

NONDESTRUCTIVE REGENERATION OF
ACTIVATED CARBON BY
NATURAL GAS

By

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1990

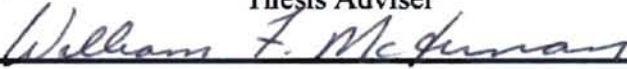
Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the degree of
MASTER OF SCIENCE
July, 1996

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NATURAL GAS

Thesis Approved:



Thesis Adviser







Dean of the Graduate College

ACKNOWLEDGEMENT

Research work rarely follows the path graduate candidates and student advisors envision in their mind prior to actually performing it. During the experiments, I felt often that I was bestowed more than a fair share of the fits and starts. The presence of Dr. John N. Veenstra was often inevitable both physically (often the equipments started to work perfectly when Dr. Veenstra appeared at the scene of experiments) and spiritually when my experimental mood could not have been characterized by the least as insatiable to more results and knowledge. Hereby, I wish to show my appreciation to him for helping me over these difficult periods.

I would also like to express my gratitude to the Committee Members, Dr. William McTernan, whose assistance on preparing cost estimations and other calculations was particularly valuable and to Dr. Khaled A. M. Gasem, who provided me with simple advices for seemingly difficult problems.

Finally, I would like to extend my special thanks to my sponsor organization, the Fulbright Committee, and to all those who made my education in the United States possible by offering their precious time, energy and finances.

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CHAPTER I

INTRODUCTION

Activated carbon treatment is one of the most efficient methods to purify drinking water and wastewater. Nevertheless, replacing the activated carbon after it is saturated by contaminants with fresh carbon would impose high operating cost on processing plants with high carbon usage rates. Besides, management of carbon spent in the purification of hazardous material containing wastewaters requires incineration or disposal at landfill sites specifically designed for hazardous materials.

The reactivation of carbon by the most commonly used method, thermal regeneration, is relatively expensive and carbon loss occur. These drawbacks generated a need to identify alternative regeneration techniques.

This thesis is intended to provide a concise overview on the currently available regeneration options and describes a novel regeneration method. Natural gas is inexpensive and readily available at larger treatment facilities, therefore its potential to regenerate spent carbon induced research interest. Natural gas regeneration of carbon exhausted by volatile compounds in gas phase proved to be successful, therefore the capability of natural gas to clean liquid phase loaded activated carbon is presented in this thesis.

The objectives of the research are:

- (i) to determine the efficacy of hot natural gas to regenerate carbon loaded by a semi - volatile material in the liquid phase,
- (ii) to analyze the effect of regenerating temperature and the length of regeneration on the regeneration efficiency that can be accomplished, and
- (iii) to elaborate assumptions on the scope of adsorbates hot natural gas can remove from the carbon surface.

CHAPTER II

LITERATURE REVIEW

1. ADSORPTION

Adsorption and desorption are counteracting processes in their effect: adsorption accumulate substances on a solid surface, which are driven off by desorption. While the literature on adsorption principles is voluminous, desorption processes did not receive particularly distinguished attention. The knowledge gained on adsorption processes however can help in describing desorption, if it is conceptualized as the reverse process of adsorption. The next chapter delineates the principles of adsorption, which are important for understanding the desorption process.

1.1. BASIC ADSORPTION PRINCIPLES

Adsorption involves the transfer of the solute (adsorbate) from either a liquid or gas phase to the surface or interface of a solid material (adsorbent), where the adsorbate is enriched due to its interaction with the surface molecules [1]. Based on the nature of the binding force between the adsorbate and adsorbent, two main types of adsorption can be distinguished: physical and chemical adsorption [2].

Physical adsorption is generated by van der Waal forces involving the London dispersion forces and electrostatic forces. The London dispersion forces were defined by London (cited by Weber [2]), who claimed that electron distributions around the nuclei are not uniform, they may have locations of high electron density. Within the electron cloud, the

place of the electron abundance varies in time, which gives a fluctuating polarity for the solute molecule. As a result, the solute particle approaching the surface may perturb the electron distribution of the surface molecule and induce the dispersion forces.

In addition to the nonspecific dispersion forces, physical adsorption also includes the more site specific electrostatic forces. In order to activate the electrostatic forces, the adsorbent molecules first polarize the adsorbate as it passes the boundary of the electric field of the surface and then the bond will be established as a result of the electrostatic interaction [2].

Chemisorption is the other large group of adsorbent - adsorbate type of interactions, which is comprised of binding forces formed via chemical reactions that take place between the solute and the functional groups located at the active sites of the surface. Although there are few solute - adsorbent chemical bonds, which exhibit low adsorption energies, usually chemisorption represents a stronger binding force than physical adsorption [2].

1.2. DISTINGUISHING FEATURES OF PHYSICAL ADSORPTION AND CHEMISORPTION

The characteristics differentiating chemisorption from physical adsorption can be summarized in four major points [3]:

- (i) strength of the binding force,
- (ii) monolayer - multilayer adsorption
- (iii) selectivity and
- (iv) temperature dependence.

1.2.1. STRENGTH OF THE BINDING FORCE

In case of physical adsorption, the molecules participating in the interaction preserve their individual structure, only electrostatic attraction exist between them. Therefore, the adsorption force is relatively weak. However, when the solute is adsorbed chemically, a covalent bond is formed with a significantly higher binding energy. The energy liberated in the adsorption process is the heat of adsorption [4, 5] and its magnitude relates to the type of adsorption. High heat of adsorption indicates chemical adsorption, low heat of adsorption is characteristic of the physical adsorption. It is to be emphasized however, that the heat of adsorption is dependent on the loading of the carbon. In *Figure 1* Q_i stands for the adsorption heat expressed in kJs, which is liberated when 1 mole of adsorbate is adsorbed on the adsorbent, the adsorption capacity, a is the amount of solute in mmol adsorbed on 1 g of adsorbent. It decreases with the increasing coverage as the adsorption process proceeds [4]. As it can be seen from *Figure 1*, the adsorption heat decreases as the adsorption capacity, a increases.

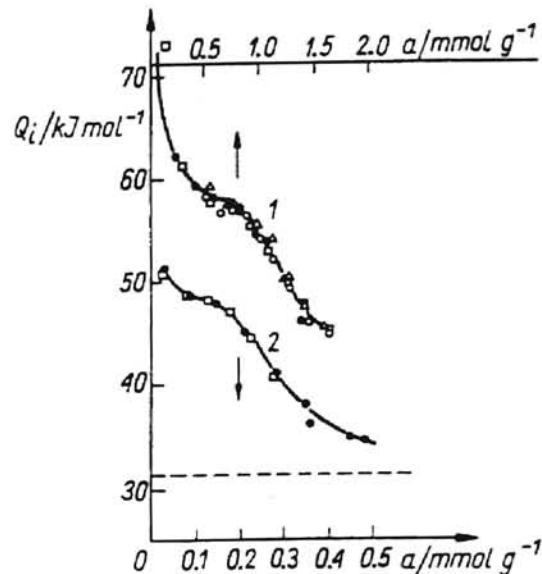


Figure 1 Adsorption heat vs. adsorbate loading

From Jankowska, *et. al* Active carbon [4]

1.2.2. MONOLAYER - MULTILAYER ADSORPTION

Chemical adsorption requires direct bond between the adsorbate and the active sites (functional group) of the adsorbent, of which the latter are only available in a limited number. Therefore, only one layer of solute may attach to the surface chemically, and after all the active sites have reacted the amount of adsorbed compound cannot be increased any further [2]. On the contrary, sites for physical adsorption are abundant and the adsorbate can be sorbed not only by the adsorbent molecules, but also by the already adsorbed molecules as well [2]. As a result, several adsorbate layers may be built up on the carbon, and more solute can be adsorbed by raising the solute concentration.

1.2.3. SELECTIVITY

Chemisorption is a selective adsorption process, it takes place only if the adsorbate exhibit chemical affinity toward the functional groups located on the carbon surface. Physical adsorption however is not restricted to specific sites with unique chemical characteristics, thus it is a nonselective process.

1.2.4. TEMPERATURE DEPENDENCE

As with the rate of chemical reactions in general, the rate of chemisorption significantly increases at elevated temperatures. For this reason, when the adsorption is carried out at a higher temperature the proportion of the chemically attached adsorbate will be greater. The opposite holds true for the physical adsorption: at high temperatures the physically desorbed solutes desorb and the proportion of the physically attached adsorbate is greater[2].

1.3. FACTORS AFFECTING ADSORPTION

The amount of adsorbed compound in equilibrium is defined by parameters in association with the adsorbate such as concentration (solubility in liquid phase), molecular weight, molecular size, molecular structure, molecular polarity and steric hindrances [2]. The

adsorption can also be influenced by the variation of three system parameters: pH (liquid phase), pressure (gas phase) and the temperature. Besides the solute characteristics and system parameters, the type of adsorbent also plays a major role in the adsorption process, which is elaborated in the next section.

1.4. ACTIVATED CARBON AS AN IDEAL ADSORBENT TYPE

Activated carbon is the most frequently encountered adsorbent type in drinking water and wastewater treatment technologies [2]. The popularity of the activated carbon can be attributed to its capability to remove a wide range of compounds due to its high porosity and the associated extensive surface area, the increased surface activity, the relative ease of manufacturing and the possibility of its economical regeneration [2].

Activated carbon with the above mentioned advantageous properties may be manufactured from a wide range of carbonaceous material (bituminous coal, bones, coconut shells, peat, sugar, wood etc.) [4]. In the manufacturing process the carbon is first carbonized by heating in an atmosphere devoid of oxygen and then activated usually by steam or carbon-dioxide [5]. Activated carbon can be produced in either granular or powdered form [6], in both cases the surface of the carbon is almost exclusively (99 %) contained in the irregular intraparticle structure of the carbon [7]. The pore size distribution is an important characteristics of the activated carbon, because that limits the size of the adsorbate molecules, which can penetrate the micropores, and the rate of achieving the adsorption

equilibrium. Dubinin cited by Gregg and Sing [1] choose the average pore diameter to classify the total range of the pore sizes into three categories:

micropores:	less than	$\sim 20 \text{ \AA}$
mesopores:		20 - 500 \AA
macropores:	greater than	$\sim 500 \text{ \AA}$

The pore size distribution of carbons produced for gas phase adsorption is different from the ones used in liquid phase adsorption: while the majority of the pore volume of the gas phase adsorbent lie in the micropore and macropore range, liquid phase carbons can be characterized by a large fraction of their pore volume being in the mesopore size range [8]. The larger transitional pore size fraction in the liquid phase carbon is necessary to overcome the limitation of adsorption due to poor diffusion in liquid phase [8]. The structure of the carbon consists of graphite-like basal planes formed randomly in the activation process (*Figure 2*). As a result of the oxidation process, micropores are developed as fissures on the basal planes, whereas the macropores are created at places where the locally more radical oxidation has cut through the basal planes. The functional groups of the carbon, which participate in the chemical adsorption are located at the edge of the basal planes [2].

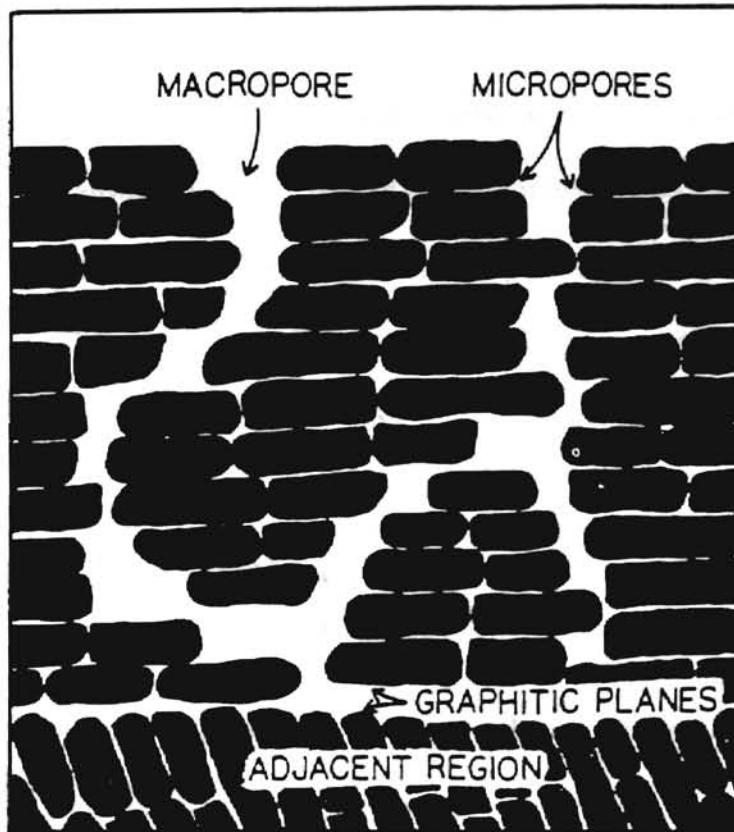


Figure 2 Symbolized presentation of the internal structure of a carbon particle

From Noll *et. al* Adsorption technology for air and water pollution control [9]

Depending on the temperature at which the carbon activation process is performed the nature of the functional groups differs. The majority of surface oxides of the carbon which is activated below about 400 -500 °C is of acidic character, and the surface of the carbon charged negatively. Carbon which is activated at 800 - 1000 °C mainly has basic groups of oxides on its surface and it exhibits a positive potential [2].

1.5. ADSORPTION EQUILIBRIUM

The adsorption process proceeds toward an equilibrium with the desorption process.

The initial rate of adsorption decreases and the rate of desorption increases rapidly as the surface area available for adsorption declines. In equilibrium adsorption and desorption rates are equal. The amount of adsorbate, held by the carbon under equilibrium condition is used to characterize the capability of both the carbon and the adsorbate for adsorption.

1.6. ADSORPTION ISOTHERMS

The two most common isotherms used to describe the adsorption equilibrium are the Freundlich and Langmuir isotherms. The Freundlich equation is based on the assumption that the energy of the sites have an exponential distribution and the fundamental equation can be written as [2]:

$$q_e = K_F c_e^{1/n} \quad (eq - 1)$$

where q_e is the amount of adsorbate per unit weight of adsorbent in equilibrium with a solution in which the solute has a concentration, c_e while K_F is the adsorption capacity characteristic of the amount of solute adsorbed, and n is the adsorption intensity, which indicates the strength of the adsorption force. K_F and n are constants.

In the Langmuir isotherm model, no interaction is assumed between the adsorbate molecules attached to the carbon surface, only one solute molecule is held by each

adsorption site, and the sites have identical adsorption energies. Under these assumptions, the adsorption capacity can be described as follows [2]:

$$q_e = \frac{Q^0 b c_e}{1 + b c_e} \quad (eq - 2)$$

where Q^0 is the amount of a monolayer adsorbate on a unit weight adsorbent surface, b is constant, which can be determined as

$$b = b_0 \exp(-E/RT) \quad (eq - 3)$$

where b_0 is a constant including the enthalpy term, E is the energy of adsorption, R is the universal gas constant, and T is the absolute temperature.

1.7. COMPETITIVE ADSORPTION

The principle of the competitive adsorption is important in the control of regeneration, because it decreases the amount of the weakly adsorbed substance. Based on the work of Frick *et al.* [10], who studied bisolute and heterosolute systems, the effect of competitive adsorption is a function of the activated carbon type, the difference in adsorbability between the weakly and the strongly adsorbed compounds and the initial concentration of the particular adsorbates.

The result of the competitive adsorption can be investigated by analyzing the shape and the position of the isotherm of the weakly adsorbed compound. The greater the difference between the adsorptivity and the concentration of the particular solutes, the steeper is the isotherm of the weakly adsorbed compound. *Figure 3* was obtained by recording the isotherms of a weak adsorbate, lignin sulfonic acid (LSA) in the presence of a strong adsorbate paranitrophenol (PNP) at initial concentrations indicated in the legend of *Figure 3*. q_{LSA} is the adsorbed solute in mg/g for various LSA equilibrium concentrations (C_{LSA} measured in mg/L). The competitive effect can also distort the shape of the isotherm obtained for the weakly adsorbed solute. *Figure 4* demonstrates that the greater the initial

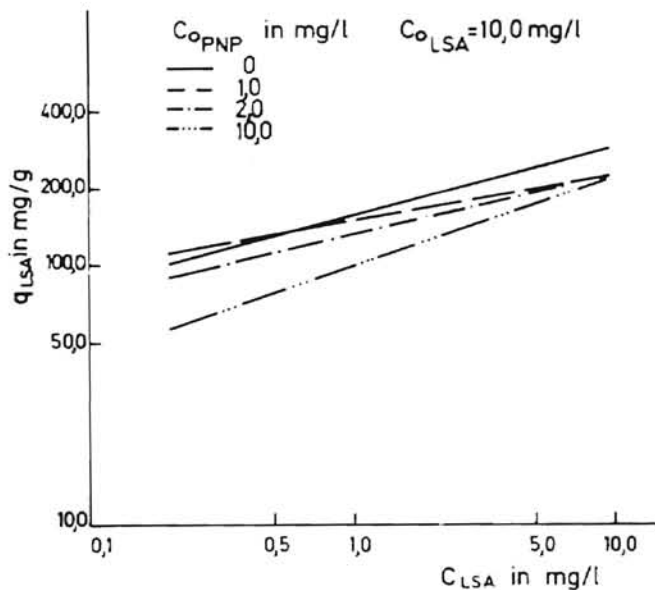


Figure 3 Adsorption isotherms of LSA in the presence of PNP in various concentrations

From Frick *et. al* Predicting competitive adsorption effects
in granular activated filters [10]

concentration of the stronger adsorbate in the solution ($C_{0\text{PNP}}$, PNP is the strong adsorbate) the more non-linear is the isotherm of the weaker adsorbate (tetrachloroethane, is the weak adsorbate in *Figure 4* and its concentration is $C_{0\text{tetra}}$). Also the isotherm of the weakly adsorbed compound will be shifted closer to the horizontal axis of the plot as the concentration or adsorbability of the strongly adsorbed substance increases. This indicates the reduced adsorption affinity of the carbon to the weaker adsorbing compound (tetrachloroethane).

