence, the equilibrium was obtained faster with smaller sorbent particles. Therefore, significant amount of amitrole solution can completely purified with residual amitrole concentration  $C_t$  being virtually zero.



**Figure 3.** Effects of different particle sizes of GAC to the dynamic adsorption of 10 mg/L amitrole

The most important data of TSA experiments were demonstrated in figure 4. TSA system was successfully operated in aqueous phase with the continuous running of numerous adsorption–desorption cycles. In the displayed adsorption cycles, the removal of amitrole can be high after effective regeneration by temperature swing method. Breakthrough curves suggest that cyclic steady-state was established. However, more studies have been aimed to be conducted in the future to gain the deeper look and improve this process of TSA in aqueous phase.



**Figure 4.** TSA adsorption – desorption cycles for *in situ* adsorbent regeneration at 125°C

#### 4. Conclusions

In this research project, the removal of the amitrole as an important pesticide by adsorption on granular activated carbon (GAC) was thoroughly studied. Initial data was obtained and the feasibility of a TSA system by the use of heat in order to establish a temperature swing adsorption in the liquid phase was proven. Future works will emphasize on different chemical compounds to identify other suitable sorptive – sorbent systems for TSA application. Moreover, TSA technique for household drinking water treatment will be studied thoroughly and in line with the current trend of the combined usage of membrane technology with TSA in liquid phase [9]. On the other hand, breakthrough curve modelling should be implemented to compare with the obtained experimental results to investigate the transport processes happened within the carbon bed depth. Mathematic models to predict the adsorption behaviours which are naturally based on thermodynamic properties should also be proposed. Moreover, the obtained results from this research can be utilized as the input data for adsorption column scaling-up and pilot model design in the future.

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