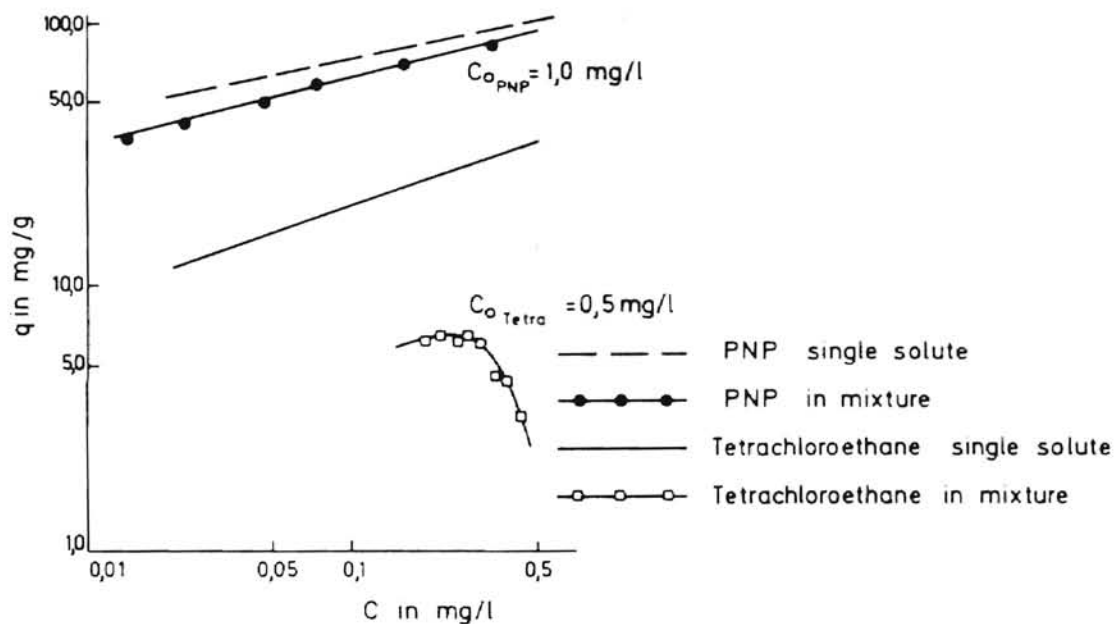


Figure 4 Adsorption isotherms of PNP and tetrachloroethane both as single solutes and in mixture

From Frick *et. al* Predicting competitive adsorption effects
in granular activated filters [10]

2. DESORPTION

As opposed to adsorption, desorption is not a spontaneously occurring process, it must be induced by supplying a given amount of energy, which is required [11]:

- (i) to split the adsorption bond between the adsorbate and the adsorbent.
- (ii) to overcome the interaction between the particular adsorbate molecules attached to the external or internal surface of the carbon, and
- (iii) to evaporate the condensed adsorbates from the micropores.

Baudu *et. al* [11], performed investigations to determine the overall desorption energy and they found that it was related to the structural properties of the adsorbate such as molecular weight, dipolar moments and molar refractions. Although the molecular weight of aromatic and aliphatic substances was in proportion to their desorption energy, the correlation was poor. The dipolar moments were reported to characterize well the desorption enthalpy of the studied aromatic compounds. In *Figure 5* the desorption energy (energy that is required to desorb one mole of adsorbate from the surface) is graphed as the function of the dipolar moment, μ (measure of the polarity of the compound). For aliphatic substances, the measurement of molar refractions provides good correlation to the desorption energy. *Figure 6* demonstrates this relationship, where the desorption energy is recorded vs the molar refraction, MR (characteristics for the ability of the solute to refract the light).

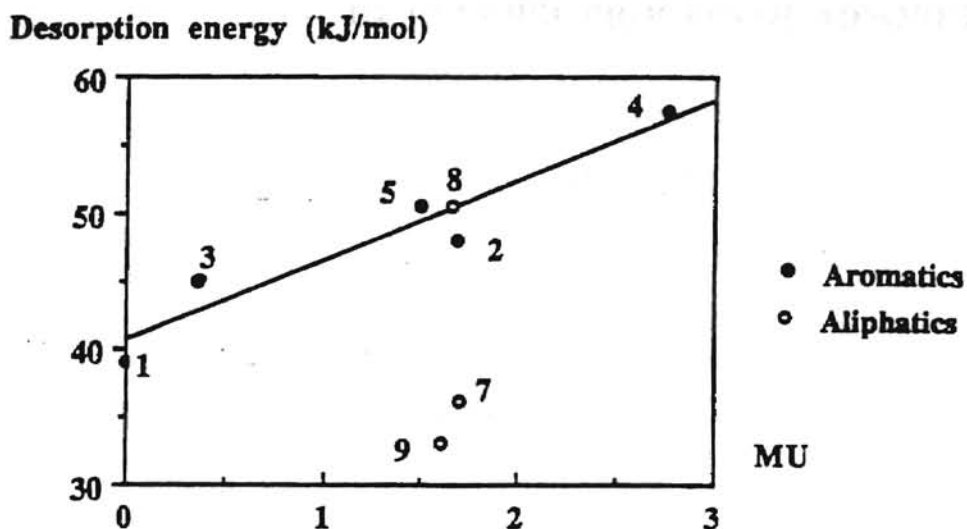


Figure 5 Relationship between dipolar moment and desorption energy for aromatic substances

From Baudu *et. al*, First approach to desorption energies of water and organic molecules onto activate carbon by differential scanning calorimetry studies [11]

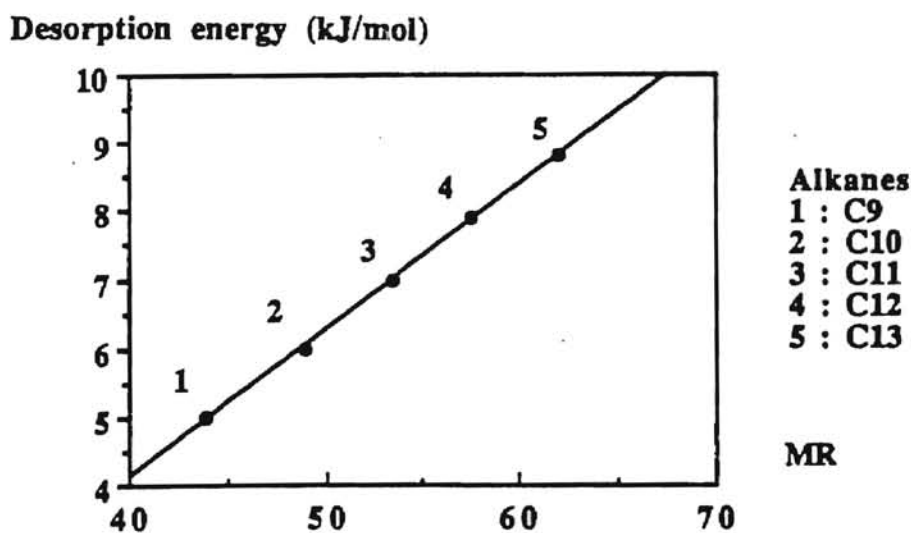


Figure 6 Desorption energy vs. molar refractions for aliphatic compounds

From Baudu *et. al*, First approach to desorption energies of water and organic molecules onto activate carbon by differential scanning calorimetry studies [11]

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2.1. DESORPTION AS THE REVERSE PROCESS OF ADSORPTION

The reversibility of the adsorption process depends on the strength of the adsorption force. As it was mentioned in section 1.2.1., physical adsorption represents a weak binding force, the adsorbate can easily desorb from the surface. On the contrary, when substances are bound to the surface by chemical adsorption, desorption becomes difficult. *Figure 7* demonstrates this relationship in terms of energetic aspects, by introducing the activation energy and the heat of adsorption [12]. It has been shown in section 1.2.1. that the type of the adsorption can conveniently be described by the heat of adsorption.

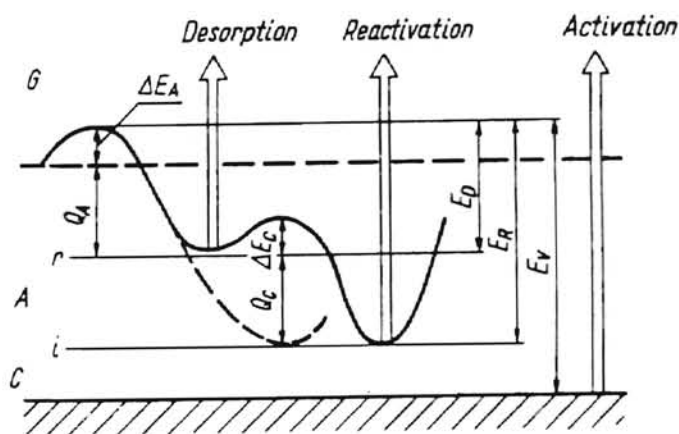


Figure 7 Adsorption and desorption energies in the regeneration process

From Jankowska, *et. al* Active carbon [4]

In *Figure 7*, the heat of adsorption, (Q_A) stands exclusively for the heat of physisorption to emphasize the difference between the heat of the physical and chemical adsorption.

In order to induce the desorption of the physisorbed adsorbate (A) from the carbon (C) to the gas phase (G) an additional energy, the activation energy, ΔE_A must also be supplied. The role of the desorption energy, E_D , the regeneration energy, E_R , and energy necessary to activate the carbon, E_V will be discussed in the next section. The activation energy in practice is very close to zero [12], consequently the energy required for the desorption can be ensured by even mild interventions, such as the increase of temperature and/or displacement by stronger adsorbate compounds in both liquid (extraction) and gas phase, changing the pH in case of liquid phase regeneration and reduction in pressure (vacuum) when the regeneration is carried out in gas phase. These methods will be further analyzed under section 1.3.

2.2. REACTIVATION FOR PERSISTENTLY ADSORBED SUBSTANCES

Activated carbon can be exhausted by chemically adsorbed compounds, and thus the above mentioned measures will not lead to adequate removal of the adsorbate. In *Figure 7* the energy required to break the bound of the chemical adsorption, is defined as the sum of the heat of the chemical adsorption or the reaction heat, Q_C and the activation energy of the chemical reaction, ΔE_C . However, for the complete removal of the adsorbate from the surface, the energy of the adsorbate should be raised above the sum of Q_C and the desorption energy, E_D [12]. The total amount of energy needed is termed as reactivation energy, and the name of the process is reactivation. E_V is the energy required to activate the carbon in the carbon manufacturing process.

Due to the high energy demand of reactivation, the adsorbates are often destroyed in the process. In thermal reactivation oxygen is supplied at high temperatures to oxidize the adsorbate. While thermal volatilization is carried out at temperatures around 100-120 °C, the thermal reactivation will be efficient only at temperatures higher than 700 - 800 °C [4]. On the basis of literature, other methods that have been successfully employed are bioregeneration, homogenous and heterogeneous regeneration, electrochemical regeneration, and wet air oxidation. The two fundamental types of regeneration and the corresponding methods are listed in Table 1.

Table 1 Summary of the mechanisms of the currently available regeneration processes

From Klein Regeneration von Adsorptionmitteln, [12] completed by boiling and bioregeneration

Regeneration Type / Phase	Desorption	Reactivation
Gas Phase	Partial pressure decrease Temperature increase	Gasification \ Oxidation
Liquid Phase	Extraction (Boiling)	Chemical reaction \ Extraction Bioregeneration

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2.3. MECHANISM OF DESORPTION

2.3.1. DESORPTION INITIATED BY TEMPERATURE - INCREASE

Desorption can be conceptualized as a first order activated reaction, and the variation in the adsorption capacity versus time can be applied to formulate the process of the desorption [12]:

$$\frac{dq}{dt} = -kq \quad (eq-4)$$

where q is the adsorption capacity, t is time and k is the rate constant. The constant k is temperature dependent and can be determined from the Arrhenius equation:

$$k = k_0 * \exp(- E / RT) \quad (eq-5)$$

k_0 is the isotherm desorption rate, and E is the activation energy of the desorption which defines the minimum energy that has to be introduced to induce desorption. The temperature dependency of these parameters imply the potential of the thermal regeneration method [12]. Assuming no reverse process (adsorption), and knowing E and k_0 , the amount of remaining adsorbate (heel) on the carbon surface can be calculated at any given time at a constant temperature [12]. However, in practical applications the isotherm desorption phase is always preceded by a non-isothermal heating-up phase, and it is known from experience that a portion of the load already desorbs in the heating phase [12]. This observation will help in determining the values of E and k_0 . By monitoring the

decreasing load of the carbon as a function of time, *Figure 8* can be obtained. In *Figure 8*, the amount of adsorbate removed from 1 g of carbon as a result of increasing the temperature by 1 centigrade (dn/dT) is presented in moles vs the applied temperature (T). Employing the assumption that the desorption is a first order reaction, the shape of the curve and the position of the peak can be used to elucidate E and k_0 . Substituting these factors into eq 4 and 5, the amount of substance, which will desorb under isotherm conditions can be calculated [12]. In practice, deviations in the shape of the curve from the one demonstrated in *Figure 8* will be experienced, which can be attributed to the

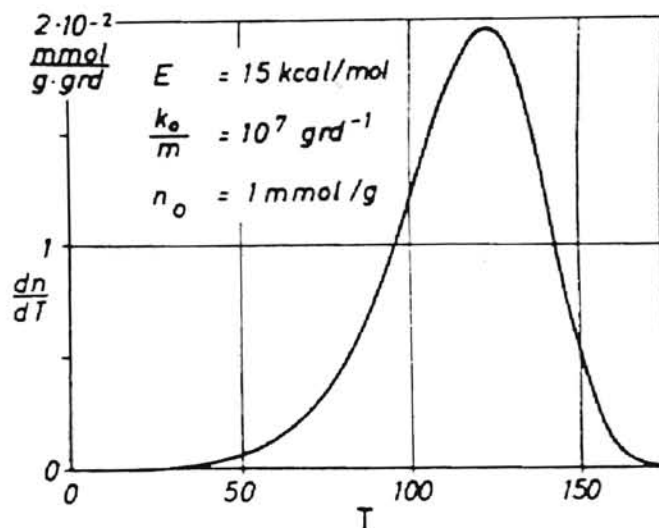


Figure 8 Desorption as a function of process temperature

From Klein *Regeneration von Adsorptionmitteln*, [12]

variations in the degree of initial loading of the carbon [12]. *Figure 9* presents the dn/dT vs T relationship for different initial loadings, where n is the loading in mmol/g, m is the temperature ramping in °C degree per minute, and v_s is the pore volume of the carbon in

cm³/g. When the initial loading of the carbon is the smallest, 0.96 mmol/g, the maximum desorption rate was achieved at 150 °C and the curve exhibited a symmetrical shape. As the initial desorption loading increased, the asymmetry of the curve became more emphasized and the maximum desorption rate shifted to the lower temperature range.

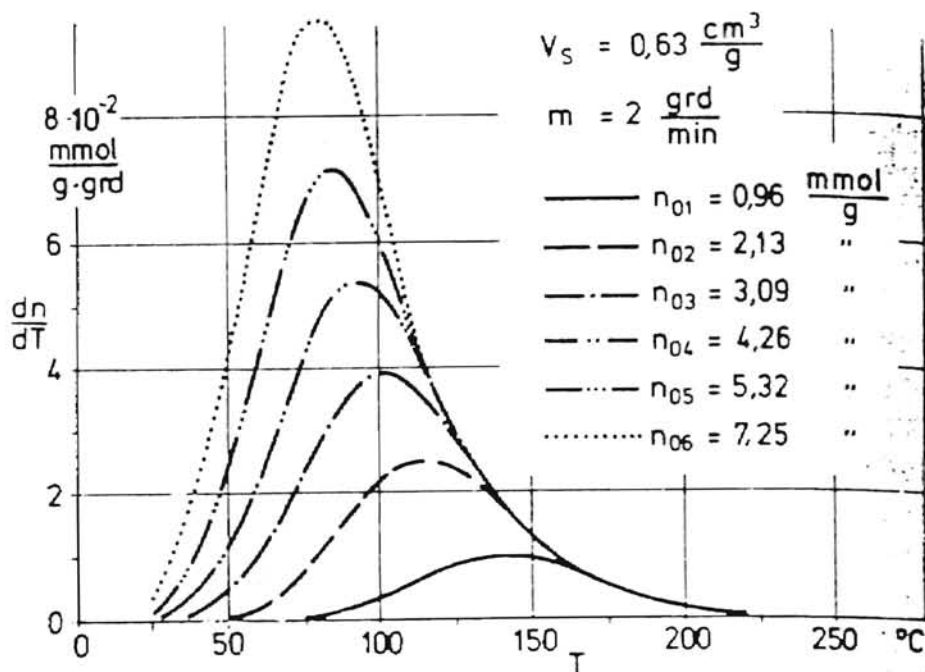


Figure 9 Desorption at various initial loadings

From Klein Regeneration von Adsorptionmitteln, [12]

2.3.2. DESORPTION BY DECREASING THE PRESSURE

In gas phase adsorption systems, when the physical adsorption force is the dominant, the course of desorption will be very similar to that of adsorption. Thus the isotherms gained during adsorption can be used to make statements on the course of the desorption process, which are useful when the optimum performance of the regeneration is to be

defined. *Figure 10* represents two isotherms, in which the adsorption capacity (q_{ads}) at the equilibrium pressure (p_{ads}) is identical, but the curves are different in their shape. The comparison of Case "a" and Case "b" isotherms shows that adsorption of compounds with Case "a" isotherms is more favorable than adsorption of compounds with Case "b" isotherms, since the pressure required to adsorb a unit amount of solute ($p_{des,a}$ in case "a"

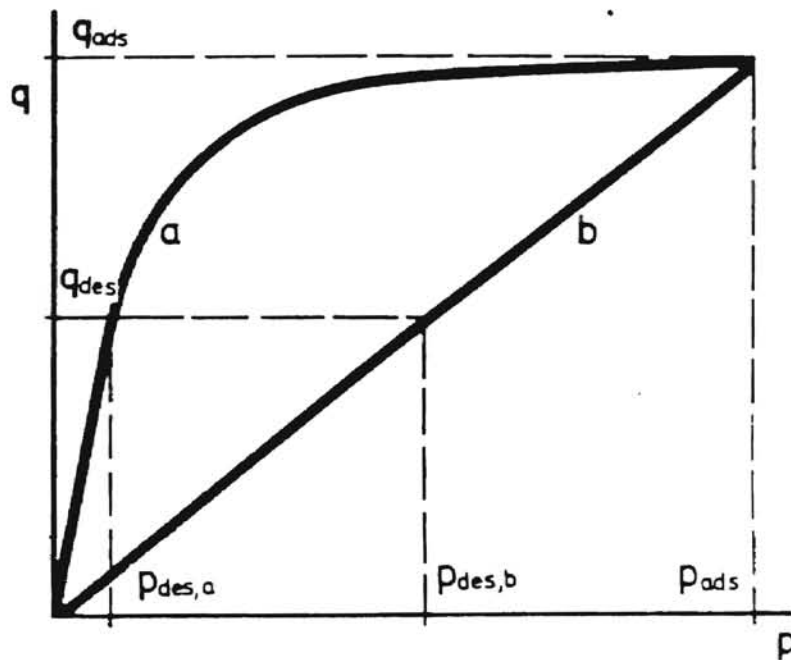


Figure 10 Two adsorption equilibrium influenced by the desorption pressure differently

From Klein *Regeneration von Adsorptionmitteln*, [12]

as compared to $p_{des,b}$ in case "b") is lower. From the point of view of desorption however, Case "b" will be more advantageous, because it necessitates smaller reduction in the partial pressure to effect the removal of the same amount of adsorbate, then in Case "a" [12].

Considering both the expenses of decreasing the pressure and the amount of substances desorbed from the surface as a function of the pressure, an optimum pressure range can be selected, in which the regeneration is the most economical. The economical feasibility of the regeneration process is also determined by the time required for regeneration: as a rule of thumb, regeneration cannot be longer than adsorption. However, complete regeneration cannot be accomplished even when the heat of adsorption of the particular adsorbate is relatively low [12, 13]. Zero surface adsorbate concentration is not reached even by decreasing the pressure considerably, which is due to the irreversibly adsorbed fraction of the adsorbate and the slow desorption rate, which results from the delaying effect of diffusion. This is shown in *Figure 11*, which illustrates the adsorption capacity vs time relationship; q_0 is the initial loading, and q_{ir} is the irreversible loading. For the irreversible adsorbed fraction, Modell *et al.* [14] hypothesized the surface oxides (section 1.5.) to be responsible, by establishing high energy chemical bonds with the adsorbate.

Pressure Swing Adsorption

Based on the effect of the pressure on the adsorption / desorption equilibrium, optimum adsorption and desorption efficiencies can be ensured in the gas phase by selecting the pressure favorable for the adsorption/desorption. This principle is utilized in pressure swing adsorption when the adsorption is carried out under pressure to increase the adsorption performance and then a vacuum is exerted on the saturated carbon to enhance dislodging of the adsorbate [5].

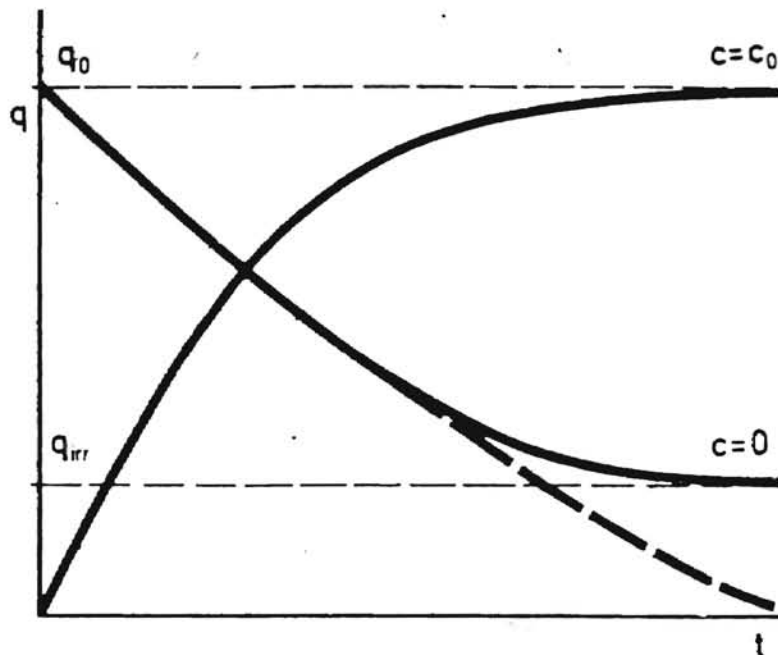


Figure 11 Desorption curve demonstrating the irreversible adsorption load

From Klein *Regeneration von Adsorptionmitteln*, [12]

2.3.3. DESORPTION DUE TO CHANGE IN PH

Activated carbon exhausted by weakly dissociable adsorbates may be regenerated in the liquid phase by varying the pH of the solution. Muller *et al.* [15] stated that the adsorption of organic materials favors a decrease in pH. One of the major factors responsible for this phenomena is the reduction in the repulsion forces between adsorbate and adsorbent [16]. The repulsion force at high pH results from the fact that both the carbon surface and the dissociated organics particles are charged negatively. Lowering the pH not only promotes

ionized organics to neutralize by uptaking a proton, but reduces the negative surface charge on the carbon [16]. In *Figure 12* the change in the surface charge (in 10^2 milliequivalent of charge per gram carbon) is graphed as the function of the pH of the solution for both used and unused carbon. The decrease in surface charge per unit pH reduction for virgin carbon is much smaller than for loaded carbon. In *Figure 12* pzc is the point of zero charge, which is around 6 - 6.5, while the used carbon has a lower pzc of

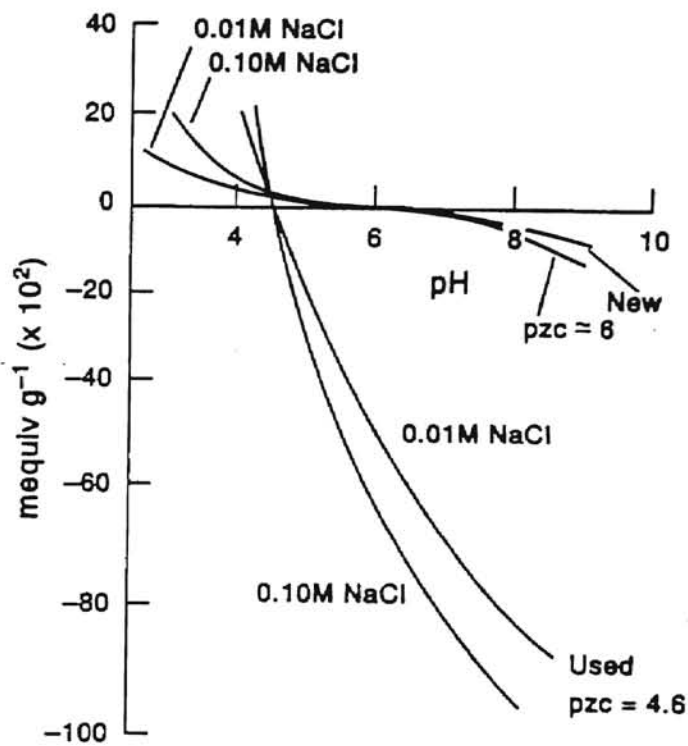


Figure 12 Variation of the surface charge for new and used carbon
as a function of the pH

From Newcombe and Drikas, Chemical regeneration of granular activated carbon
from an operating water treatment plant [16]

pzc, the carbon has a negative potential and the used carbon surface is negative in a greater pH domain than the new carbon. This finding explains how it was possible to obtain a regeneration efficiency (RE) above 100 % in several regeneration studies. (For definition of indexes for determining regeneration performance, see Appendix A). Forexample, when humic acid was desorbed the RE reached 160 % in the 2nd, 3rd regeneration cycles [17]. The RE in these experiments was determined by measuring the decrease in adsorption capacity in consecutive cycles. As a result of decreasing the pH, the repulsion between adsorbate and adsorbent was decreased, which improved the adsorption capacity in the consecutive cycles.

2.3.4. ELUENT REGENERATION

The type of the mechanism utilized in an eluent regeneration depends on the affinity of the adsorbate for the regenerating solution. Chemical reaction is experienced in certain situations *e.g.* when hydrochloric acid is the regenerating chemical for cleaning a phenol laden carbon [18]. If a reaction between adsorbate and adsorbent is unlikely, the regenerant extracts the adsorbate from the carbon surface, and then it is dissolved in either the regenerant itself, or another solvent [18]. Based on literature organic solvents are frequently employed as eluents.

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2.3.4.1. Selection of the Organic Eluent

The proper choice of the regenerating solvent is of crucial importance for the success of the eluent regeneration, therefore the following characteristics of the solvent candidate should be evaluated. First, the solvent must be more strongly adsorbable than the adsorbate, because the solvent must be capable of displacing the adsorbate. Secondly, the adsorbate must be highly soluble in the solvent to avoid the readsorption of the compound. Thirdly, the desorption of the solvent should not leave any residual load on the surface and finally, the separation of the solvent from the adsorbent and adsorbate should be easy [19]. The method developed for the selection of an appropriate solvent can be found elsewhere (Kanavets *et al.* [20])

2.3.4.2. Favorable Adsorbate Structural Characteristics

(i) Molecular Weight

It has been demonstrated by numerous researchers that the molecular weight of the solvent agent significantly affects the effectiveness of the eluent regeneration. If the eluent regeneration is based exclusively on displacement mechanism, it is expected that the smaller the solvent molecule as compared to the size of the adsorbate, the greater the RE is [18].

(ii) *Substituents on the Aromatic Compound*

Tamon *et al.* [21] performed investigations to obtain insight into the capability of ethanol to remove a wide range of aromatic substances from activated carbon. The regenerability of the carbon was proved to be a function of the reactivity of the adsorbate, which is determined by the induced and mesomeric effects present in the substituted aromatic ring. The induced effect is the result of the attachment of an electron donor group, and the mesomeric effect is brought about by a substitution with an electron acceptor functional group. As a consequence, while desorption is generally efficient if an electron attractive group (*i.e.* -NO₂, -OH) is attached to the benzene ring, aromatic constituents substituted by an electron donor group (*i.e.* alkyl groups) usually is harder to desorb. Halogen substituted compounds do not follow this rule. Even though they are attracting electrons from the benzene ring, the deactivation caused will only be slight, because the mesomeric effect partly counterbalance the inducing effect [21].

2.3.4.3. Recovery of the Carbon

The removal of the organic solvent from the activated carbon is realized in steam regeneration. Therefore, the volatility of the solvent and the ease of its recovery from the condensate are important factors for the process to be economical [21]. When the adsorbate is desired to be recovered from the adsorbent or it is sensitive to heat, eluent regeneration is a good candidate to substitute for thermal regeneration.

2.3.4.4. Supercritical Fluid (SCF) as an Extracting Agent

Even though most of the organic adsorbates exhibit high solubility in apolar solvents, the regeneration rate that can be attained by solvent regenerants are often very slow due to the low diffusion rate of the adsorbates from the carbon surface into the solvent [15].

Supercritical fluids (SCF) such as ethane, ethylene, fluoroform, sulfur hexafluoride, *etc.*, nevertheless, have a density which is generally one third of liquids under normal conditions, enabling both good solubility and high diffusion. Also, the efficiency of the SCF regeneration is not dependent on the type and mesh size of the carbon, and it is easy to separation from the solute by slightly changing the temperature or the pressure.

The physical characteristics of the carbon dioxide as a supercritical fluid are very favorable: its critical temperature (31 °C) and pressure (7.38 MPa) are low and exhibits high solubility for a variety of compounds [14]. The mechanism of the regeneration with supercritical carbon dioxide (SCD) is probably similar to organic solvent extraction: neither of them is likely to enter into a chemical reaction with the adsorbate, therefore presumably the desorption must be performed by the displacement mechanism. The small molecular size of the carbon - dioxide also support this hypothesis.

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2.4. MECHANISM OF REACTIVATION

Reactivation may involve chemical or biological oxidation reactions. Chemical oxidation types used for reactivation include thermal reactivation, wet air oxidation, homogenous and heterogeneous oxidation and electrochemical oxidation.

2.4.1. THERMAL REACTIVATION

The process of thermal reactivation utilizes the combined effect of an increase in the temperature and chemical oxidation to attain a high degree of regeneration. When the activated carbon is exhausted by an array of contaminants, the individual adsorbates will behave differently during the heating - up phase of the reactivation [22]:

1. the highly volatile adsorbates will leave the carbon first, (at temperatures below around 200 °C)
2. volatile adsorbates continue to evaporate and the unstable adsorbates start to decompose and to form volatile products (between 200 to 500 °C)
3. non - volatile adsorbates pyrolyse, and the products of the pyrolysis reaction cover the carbon surface with a carbonaceous residue (from 500 to 700 °C)

4. the residue is selectively oxidized by steam, carbon dioxide and other oxidizing agents as well as the combinations of all aforementioned compounds.

The control of the temperature in the pyrolysis and selective oxidation process is of extreme importance, because at low temperatures the rate of the desorption is small or the adsorbate is pyrolyzed and oxidized; at high temperatures not only the adsorbate, but the carbon surface is also oxidized and as a consequence the available surface area declines[22].

In addition to the reactivation temperature, the temperature of adsorption will also have a significant effect on the course of the reactivation curves. In *Figure 13*, the amount of adsorbate in grams removed from 1 g of carbon by increasing the temperature by 1 centigrade (dn/dT) vs the reactivation temperature (T) is presented when the carbon was loaded at temperatures ranging from 25 - 112 °C (v_s is the pore volume in cm^3/g in *Figure 13*). The graph recorded at an adsorption temperature of 25 °C has only one peak at a temperature of about 170 °C. As the adsorption temperature increased however, two additional peaks appeared at around 350 and 550 °C. When the adsorption temperature was the highest, 112 °C, the largest proportion of the adsorbate desorbs at approximately 350 °C. The two additional peaks at higher reactivation temperatures can be explained by polymerization and condensation reactions taking place during adsorption at elevated temperatures [12]. The decomposition products of these reactions can desorb at a temperature of 700 °C. However, a fraction of the loading will tenaciously stay on the

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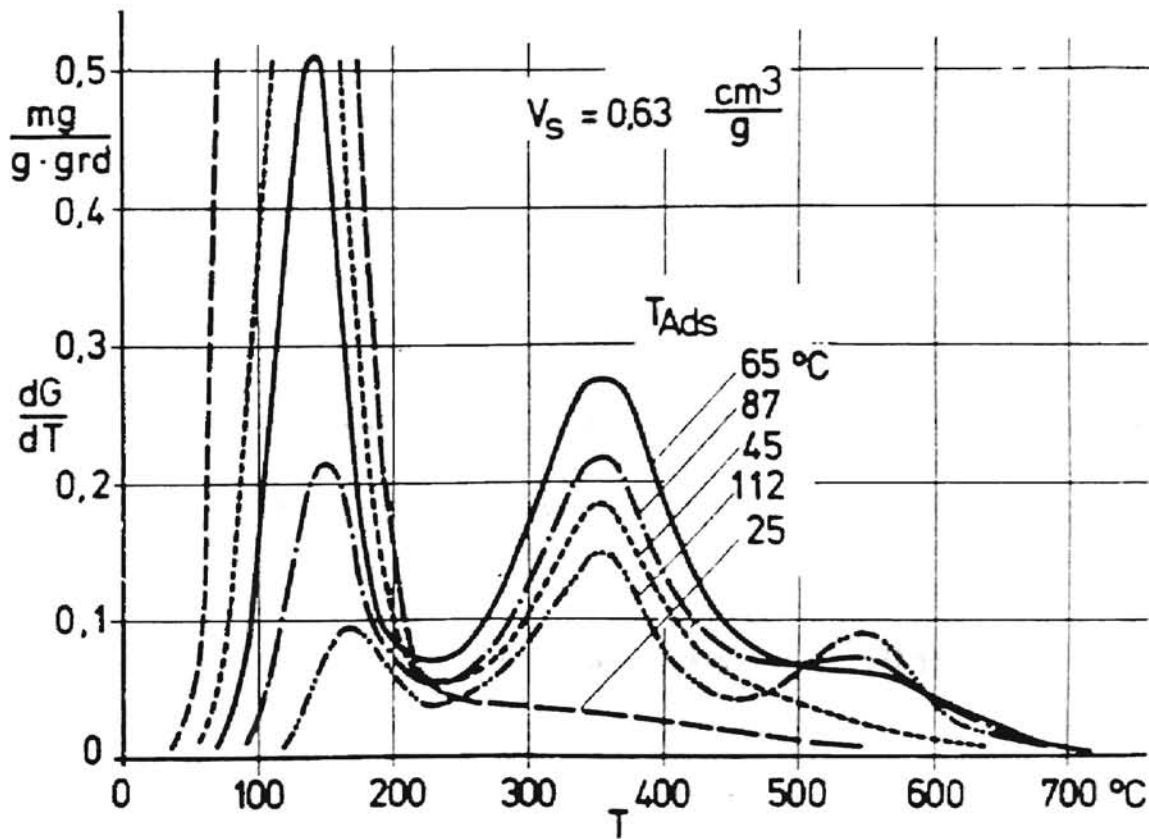


Figure 13 Amount of removed adsorbate loaded previously
at different adsorption temperatures

From Klein Regeneration von Adsorptionmitteln, [12]

carbon even when heating up to temperatures of 900 °C. These compounds can only be removed by utilizing the oxidizing power of water steam, carbon dioxide and other oxidizing media at high temperatures to selectively oxidize the adsorbate [22].

2.4.2. CHEMICAL OXIDATION PROCESSES

Practical experience and knowledge of chemical oxidation are extensive, therefore its application as a regeneration method is very desirable. Numerous water - soluble solid compounds (potassium permanganate, potassium bichromate), liquids (hydrogen peroxide) and gas substances (ozone, air), which exhibit oxidizing power, can be found. For the destruction of organic compounds, the most efficient processes use hydroxyl radical, one of the most powerful oxidants, as an oxidizing agent.

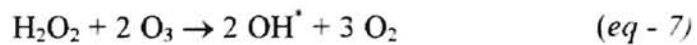
2.4.2.1. Mechanism of Hydroxyl Radical Reaction with Organics

When hydroxyl radical is applied to the liquid phase, it may act on organic substances by a hydrogen abstraction, electron transfer or radical addition [23]. The reaction of the hydroxyl radical with organic materials takes place according to a second order reaction rate as stated by Farhataziz and Ross (1977), cited by Mourand *et. al* [24]. The efficiency of the oxidation in the bulk solution can be raised by increasing the pH [25, 26] and the temperature [27] of the solution. The hydroxyl radical can be produced by either combining H_2O_2 and ozone, or activating the hydrogen peroxide molecule by UV light. Procedures employing UV light to generate OH^* radical are referred to in literature as advanced oxidation processes.

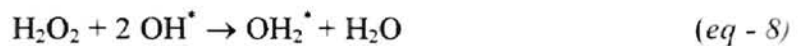
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2.4.2.2. Formation of Hydroxyl Radical from Ozone and Hydrogen - Peroxide

Hydroxyl radicals can be formed by the following reaction equation [27]:

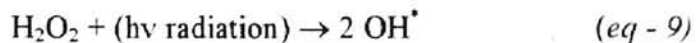


Raising the H_2O_2 concentration may increase the rate of the reaction, but it also enhances the production of OH_2^\bullet with excess hydrogen peroxide, which decreases the amount of the OH^\bullet radical:



2.4.2.3. Homogenous Advanced Oxidation

Conversion of hydrogen peroxide to hydroxyl radicals can be brought about by exposing the hydrogen peroxide molecule to protons carrying adequate energy [27]:



The efficiency of the oxidation can be influenced by the wavelength of the UV light, the H_2O_2 concentration and the intensity of the light. The production rate of the hydroxyl

radical is adequate if the wavelength of the UV light ranges from 200 - 280 nm. When the quantity of the H_2O_2 applied was raised to as high as 10 times required by the stoichiometrical reaction equation, the effectiveness of the reaction was acceptable for destroying various aromatic compound [28].

Destruction of the organic matter also depends on the light transmission. Light transmission can be higher in a carbon regeneration process than in treating wastewater in liquid phase, because of greater control of the process. As a consequence, the oxidation rates are higher when the organics is adsorbed onto the carbon.

2.4.2.4. Heterogeneous Advanced Oxidation

In addition to UV light or ozone, hydroxyl radicals can also be generated by the activation of a solid phase photoactive metal oxide catalysts such as titanium - dioxide (TiO_2) and platinized titanium - dioxide ($Pt-TiO_2$) [29]. The electrons of the photoactive catalysts can be excited by exposing them to UV light having a wavelength between 376 - 413 nm [29]. The hydroxyl radicals are formed from electrons and/or holes (electron deficient location). An electron may act on an oxygen molecule adsorbed on the catalyst and H_2O_2 will be formed through the intermediate HO_2^* and HO_2^- compounds. The OH^* molecules are produced then from the H_2O_2 by radiation or conduction band electrons. The hole may react with either H_2O_2 or OH^- to form the hydroxyl radical [29].

2.4.2.5. Wet Oxidation

As a definition, wet air oxidation is the process of oxidizing a compound in solution by oxygen, which is driven through the gas - liquid interface from the gas phase[30]. If the oxygen is provided in the form of air the method is termed as wet air oxidation (WAO).

The wet air oxidation process consists of four major steps [30]:

- (i) Desorption of the adsorbate from the interior surface of carbon and its diffusion to the external carbon surface,
- (ii) Transport of the adsorbate from the external surface to the bulk of the liquid.
- (iii) Transfer of oxygen from the gas phase to the liquid phase, and
- (iv) Reaction of oxygen and the dissolved adsorbate [26].

The rate controlling steps in the process of wet air oxidation are the (i) mass transfer of the oxygen gas from the gas phase to the liquid phase, and the (ii) adsorbate - oxygen reaction. The limitation of the oxygen gas transfer can be overcome by agitation [26].

The efficiency of the WAO process is affected by variations in temperature, total pressure, partial pressure of oxygen, gas - liquid mixing, concentration of oxidizable substances, pH and type of catalyst. Of these parameters, the temperature has the greatest influencing effect.

2.4.2.6. Electric and Electrochemical Regeneration

In electric methods, the costly thermal heating is partially substituted by electric heating, in which current is directed through the carbon particles to increase the temperature of the carbon bed [4, 31]. This innovation permits the maintenance of a lower flue gas temperature in the furnace, resulting in cost savings.

Two major types of electrochemical regeneration are discussed in literature: anodic oxidation of the adsorbate and cathodic polarization of the sorbent. In both methods, the oxidation resistant electrodes are placed in an electrolyte solution (in most cases alkali metal salts, [32, 33]) containing the exhausted carbon dispersed in it. In anodic oxidation the contaminants desorbing from the surface will migrate to the anode where they will be oxidized. Instead of mixing the carbon into the electrolyte, however, it can be connected *into the electric circuit as one of the electrode*; when this procedure is followed it is called the cathodic polarization method. The cathodic polarization may be preferred to the anodic oxidation due to the following drawbacks of the anodic oxidation [34]:

- (i) the initial RE of the anodic oxidation cannot be maintained in consecutive regeneration cycles, and the virgin adsorption capacity cannot be restored even by repetitive alkaline washing.
- (ii) due to the high pH necessary to attain acceptable REs when applying anodic oxidation, the anode disintegrates in a very short time period.

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2.4.3. BIOREGENERATION

In the past, microbial activity on the carbon surface was considered by water treatment plant operators as a liability rather than an asset. Microorganism consortiums do initially deteriorate the adsorption capacity of the carbon due to development of bacterial colonies, but the regeneration of activated carbon was eliminated for a long time period in some treatment units [35]. Although the subject of the biologically enhanced activated carbon process (Biological Activated Carbon (BAC) process) induced an extensive scope of investigations, there is still a continuing debate in literature on the viability of the process [35 - 38].

The phenomena of the bioregeneration is assumed to be the result of the mutually enhancing processes of adsorption and biological mineralization. Theoretically, the activated carbon concentrates the organics on the surface, which enhance the bacterial mineralization by a great measure. Although the microorganisms, due to their excessively large size, would be unable to reach the organics adsorbed within the micropores, they are hypothesized to excrete an extracellular enzyme which desorbs the organics. The released organic substances will diffuse out of the micropores to be consumed by the microorganisms located at the entries of the pore network. This hypothesis was attacked by Xiaojian *et. al* [38], among others, but it has also been demonstrated that some BAC treatment units under particular circumstances are capable of operating without the need of regeneration for a time period of more than 260 days [35] with a removal efficiency, which cannot be obtained with conventional attached biofilm treatment units.

3. REGENERATION METHODS

The individual principles described in the previous chapter are rarely applied as single techniques. Rather they are combined with each other to enhance the degree of regeneration that can be obtained with them alone. In the next chapter a concise overview is given on the industrial regeneration types, their regenerating capabilities and the optimal operational conditions.

3.1. THERMAL REGENERATION

The most common regeneration method in use today is the thermal regeneration [38] due to the fact that the RE achieved by thermal regeneration is high for a wide range of adsorbates [39].

3.1.1. OPERATIONAL CONDITIONS

Thermal regeneration is realized in practice by oxidizing the carbon surface with hot gases, therefore thermal regeneration is often referred to as flue gas regeneration [4].

The regenerating gaseous media is most frequently comprised of air (oxygen), carbon - dioxide and/or steam. A steam - carbon ratio of 1 : 1 is recommended by Lombana and Halaby [40], and Kotzeburo cited by Jankowska *et al.* [4], but the beneficiary effect of

steam is debated in literature. Inert gases such as nitrogen [41], or helium [42] can also be constituents of the regenerating media. Thermal regeneration is carried out in the temperature range of 900 - 1000 °C, if inert gases or steam is added into the regenerating media, the optimum temperature is lower (750 - 850 °C) [4]. The residence time required for proper regeneration may range from 20 to 60 min. [43].

3.1.2. DRAWBACKS AND TYPES OF THERMAL REGENERATION

Although substantial restoration of adsorption capacity can be achieved with thermal reactivation for numerous adsorbates, the disadvantages limit its application. The major concern with thermal regeneration is carbon loss, which amounts to 5 - 10% of the initial carbon mass in a well controlled furnace [18]. The loss results from the reactivation process (nonselective oxidation, physical attrition of the carbon in the regenerating furnace) and the transport of the carbon.

Thermal regeneration on site requires large capital investments, therefore the carbon is often hauled to a regenerating center. This is a service-type relationship, which is termed as off-site regeneration. Although this option offers a more desirable fuel consumption and regeneration for treatment facilities with small capacity, due to the transport of the carbon, carbon loss occurs.

The operation of the regenerating plants is also frequently interrupted to replace parts of the furnace deteriorated under the severe regeneration conditions or to carry out regular maintenance activities. The reactivating furnace must be equipped with afterburners and

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scrubbers with dust filters all of which create additional wastestreams, and some pollutants (NO_x , radioactive substances, *etc.*) that are hard and/or costly to remove. Thermal regeneration is ineffective to dislodge inorganic salts [4], and carbon which are laden by flammable [44], explosive [45] or corrosive materials cannot be regenerated thermally. The above detailed disadvantages initiated a quest to find alternative options over thermal regeneration.

3.1.3. IN-SITU REGENERATION

In order to eliminate the transportation costs, development efforts were focused on new regeneration techniques, which can be carried out at the generation site of the spent carbon. When regeneration is performed in the adsorber without discharging the carbon, the procedure is referred to as in-situ regeneration. In situ techniques were principally developed to reduce carbon loss, but they also provide inherent advantages, which include savings in time and work power.

3.2. DESTRUCTIVE VS NONDESTRUCTIVE METHODS

Destructive processes often harm the carbon surface due to vigorous oxidation. Nondestructive processes are less austere, they remove the adsorbate, but leave both the adsorbate and the carbon intact. As a result they preserve the virgin adsorption capacity of the carbon as well as provide the option of the recovery of the desorbed substances.

Nondestructive regeneration types are often more economical than the destructive ones[46], and they can be operated as in situ technologies. In spite of these desirable beneficial characteristics of the nondestructive processes, the carbon may have to be periodically reactivated by destructive processes.

3.2.1. NONDESTRUCTIVE METHODS

Based on their mechanism, the temperature swing, pressure swing, pH reduction and eluent regeneration can be categorized as nondestructive regeneration processes.

3.2.1.1. Temperature and Pressure Swing

Although these technologies are widely employed in industry, very few studies have been performed to explore in detail the principles and the optimal operating conditions of these techniques.

(i) Temperature swing

Temperature swing is conducted at low temperatures at which loss of carbon due to non-selective oxidation is low. Inert gases (nitrogen, helium, argon) often employed as regenerating media. When regenerating with inert gases the favorable effect of both the temperature and the pressure is utilized to shift the desorption - adsorption equilibrium.

Desorption is promoted in part by increasing the temperature of the carbon surface, and a

reduction in the partial pressure of the adsorbate, which results from the diluting effect of the inert purge gas.

Hot air is used at either atmospheric or slightly higher pressure. The temperature has a major effect on hot gas regeneration, a maximum regeneration efficiency of nearly 80 % was experienced by Klobucar and Pilat [47] for the desorption of VOC's at the highest temperature studied (92 C°). In the 100 - 300 C° temperature range, less volatile compounds (such as n-octane, [48]) can be desorbed. Hot air desorption cannot be employed when the adsorbate oxidizes, polymerizes, or decomposes when in contact with carbon [49].

(ii) Steam regeneration

Steam regeneration is one of the most commonly employed desorption techniques in practice for the removal of organics with low boiling point [3]. The mechanism of desorption initiated by steam can be described as the integrated effect of condensation, competitive adsorption and purging of the bed [50]. The principle of steam condensation can account for some of the advantages of steam regeneration over other gaseous regenerants[3]:

1. condensation of steam provides an additional source of heat.
2. consequently, the required temperatures for steam regeneration are lower, which facilitates the desorption of heat sensitive adsorbates.

3. adsorbates can be easily recovered from the steam leaving the carbon by condensation or distillation,
4. the rest loading of the steam can simply be removed by directing cool air through the carbon bed.

The most dominant regeneration temperatures fall in the range of 100 - 120 C°, but higher temperatures have also been reported [4]. The degree of regeneration depends greatly on the quantity and quality of the steam [51], in addition to the type of adsorbate (volatile, non-volatile).

(iii) Pressure swing adsorption

Pressure swing adsorption has widespread commercially successful applications as a separation and purification process of bulk gases. Successful applications include gas drying, enrichment of oxygen and nitrogen in air fractionation streams, separation of methane and carbon dioxide from landfill and natural gases to be cleaned, production of carbon monoxide and dioxide from blast furnace off-gases, n-paraffin purification from olefins and branched chain hydrocarbons, treatment of waste gases by removal and recycling of solvent vapors [52]. In pressure swing adsorption process, either the adsorption pressure is increased above atmospheric pressure or the pressure of desorption is decreased (vacuum regeneration) by 2000 - 200 kPa.

3.2.1.2. Eluent Regeneration

A variety of eluents have been tested for carbon regeneration: boiling water, alkaline and acid solutions, iodine solution, supercritical fluids, and the most commonly employed washing liquids, the organic solvents. Eluent methods are often carried out at elevated temperatures to accelerate the extraction process or the chemical reaction between the adsorbate and the regenerant (HCl regenerant for phenol removal). They are usually preceded and followed by rinsing with hot / cold water. The regeneration efficiencies of inorganic eluents reported in the available literature are summarized in Table 2.

Table 2 Results from inorganic eluent regeneration studies

Adsorbate	Regenerating Media	RE [%]	Time [min]	Adsorbent	Reference
Aromatics	Boiling water	3 - 90	260	AC	18, 53
Hydroxyamines	Hydrochloric acid	99.95	NA	AC	54
Aromatics	Aliphatic acids	- 11.9 - 99.1	1440	F - 400, AC	18, 53
Aromatics	Hydrochloric acid	- 27.6 - 72.2	1440	F - 400, AC	18, 53
Aromatics	Sodium hydroxide	5.2 - 72.4	1440	F - 400, AC	18, 53
Organics	Alkali Hydroxide + organic solvent in water	"directly reusable"	> 60	AC	55
Organics	Iodine in aqueous and organic solution	"complete regeneration"	NA	AC	56
Organics	5-10 % caustic soda + hot water + acid wash	94.0	> 280	AC	57

Sodium hydroxide in a 4 % solution has been found commercially effective for carbon regeneration that has been exhausted by phenol (Himmelstein et al (1973) and Fox et al (1970) cited by Martin and Ng,[18]). However, the group of benzene and phenol derivatives investigated in literature are very poorly desorbed by hydrochloric acid and

sodium hydroxide (less than 33 %) [18]. Sodium-hydroxide and hydrochloric acid were also studied as a pre- and posttreatment method to the thermal regeneration, but the obtained efficiencies were poor [58]. Low molecular weight carboxylic acids (up to 4 carbon atoms) can provide acceptable REs (greater than 66%,) for some benzene and naphthalene derivatives, but they are not efficient for substituted phenols [18]. Iodine is declared to be the “strongest displacing agent” [56], and regeneration is reported to be complete by iodine in both aqueous and organic solvents. The scope of the amenable adsorbates was not stated in the patent.

(i) Organic solvents

Regeneration processes using organic solvents have been thoroughly investigated (Table 3). The highest REs were reached in pure solvents, while the RE deteriorated in aqueous solution in proportion to the volume of water in solution [18]. Common steps in the regeneration process with an organic eluent consists of drying, rinsing with the solvent, removal of the solvent and recovery of the adsorbate. The drying step is not necessary in the case where solubility of the water in the eluent is high (dimethyl ether). The separation of the desorbed substances from the solvent can be accomplished by distillation, extraction, decanting or sedimentation [4]. Since many of the solvents have low boiling point, distillation can be a cost effective option. Of the chloromethanes, only the dichloro methanes demonstrated acceptable RE for substituted benzene- and some phenol derivatives [18, 53]. Similar observations were made with regards to acetone. Alcohols

and amines containing less than five carbon atoms, however showed outstanding regeneration performance for both phenol and benzene solute groups [53].

Table 3 A brief overview on the organic eluent regeneration techniques

Adsorbate	Regenerating Media	RE [%]	Time [min]	Adsorbent	Reference
Aromatics	Aliphatic alcohols	66.4 - 100.0	1440	F - 400, AC	53
Aromatics	Acetone	26.4 - 93.6	1440	F - 400, AC	53
Aromatics	Benzene	- 4.5 - 74.0	1440	F - 400, AC	53
Aromatics	Amines	42.7 - 95.9	1440	F - 400, AC	53
Aromatics	Chloromethanes	- 4.5 - 81.4	1440	F - 400, AC	53
Bentazone	Chloroform	40	NA	AG-3, AC	59
Bentazone	Ethanol	33	NA	AG-3, AC	59
Nitrobenzene	Aliphatic acids	46.9 - 70.5	1440	F - 400, AC	18
Nitrobenzene	Chloromethanes	43.4 - 93.2	1440	F - 400, AC	18

(ii) Successive regeneration

An important measure of capability of a method to regenerate spent carbon is the number of regeneration cycles, in which the adsorption capacity of the carbon is adequately restored. Ethanol, acetone and methanol were used in consecutive regeneration cycles, to drive Rhodamine B from carbon particles. After the first several cycles of high regeneration efficiency, the RE decreased and at the end of the 15th cycle it amounted to less than 80 % [17]. In the same experiment, formic and acetic acid were also employed for 15 successive cycles, and the RE by these substances did not fall below 90 %. *Figure 14* demonstrates the decrease in RE (measured in %) graphically as the function of the

number of regeneration cycles. In another research [21], when ethanol and toluene were the regenerants, the loss of adsorption capacity greatly declined in the consecutive regeneration cycles.

(iii) Consistency of eluent regeneration techniques

Employing ethanol as a regenerating media was studied by several authors for a broad range of compounds. The data from these studies are summarized in Table 4 and it can be established that there is a wide variability in the results.

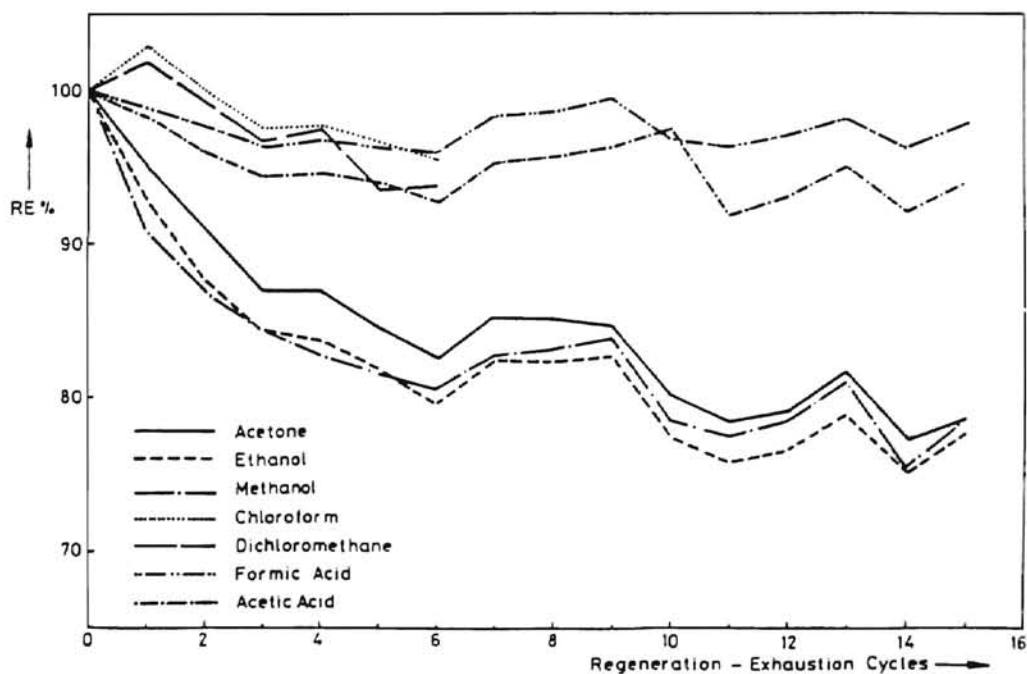


Figure 14 RE vs. regeneration cycles for carbon laden by Rhodamine B

From Martin and Ng, The repeated exhaustion and chemical regeneration of activated carbon [17]

(iv) Supercritical carbon dioxide

Supercritical carbon dioxide has been investigated mainly for recovering the adsorptivity of carbon exhausted by volatile substances. The virgin adsorption capacity of the carbon has been preserved almost intact through 9 successive regeneration cycles for benzene and toluene [60]. For non-volatile compounds such as pentachlorophenol, and hexachlorobenzene, the measured efficacy of regeneration was lower, but still acceptable (75 % [61]). Based on literature data desorption studies with supercritical carbon dioxide are generally performed in the temperature range of 27 - 77 C °, and at pressures 10 - 20

Table 4 Carbon regeneration efficiencies obtained by different researchers with ethanol eluent

Adsorbate	RE [%]	Load [mg/g]	Temperature [C°]	τ [min]	AC type	Reference
Aniline	48	233	35	6 days	CAL	21
Aniline	77.8	NA	NA	120 + shaking	F-400	18
Aniline	96.8	157.57	NA	6 days	IONAC	39
Benzaldehyde	95	235	35	360	CAL	21
Benzaldehyde	78.8	NA	NA	120 + shaking	F-400	18
o-Cresol	42	304	35	6 days	CAL	21
o-Cresol	27.6	NA	NA	120 + shaking	F-400	18
β -Naftol	90	469	35	6 days	CAL	21
β -Naftol	74.4	NA	NA	120 + shaking	F-400	18
β -Naftol	27.81	508.38	NA	NA	IONAC	39
Nitrobenzene	80	374	35	6 days	CAL	18
Nitrobenzene	85	NA	NA	120 + shaking	F-400	18
Phenol	68	199	35	6 days	CAL	21
Phenol	92.6	NA	NA	120 + shaking	F-400	18

MPa [14, 62, 63]. The time required to reach adequate regeneration is reported to be 0.5 (weakly adsorbed compounds: *e.g.* acetic acid) - 3 (highly adsorbable substances: *e.g.* phenol) hours [21]. Madras *et. al* [61], compared the breakthrough curves of carbon regenerated by steam and supercritical carbon dioxide. The supercritical carbon dioxide regenerated carbon was shown to be superior to the steam regenerated one. A practical advantage of the desorption with supercritical carbon dioxide is that it eliminates drying of the carbon before regeneration, because the solubility of the water in the supercritical fluid is sufficiently high to transfer the adsorbate from the surface of the carbon into the carbon dioxide under the conditions employed in the desorption procedure [61]. A detailed overview on the performance of the SCD regeneration studies available in literature is demonstrated in Table 5.

Table 5 Summary of regeneration efficiencies and conditions of some SCF studies

Adsorbate	RE [%]	Regeneration Time [min]	Adsorbent	Reference
Benzene	85	300	Degussa (WSIV), AC	58
DDT	60	900	F-400	62
Ethyl acetate	70	NA	AC	60
Toluene	85	300	Degussa (WSIV), AC	58
Toluene	85	NA	F-400	61

3.2.2. DESTRUCTIVE REGENERATION METHODS

3.2.2.1. Regeneration by Chemical Oxidation

(i) Homogenous oxidation

The low RE's obtained from homogenous oxidation methods (Table 6) shows that the carbon cannot be regenerated adequately. In order to raise the efficiency of the regeneration the dosage rates can be raised. Nevertheless, the excessive oxidant requirement increases the cost of the method and therefore it questions the economic feasibility of the whole adsorption process (including regeneration) to remove pollutants as compared to a direct oxidation process in bulk liquid.

Table 6 Regeneration performances and operational conditions of several oxidation regeneration techniques

Adsorbate	Regenerant	RE [%]	Time [min]	Adsorbent	Reference
Phenol	"wet air"	90 - 95 70 - 80	180	AC, F 400 Narbada	65
TCE	Hydroxyl radical	89 in 2 cycles	4320	Pt-TiO ₂ impregnated F 400	29
Mono - substituted benzene	10 % potassium permanganate	- 18.2 - 41.3	4320	AC, F 400	18
	10 % potassium bichromate	- 6.9 - 36.2			
	0.35 % sodium hypochlorite	- 7.4 - 68.0			
Aromatics	10 % potassium permanganate	1.2 - 26.2	4320	AC, F 400	53
	10 % potassium bichromate	2.4 - 18.6			
	0.35 % sodium hypochlorite	- 26.3 - 35.0			

(ii) Heterogeneous advanced oxidation

The efficiency of the oxidation process can be increased if the oxidant is generated at the vicinity of the carbon. This principle has been realized in a heterogeneous advanced oxidation process, in which a Pt-TiO₂ impregnated carbon was excited by artificial light. The regeneration time by this method has been reduced to one fifth of the adsorption time and 89 % of the adsorption capacity has been restored after the second regeneration cycle [29].

In wet air oxidation the carbon suspended in water is exposed to the oxidizing effect of air or pure oxygen at an oxygen partial pressure of 0.5 - 20 MPa, and at the temperatures extending from 125 to 320 °C. Mundale *et al.* [65] determined the optimum regeneration temperature: at temperatures higher than 150 °C significant deterioration in adsorption capacity was observed. A drawback of the chemical oxidation processes, analogue to the thermal oxidation processes, is that the carbon will be damaged due to partial oxidation of the surface. To minimize this effect very careful process control is required within defined parameter ranges, which limits the achievable level of regeneration.

3.2.2.2. Electric and Electrochemical Methods

Although the failure of electrochemical regeneration for activated carbon exhibiting an extensive micropore system has been reported; high recoveries have been obtained with cathodic oxidation of activated carbon fibers [34, 66, 67]. Data supporting these

observations along with the type of electrolytes, the activated carbon regenerated and the regeneration efficiencies and the electric current applied are provided in Table 7.

Table 7 Typical regeneration efficiencies gained by electrochemical regeneration methods

Adsorbate	Electrolyte	RE [%]	Time [min]	Adsorbent	Reference
Dyes (3)	Sodium sulfate	64 - 75	NA	AC	67
p-Nitrotoluene	Sodium chloride (0.2-0.6 M)	97.4 in 3 cycles	30	AC	66
Phenol	Potassium sulfate	85 in 12 cycles	NA	unwoven carbon fiber	34
Wastewater	NA	61	NA	AC	68

3.2.2.3. Bioregeneration

Bioregeneration has been attempted for a number of compounds including phenol, p-cresol, p-nitrophenol and dichloro-methane. Generally, the rate of the biodegradation was not satisfactory, the shortest regeneration time mentioned in the available literature was 29 hrs [69], but regeneration times as high as 160 hrs have been reported [69].

Bioregeneration in practice will almost exclusively be employed in a BAC unit, because in bioregeneration a biological mat develops on the carbon surface, which obstructs adsorption on a fraction of the surface area.

3.3. NATURAL GAS REGENERATION

Based on literature natural gas is employed in thermal regeneration as a fuel to provide the temperature required for the chemical oxidation. Methane gas is reported to be widely applied in industry to dry molecular sieves [48], but regeneration of activated carbon (other than molecular sieves) for organic compounds is not discussed. Therefore, it is assumed that the principle of regeneration with natural gas is a novel idea.

4. REGENERATION ECONOMICS

4.1. THERMAL REGENERATION

The total capital and operational cost of a thermal reactivating facility in 1978 US dollars are demonstrated in Table 8. The capital cost of the multiple hearth furnace is the highest of the four most commonly used furnaces: multiple hearth, rotary kiln, infrared and fluidized bed furnace[71]. The lowest equipment and implementation cost was reported for the infrared furnace [71].

Energy is demanded in the form of electricity, fuel, and steam. A significant fraction of the operating cost is the make-up carbon cost and the replacement costs of the parts of the furnace.

Table 8 Capital and operational costs of thermal regeneration facilities

Cost \ Furnace	Multiple Hearth [5,000-30,000 lb/day]	Rotary Kiln [5,000-30,000 lb/day (estimated)]	Infrared [2,400- 24,000 lb/day]	Fluidized Bed [6,000-24,000 lb/d]
Capital Cost [\$ 1000]	850 - 4200	NA	250 at 2400 lb/d	740 - 992
Operational Cost [¢/lb]	18.8 - 12.2	15 - 25	13 - 5	9.5 - 6.2

Note: NA = non-available

The price of off-site thermal regeneration alone is \$ 87 / lb (assumed to be in 1995 dollars). The total regeneration cost including the discharging of the carbon of the adsorption vessel and transportation of the carbon is \$ 1.55 / lb if the amount of carbon to be regenerated is above 10,000 - 20,000 lbs [72].

4.2. STEAM REGENERATION

Parmelee and Allen [46] have determined the cost of steam regeneration for exhausted carbon from groundwater treatment. Assuming a hypothetical carbon requirement of 1 lb C / 1000 gal groundwater, the steam regeneration will cost \$ 51/1000 gal groundwater. The cost calculations incorporate a 3 % loss of adsorption capacity and a steam - carbon ratio of 5 lb / lb. Both data were estimated for groundwater treatment from experiences on regeneration of carbon saturated in wastewater treatment. In the regeneration of the carbon used in the wastewater treatment a 1% carbon capacity loss and 1 lb steam / lb carbon ratio have been observed. The regeneration costs were recalculated with these costs (Appendix B) to determine the price of regeneration of carbon from wastewater treatment. The calculations yielded \$ 17/lb carbon regeneration cost for the regeneration of carbon spent in the purification of 1000 gal wastewater, all these data assumed to be in 1982 dollars.

4.3. ELUENT REGENERATION

4.3.1. Solvent Regeneration

The cost of solvent regeneration was provided by Chang and Wu [39] to be US\$ 609,905 annual cost. This estimation was obtained for substances with high RE's, and unit expenses for the regeneration of compounds which are difficult to desorb will be higher. The calculations do not consider the profit that can be gained from the recovery of the valuable adsorbates.

In another survey, Parmele and Allen (1982), [46] describe a "self-financing" carbon regeneration project. Pilot plant studies demonstrated that cost of regenerating the carbon used to treat phenol-formaldehyde containing wastewater amounted to \$ 0.02 / lb carbon, and the worth of the desorbed and recovered substance was \$ 0.03 / lb carbon.

4.3.2. Supercritical Carbon-dioxide (SCD)

Tomasko *et al.* [63], estimated the capital cost of SCD regeneration to be \$ 3,310,900 in 1991 \$s, which illustrates that on site regeneration with SCDs will be prohibitively high for many adsorption treatment applications. Recycling of the carbon dioxide partly counterbalanced the high depreciation and tax costs. The operational cost amounted to 10.6 ¢ / lb at a daily regeneration rate of 52,800 lb carbon/day [63]. The earnings from the solute recovery may partially reduce these costs.

4.3.3. Inorganic Eluents

Since the removal of chemical regenerating agents such as alkalis, acids and oxidants can be performed by simple water rinsing, the costs involved with nonsolvent regeneration are low. For example, Dow Chemical Company reported the operating cost before credit to be \$5/1000 gallons (influent flowrate: 0.144 MGD) to regenerate carbon spent in purifying wastewater containing phenol and sodium acetate [45]. The construction of the necessary units to regenerate laden carbon costed \$ 692,000.

4.3.4. ELECTROCHEMICAL REGENERATION

In-situ regeneration of carbon with electrochemical methods requires the insulation of the adsorber, the electrodes have to be built in the adsorber, which raises the capital cost of the regeneration. The operational cost of electrochemical regeneration depends largely on the consumed electricity. Owen and Barry [68] calculated the cost for rinsing and regenerating the carbon as 0.66 cents to purify 1000 gal of a "Lake Tahoe type" wastewater at a price of 1.2 cent per kWhr electricity. The treatment of the wastewater required 0.21 lb carbon / 1000 gal effluent.

4.3.5. BIOREGENERATION

In order to increase the biodegradability of the influent waste stream, BAC is often preceded by ozonation. Ozonation however is capital intensive, and its cost is only justified if the savings realized by the less frequent regeneration will counterbalance the high construction costs.

Rice and Robson [73] calculated the cost of a plant assembled from technological units documented in literature. The plant is capable of producing drinking water up to 75 MGD, and the average daily output is 50 MGD. The capital cost for a combined ozonation BAC unit for this flowrate, based on experiences with European treatment plants, is \$10.5 million when an ozone dosage rate of 2 mg/L is applied (assumed to be in 1982 dollars). Operating costs amount to \$550,000 - 650,000 annually. Reviewing these data in light of the carbon adsorption with thermal reactivation, it can be established that the conventional carbon treatment requires lower capital investments (\$ 10 million), but the operating costs are much higher (\$1.1 million).

5. COST COMPARISON OF SPENT CARBON MANAGEMENT ALTERNATIVES

In order to make a cost comparison upon the available carbon regeneration methods, the cost of the above mentioned methods were updated to 1996 dollars. The cost of the SCD

regeneration in 1996 was computed by substituting the cost indexes published in the *Journal of Chemical Engineering* in the following formula:

$$\text{Present cost index} = \text{original cost} * \left(\frac{\text{cost index value at present time}}{\text{cost index value at time original cost was obtained}} \right) \quad (\text{eq} - 10)$$

The summary on the cost of handling 1000 lb exhausted carbon by different methodology is provided in *Figure 15* and Table 9. The cost estimation of each option includes the price of disposing and transporting the fraction of the carbon, which was not reactivated due to incomplete regeneration. The cost of solvent regeneration may vary widely depending on the price of the solvent in relation to the value of the recovered material. It may even earn profit as it was reported by Parmele and Allan [46].

The cost of steam regeneration is the lowest, it is only a fraction of the thermal regeneration expenses. The survey showed the SCD process to be inexpensive to operate as compared to thermal regeneration, but it is to be emphasized that the capital cost of the SCD process is high (\$ 3.3 mil., as compared to \$ 3.9 mill. construction cost for a multi-hearth furnace with the same capacity, in 1978). Therefore, it is questionable whether SCD is economically feasible as an in situ option. Although the capital cost of the electrochemical method was not included in the calculations, the estimated operational cost is relatively high. Thermal regeneration is the most expensive of the presented regeneration methods. The cost of carbon replacement, when the total amount of spent

carbon is disposed and substituted for fresh carbon, was also calculated and it proved to be the most expensive waste carbon management alternative.

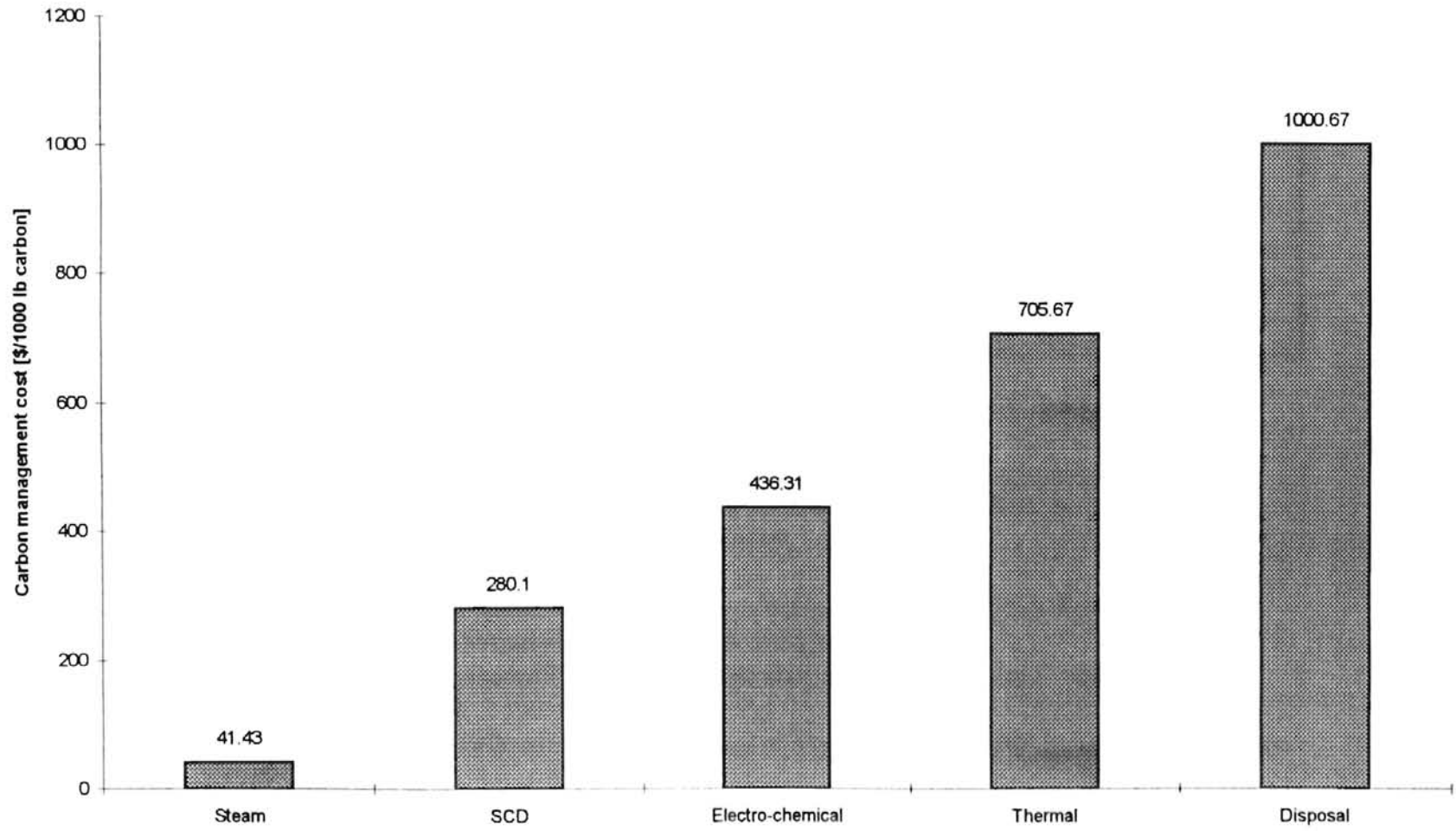


Figure 15 Spent carbon handling cost by various options

Table 9 Cost of spent carbon management techniques^a

Carbon Management	Unit cost	Disposal	Thermal	Steam	Electro-chemical	SCD
Make up - Carbon Cost ^b	980.00	980.00	-	29.40	382.2	147.00
Shipping ^c	15.67	15.67	15.67	0.59	6.11	2.35
Disposal ^d	5.00	5.00	-	0.19	1.95	0.75
Regeneration	-	-	690.00 ^e	11.25 ^f	46.05 ^g	258.67 ^h
Total Cost	-	1000.67	705.67	41.43	436.31	280.1

Notes:

- a. A carbon consumption of 30,000 lb/week had been assumed, which corresponds to the requirement of a wastewater treatment plant with a capacity of 5 MGD, assuming a carbon dosage of 1 lb carbon / 1000 gal wastewater [46]
- b. makeup carbon cost: \$ 98/lb carbon [75],
- c. shipping cost in a distance of 70 miles for commercial volumes: \$ 235/yd³ [76],
- d. disposal cost (non-hazardous materials): \$ 15.50/yd³ [76],
- e. price of off site regenerated 840 R carbon (similar in characteristics to F - 400): \$ 69/lb carbon [75]
- f. cost of steam: \$ 2.00/lb estimated from prices of 50 psia steam (\$ 1.80/lb), and 160 psia steam (\$ 2.20/lb) [77]
- g. capital cost is not included, price of electricity for industrial costumers averaged from winter and summer prices: \$ 9.67/kWh, RE from [78]
- h. \$ 500/month renting cost of a tank to store the CO₂ on site included, cost of carbon dioxide: \$ 5/lb CO₂ [79]

CHAPTER II

EXPERIMENTAL BACKGROUND

1. REGENERATION WITH NATURAL GAS

Natural gas offer several advantages over other thermal treatment of the activated carbon such as:

- (i)* inexpensive and available at most water and wastewater treatment plants for heating purposes,
- (ii)* it can be applied in situ,
- (iii)* the pollutants removed from the contaminated carbon can be disposed by simply igniting the effluent natural gas leaving the carbon,
- (iv)* the contaminated natural gas can also be recycled by condensation, and the pollutant can be recovered if it is valuable.

The step of the experiments developed to evaluate the efficiency of the method are as follows:

- (i) isotherm studies to determine the adsorption capacity of the carbon.
- (ii) preliminary experiments to gather information on parameters needed for the main experiments, and
- (iii) loading and regeneration studies.

2. MATERIALS

The activated carbon employed in the experiments (Filtrisorb 400, Calgon) is very commonly used in regeneration studies (see Tables in Chapter I, Section 3). The carbon for the isotherm adsorption, column adsorption and regeneration studies was washed to remove fines, heated at 105 C° for 24 hrs, then cooled and stored in dessicator until use in the study. Orthochloro - phenol (OCP) of 98 % purity was purchased from the FLUKA Chemika, acetone employed as a diluting agent for the gas phase calibrations was of HPLC grade and purchased from the Fischer Scientific.

3. EQUIPMENTS

3.1. ADSORPTION EQUIPMENT

The physical arrangement of the adsorption equipment is presented in Figure 16. The OCP solution is moved by a positive displacement pump (Masterflex, Model No 7520, manufactured by the Cole Parmer, Inc.) from the influent bottle to point A of the

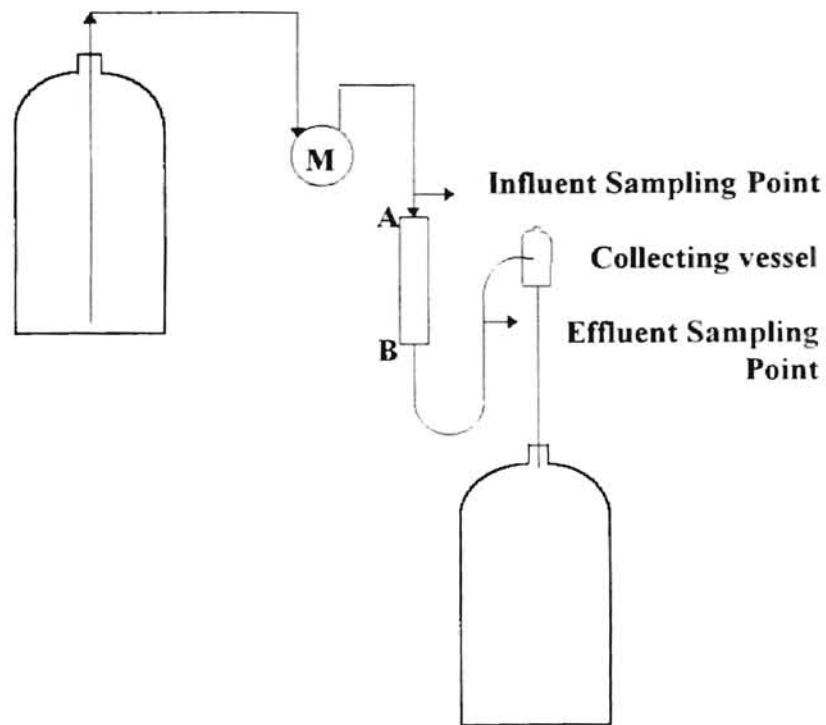


Figure 16 Experimental setup for the adsorption phase

adsorption column through Vyton tubing (Masterflex, 6412-14), and from point B of the adsorption column the solution was removed from the column by gravity. The solution was led by an 11 mm I.D. polyethylene tube, which was narrowed down to 5 mm I.D. bent in the shape of a gooseneck. Initially, the exit of the column was directly connected to the effluent bottle and the OCP solution by its weight flew out of the column through the gooseneck and left the column empty. Therefore, the top of the gooseneck was connected to a vessel in which the solution was collected and the pressure in the polyethylene tube between the collecting vessel and the effluent bottle was equilibrated. Samples were taken every approximately 120 minutes at the influent and effluent sample ports in Hach tubes. 120 minutes was chosen for sampling time, because the change in the effluent concentration was slow. The volume of the Hach tube was adequate to rinse the quartz cuvet three times in which the measurement of OCP concentration was performed by a UV spectrophotometer (Secomam, S.1000) at a wavelength of 274 nm. The calibration curve was prepared using 4 OCP concentrations: 10, 40, 70 and 100 mg/L. The regression squares (R) of all calibration curves were 0.999.

3.2. REGENERATION EQUIPMENT

The regeneration of the loaded carbon was carried out in the experimental device illustrated schematically in Figure 17. The natural gas was first introduced into a fluidized sand furnace (Fluidized Bath SBL-2D, Tecam ®) to heat the gas to the desired

temperature. The sand in the furnace was fluidized by blowing compressed air in an upflow direction through the sand bed. The furnace at the start of the experiment was heated without gas flow through it until it reached around 250 °C, and then the heating of the natural gas was commenced by passing the natural gas through a bronze tube (50 feet) submerged in the furnace. Until the temperature of the natural gas reached the regeneration temperature it was allowed to escape into the air through the bypass shown in Figure 17. When the temperature of the natural gas approached the selected regeneration temperature, the bypass was closed and the regeneration was started by allowing the hot gas through the column. Point A of the column was joined to a threaded #7 glass connector by a polyethylene tube, tightened by aluminum bands. The threaded connector then was fitted on the threaded aluminum tube, which was connected to the effluent of the sand furnace. Effluent of the sand furnace.

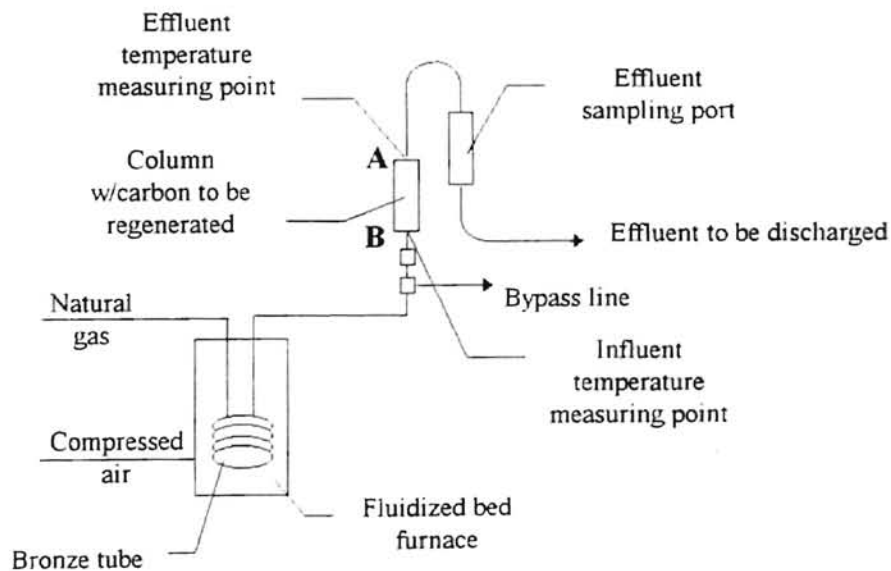


Figure 17 Experimental setup for the regeneration equipment

Point B of the column was inserted into a polyethylene tube, and the tube was tightened by aluminum bands on the column to prevent leakage. The effluent gas stream then was directed through an aluminum tube, which led into a glass sampling port, with a rubber septum to prevent leakage when taking sample.

Sampling was carried out every 5 minutes by taking 400 μL volume of the sample. Gas phase concentrations were determined then by a GC (Sigma 3B, Perkin Elmer, integrator: Sigma 15, Perkin Elmer) at 180 °C injection-, 180 °C detector- and 150 °C oven temperature, in which nitrogen gas was applied as carrier gas at 30 ml/min flowrate. The GC was equipped with an SP 1240 DA column on Supelcoport (80-100 mesh), supplied by Supelco, Inc.

The range of the OCP concentration in the effluent gas stream was not possible to estimate in advance. Although, as it was shown in section 2.3., it is known that the large part of OCP will be removed soon after commencing the regeneration, the exact proportion of the OCP released from the carbon is not known. Therefore, some of the regeneration studies had to be repeated until the calibration of the GC in the desired concentration range was successful.

The calibration of the GC was carried out at five OCP gas phase concentrations: 39.39; 78.77; 118.16; 157.54 and 196.93 ppm. At lower temperatures, when smaller amount of OCP regenerated was expected, the calibration concentrations were: 4.93; 9.85; 14.77; 19.69 and 24.62 ppm. In order to obtain these concentrations the OCP was first dissolved in acetone in a ratio of 200 μL OCP / 10 mL acetone for high regeneration temperatures

or 25 μL OCP / 10 mL acetone for low regeneration temperatures. From this solution 1 - 5 μL was transferred at room temperature into washed and dried glass bottles, sealed by Standard seal, 20 mm for 5 ml vial supplied by Supelco (2-7227), and Teflon®/Rubber 20 mm septa (2-7233). The resulting gas phase OCP concentrations were calculated by the following formula:

$$\begin{aligned} \text{OCP concentration in ppm} = & \text{volume of OCP solution injected (1-5 } \mu\text{L)} * \\ & 24.45 \text{ L/mole} / 128.5 \text{ g} * \text{density of OCP (1.242 g/L)} * \text{dilution ratio (0.2 / 10 or} \\ & 0.025/10) / \text{volume of glass bottle (120 ml)} * 10^6 \end{aligned} \quad (\text{eq - 11})$$

3.3. COLUMN DESIGNS

The final glass column design used in the experiments had been preceded by several other designs, which however failed to operate in the natural gas regeneration method. Two major types of column were first attempted. The second type of column was made of two separate glass tubes with an edge, pressed together with a clamp. In order to avoid breaking of the glass tubes and to prevent leakage, one Vytan O - ring was placed on both glass tubes. A 50 mesh size screen was placed between the two O - rings. The diameter of the glass elements were 40.64 mm, and their length were 115 mm. The elements were narrowed down at their ends to 11 mm O.D.

Prior to the commencement of the regeneration studies it was anticipated that the saturation of the activated carbon in liquid phase may require an excessively long time. In

an attempt to lower the loading time and to be able to scale up the natural gas regeneration method, the first version of the adsorption column was designed by following the principles Crittenden and coauthors defined for a rapid small scale column [80 - 82] (Figure 18). The I.D. of the glass column was 10.5 mm, and its length was 60 mm. It contained a coarse frit (a porous plate made by melting fine glass beads together) to support the carbon in the column. Nevertheless, the "course" glass frit welded into the column was not porous enough to allow the 30 ml/min flowrate suggested by the authors through the column. The openings of the next slightly more porous frit was the "extra course" frit turned out to be larger than the average carbon particle diameter, therefore it was rather decided to enlarge the pore openings of the "course" frit by washing it with a concentrated hydrogen fluoride solution. The improvement in the throughput volume of the column however was not satisfactory. Therefore, a new column was built with the extra course frit, and although at the beginning some of the carbon came through the frit, the carbon particles finally blocked the excessively large openings and loading of the carbon at 30 ml/min flowrate became possible. With this column at 100 mg/L OCP concentration, a loading time of approximately 7 hrs. was necessary to exhaust the carbon due to the accelerated adsorption rate achieved by decreasing the particle size of the carbon from 12 X 40 to 50 X 80 mesh size. However, regeneration of the carbon bed was not possible, because the wet carbon bed, composed of carbon particles with an average radius of 0.00525 cm [86], was not penetrable for the natural gas at the applied 7.41 L/min flowrate. Thus, the next column was constructed of glass tubes with the same diameter (10.5 mm I.D.) and of 60 mm length, but instead of the frit an 80 mesh size wire

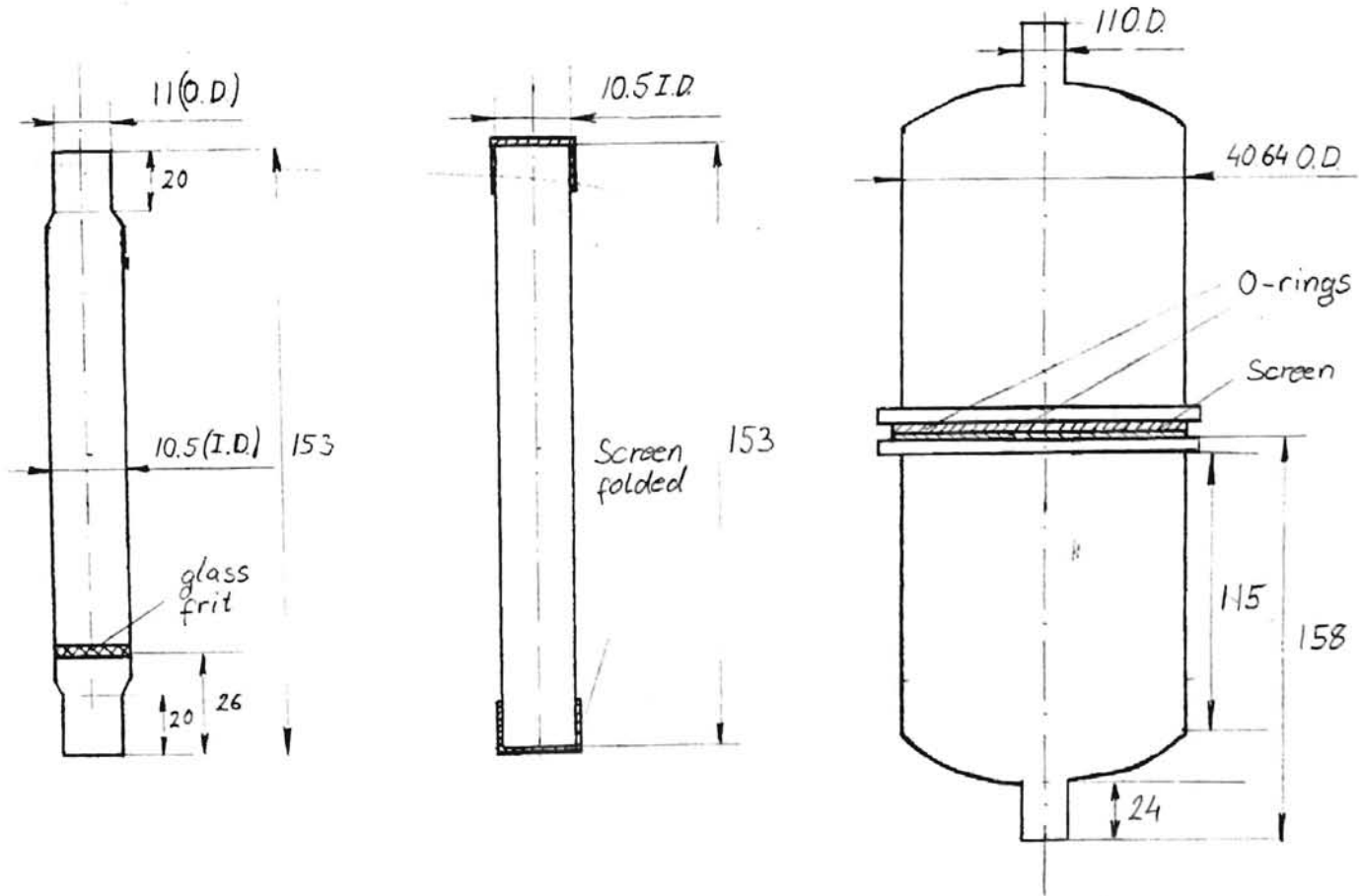


Figure 18 Development of column design

screen was employed to support the carbon bed. Screen wires were placed on the top of the column as well to prevent the hot natural gas to carry the carbon out of the column during regeneration. Nevertheless, the regeneration experiment has shown that the temperature of the natural gas was not high enough to quickly evaporate the water from the carbon bed, and the wet carbon bed blocked the gas stream across the column. This series of trials made it clear that the scaling efforts of the natural gas regeneration cannot be successful, since the small particle size is the precondition for short loading time, which causes at the same time the plugging of the column. Thus, the research was focused on only proving the principle of the natural gas regeneration.

In the modified design, the carbon was used in the commercially available particle size (12 X 40, average particle radius: 0.0513 cm), and the diameter of the column was increased from 10.5 mm in the initial design into 40.64 mm. The amount of the carbon in the bed of both columns was approximately 3 g. Since the screen does not distribute the flow uniformly, there was a concern that channeling might occur. To avoid channeling, laminar flow was enhanced in the column, by selecting column length of 10 cm. Initially, the flowrate (30 ml/min) through the column was adjusted by a clamp. However, stable flowrate was not possible to ensure by clamp, therefore a gooseneck was added to the experimental setup.

3.4. SOFTWARE

In order to calculate the regeneration efficiency a mass balance was set up for the loaded and regenerated amount of OCP. The area under the loading and regeneration curves, when was converted to mass units was determined using Graftek software [83]. For calculating the standard deviation of the calibration curves, the built-in functions of the Microsoft Excel software product were used [84].

4. CHOICE OF ADSORBATE

The selection criteria for the compound for the experiments were as follows:

1. detectable in both liquid / gas phase by UV spectrophotometer and GC, respectively
2. adsorbable,
3. semi-volatile, but volatile enough to be present at measurable concentration in gas phase for calibrating the GC,
4. liquid in room temperature,
5. "problem compound" (included as one of the National Priority Pollutants, and/or listed by EPA as a hazardous waste).

Based on these considerations, OCP was chosen as the subject compound for the experiments. The physical characteristics of OCP are summarized in Table 10. Both the column and the isotherm studies were run at an OCP concentration near 100 mg/L. This

OCP concentration is a typical influent OCP concentration to feed carbon adsorption units used to clean up sites contaminated by OCP as a result of rail car spill [85].

Table 10 Physical characteristics of OCP

Partial Pressure [kPa] ^a	Boiling Point [C°] ^b	Melting Point [C°] ^b	Molecular Weight [g] ^b	Solubility [mg/L] ^b	Adsorption intensity [mg/L] ^c	Adsorption coefficient [(mg/L)* (g/mg)] ^c	Henry constant [dimensionless] ^d
~ 0.2	175	9.3	128.5	28'500	51.0	0.41	3.70*10 ⁻¹

Note:

- a. [86]
- b. [87]
- c. adsorption parameters are obtained from [88].
- d. Henry constant is calculated at 20 °C as [89]:

$$H = 16.04 \frac{PM}{ST} \quad (eq -12)$$

- where
- P - pressure [Hgmm]
 - M - molecular weight [g]
 - S - solubility [mg/L]
 - T - temperature [K] (= 293 K)

5. STATISTICAL ANALYSIS OF THE RESULTS

In order to calculate the inaccuracy (error) of the RE data obtained from the experiments, first the inaccuracies of determining the amount of both loaded and regenerated OCP were calculated. It is claimed by Doebelin [90] that measurement data obtained from engineering applications are adequately close to a Gaussian distribution. If a random variable can be described by the Gaussian distribution, there is 95 % probability that the values obtained by measuring the variable will be scattered within $\pm 2 \sigma$ (standard deviation, S.D.) range from the mean value (μ) of the variable [90]. Consequently, it can be stated that if it is assumed that the true OCP concentration follows Gaussian distribution, then the values of the true concentrations fall with high certainty in the $\pm 2 \sigma$ range. Thus, the inaccuracy of determining the regenerated amount of OCP can be expressed as the area, which extends between the curve of time vs. measured OCP concentration - 2σ and the curve of time vs. measured OCP concentration + 2σ (Figure 19).

Calculating the inaccuracy of determining the quantity of the loaded OCP was achieved by subtracting the influent and effluent concentrations at each time point. In order to provide the differential area with a statistical bound (absolute error), the variance of two independent variables with identical variance must be computed as [91]:

$$\sigma_L^2 = 2 \sigma^2 \quad (\text{eq - 13})$$

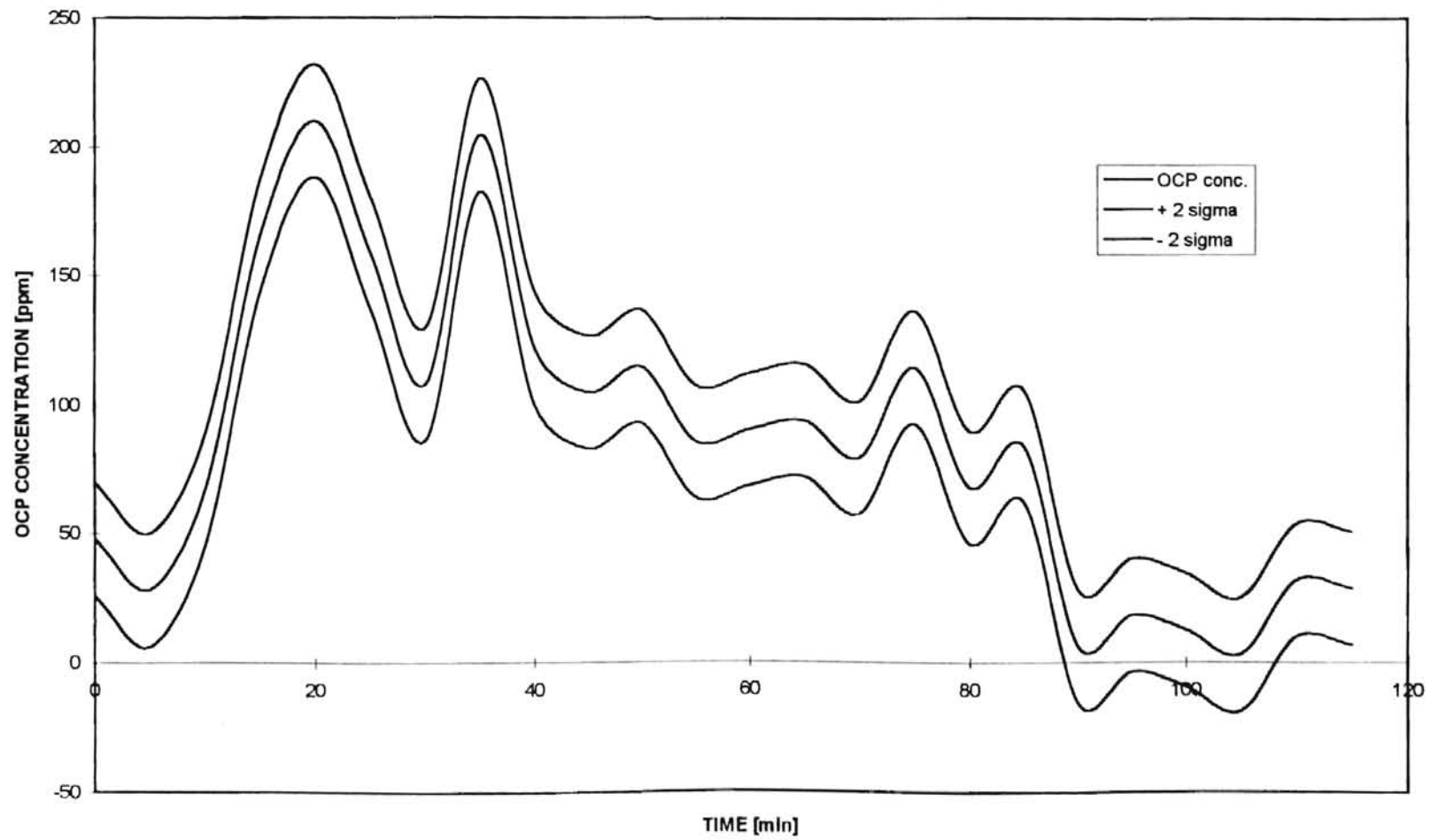


Figure 19 Representation of areas used to calculate the absolute error demonstrated on the regeneration curve of experimental run No 3.

where σ_L^2 is the variance of the difference,
 σ^2 is the identical variance of the independent variables.

Since the S.D. (σ) is the square - root of the variance (σ^2), the concentration values were altered by $\pm 1.41\sigma$ to obtain the statistical bounds. The value of σ can be determined from the calibration curve, as follows:

$$s_A^2 = 1/N \sum (mC + b - A)^2 \quad (eq - 14)$$

where s_A - S.D. of the measured area / absorbance depending on which device was calibrated by the curve (GC or spectrophotometer).
 N - number of samples of known concentration used for calibration.
 m, b - slope and intercept of the calibration curve calculated by Microsoft Excel software,
 A, C - measured area/absorbance and concentration values.

Then, the S.D. of the concentration (s_C) from s_A :

$$s_C^2 = s_A^2 / m^2 \quad (eq - 15)$$

When the function of two independent variables is known, the combined inaccuracy of the individual variables can be calculated by the next formula [90]:

$$I = \left| \Delta u_1 \left(\frac{\partial f}{\partial u_1} \right) \right| + \left| \Delta u_2 \left(\frac{\partial f}{\partial u_2} \right) \right| \quad (eq - 16)$$

where I - combined inaccuracy

f - function of the quantity to be determined vs the variables

u_1 and u_2 - variables

Δu_1 and Δu_2 - statistical bond on the variables.

Thus, for calculating the error in RE, (eq - 6) has to be derivated according to (eq - 15).

$$I_{RE} = \Delta R / A + [R / A^2] * \Delta A \quad (eq - 17)$$

where A - adsorbed OCP,

ΔA - absolute error of measuring the adsorbed OCP

R - regenerated OCP, and

ΔR - absolute error of measuring the regenerated OCP.

Note: ΔA was found in general to be higher than ΔR , due to fact that the length of loading (~ 3000 min) is considerably longer than the length of the regeneration (115 min), and thus the absolute error was obtained by integrating in a longer time period. Consequently, the accurate measurement of the OCP concentration during loading is of crucial importance to produce accurate REs.

6. ADSORPTION ISOTHERM STUDIES

The preparation of the carbon for the adsorption study included the grinding of the carbon from the original 12 X 40 mesh size into 50 X 80, which was followed by rinsing with distilled water to remove the fines and then drying the carbon as described previously.

6.1. ADSORPTION EQUILIBRIUM STUDIES

The time required to reach the adsorption equilibrium was determined by adding nearly the same amount of activated carbon (Table 11) to 300 ml of OCP solutions with identical concentration (100 mg/L). The remaining OCP concentration of each solution was recorded after thoroughly mixing on shaking table for various period of time.

Table 11 Carbon dosages in adsorption equilibrium study

Time elapsed [hrs]	Dosed carbon [mg]
12	48.9
14	49.6
16	51.0
19	51.0
23	51.6

6.2. DETERMINATION OF ADSORPTION CAPACITY

In order to obtain the adsorption capacity, various amounts of carbon (Table 12) were added to 109 ± 16.13 mg/L OCP solutions of identical volume. In the first experiment carried out to determine the adsorption capacity, the carbon dosage was chosen to be similar to dosages recommended in literature for F - 300 carbon [88]. The F - 400 carbon applied in the experiments, however showed an outstanding adsorption affinity, and the adsorption capacity studies had to be repeated twice with smaller amounts of carbon, until OCP remained in measurable quantities in the solution after adsorption.

Table 12 The range of the carbon dosages applied in the adsorption isotherm experiments

Carbon dose [mg/L]	68.00	137.33	210.00	230.67	303.00	347.00
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6.3. RECOVERY OF OCP FROM EXPERIMENTAL SETUP

Due to the high affinity of OCP to adsorb, it was expected to be adsorbed on the wall of piping employed in the experimental setup. In order to select a tubing, on which OCP does not adsorb in a significant amount, and to determine the amount of OCP removed by the piping, static and dynamic “adsorption” studies were performed. For static studies, the

weight of the piping was measured before and after 24 hr exposure to OCP solution of 100 mg/L; in the dynamic studies the 100 mg/L OCP solution was recirculated in the tubing for a duration identical to that of the experiments.

7. GAS PHASE EQUILIBRIUM STUDY

The time required for the OCP to diffuse in the glass bottles was determined by monitoring the OCP concentration as a function of time. For that reason, the OCP concentration was measured every 5 minutes from the time of injecting the OCP solution into the glass bottle as described above in Section 2.2, Chapter II.

CHAPTER III

RESULTS AND DISCUSSION

1. ADSORPTION EQUILIBRIUM STUDIES

The OCP concentrations remained in the adsorption vessel after a particular period of time are tabulated in Table 13 and illustrated in Figure 20. The OCP equilibrium concentration does not change significantly after the first sampling (12 hrs), therefore it was assumed that the equilibrium was essentially complete and to include a safety factor 24 hrs was chosen for the duration of the isotherm studies.

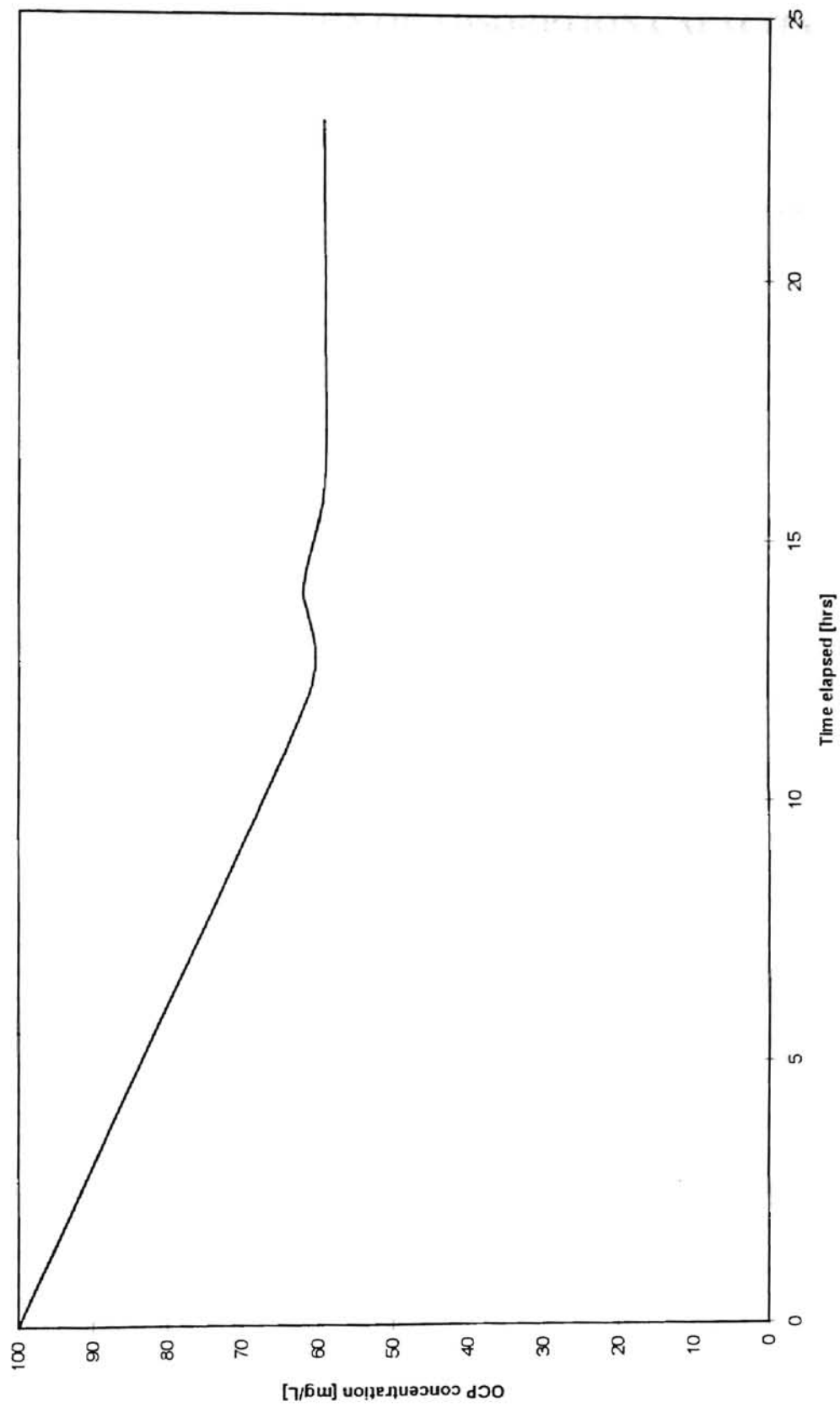


Figure 20 Adsorption equilibrium study

2. DETERMINATION OF ADSORPTION CAPACITY

The adsorption capacity of the carbon were determined with the Freundlich, Langmuir high and low form and BET isotherms. Of all these isotherms the best fit was yielded by the Freundlich and the Langmuir low form (equations given in Chapter I, section 1.6). The linear regression parameters in Table 13 (using Microsoft Excel to generate the equation of the line) show the Langmuir low form to be more accurate than the Freundlich isotherm, however the standard error of the adsorption capacity is higher for the Freundlich isotherm (Table 13, Figure 21 and 22, isotherm data in Appendix C).

Table 13 Results of the statistical analysis of the isotherm studies

Statistical Parameters	Type of isotherm	
	Freundlich	Langmuir low
R Square	0.724	0.993
Adjusted R Squared	0.669	0.992
Standard Error ($\pm 2 \sigma$)	2.12	3.392
Observations	6	6

Table 14 Parameters of the isotherm models

	Type of isotherm	
	Freundlich	Langmuir low
Adsorption capacity at 100 mg/L equilibrium OCP conc. [mg/g]	296 ± 2.12	237 ± 3.39
Adsorption coefficient, b	NA	-9804.55
Slope	0.128	0.004
Intercept	2.216	-0.023

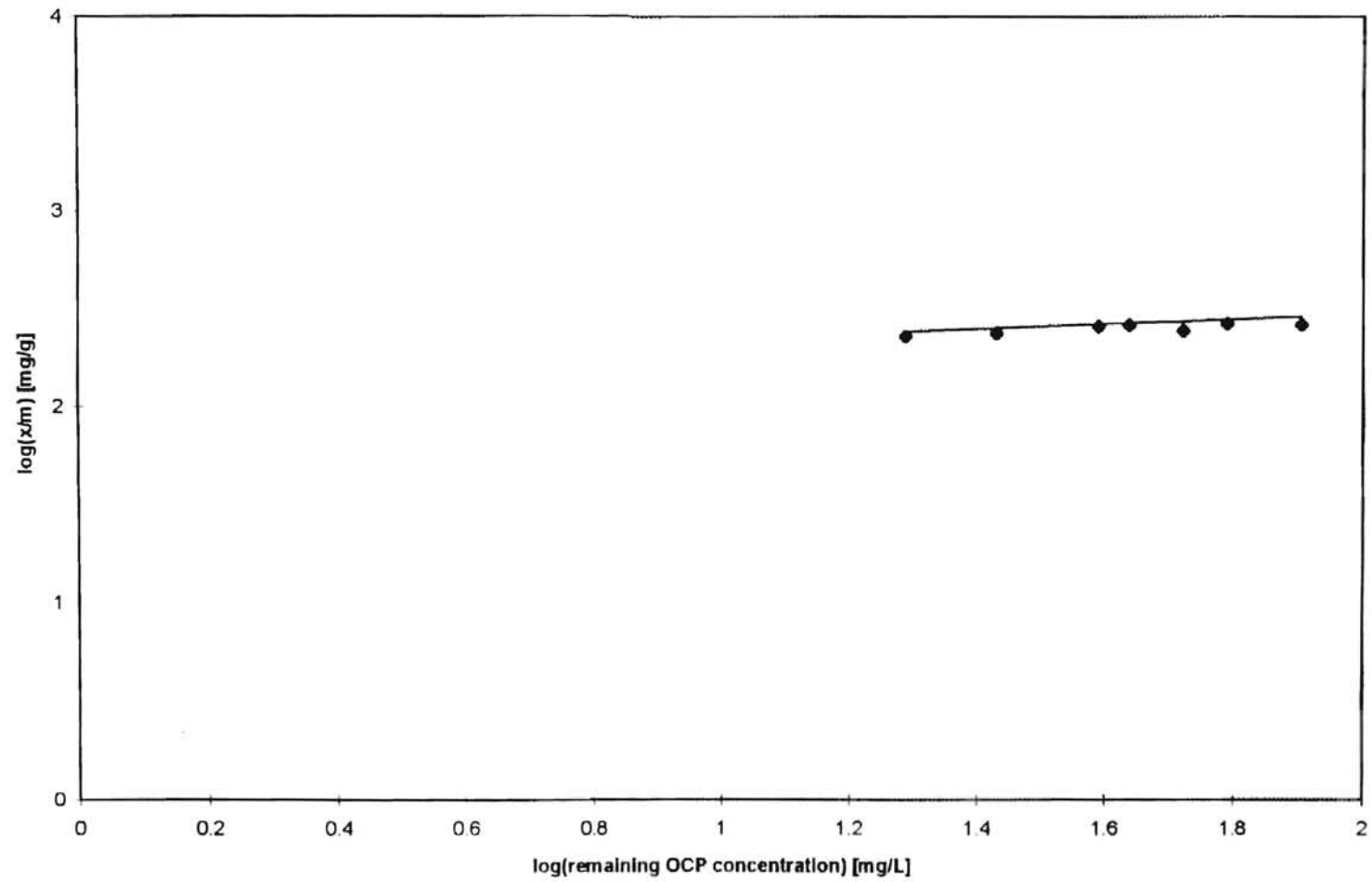


Figure 21 Freundlich adsorption isotherm

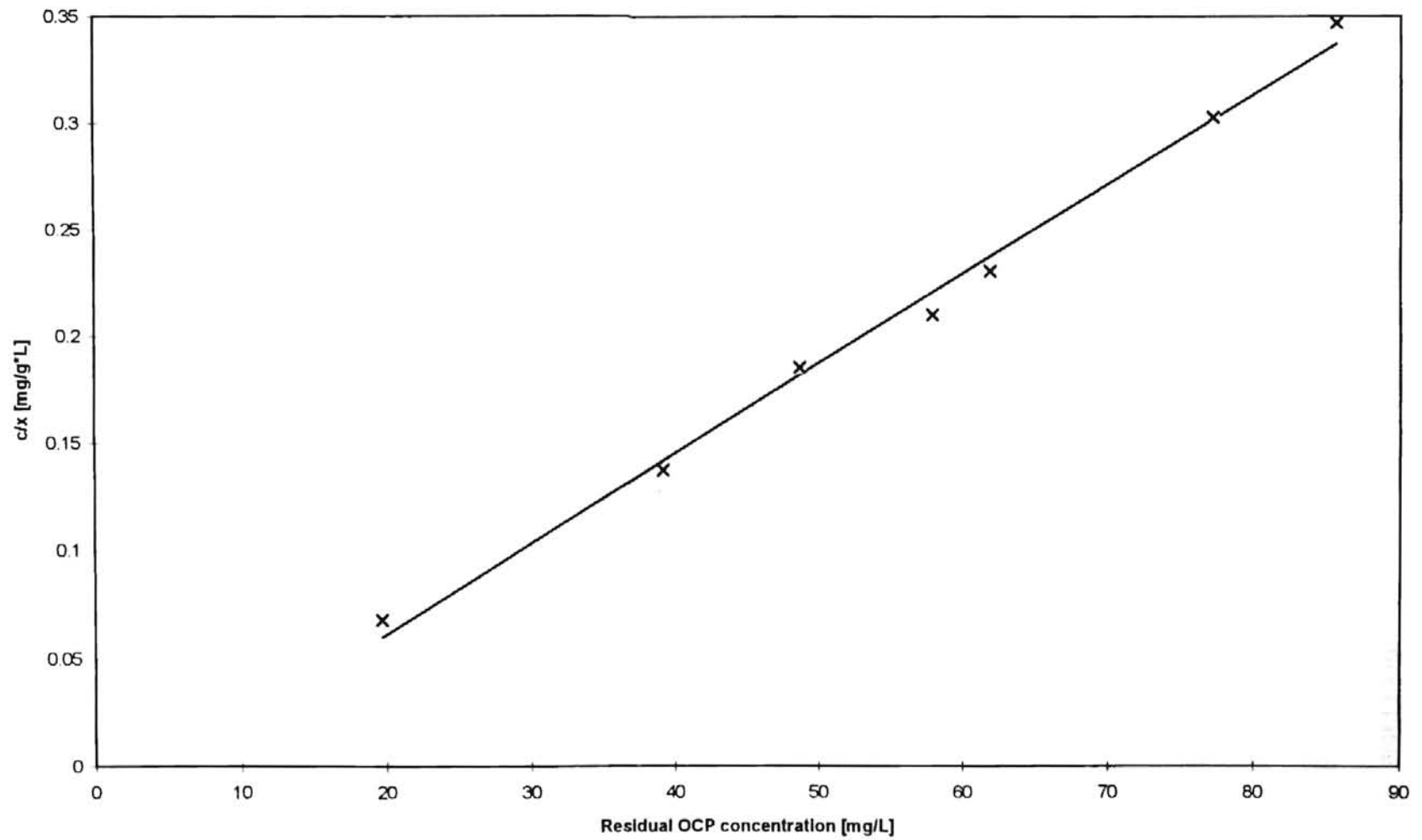


Figure 22 Adsorption isotherm, Langmuir low form

Also the adsorption coefficient, b of the Langmuir form is negative (Table 14), therefore the Freundlich form has been accepted. Thus, the adsorption capacity at the chosen influent OCP concentration (100 mg/L) obtained from (eq - 1) is 296 ± 2.12 mg/g carbon. The pH of the adsorption systems in equilibrium ranged from 5.1 to 5.9, the ambient temperature was 20 °C, but it was suspected that the heat of motor driving the shaking table may have increased the temperature of vessels moving directly above.

3. RECOVERY OF OCP FROM THE EXPERIMENTAL SETUP

Three types of tubings were tested: poly-vinyl-chloride (PVC)-, silicon- and polyethylene - based. Both the PVC - and the silicon - based tubing adsorbed considerable amounts of OCP, only the polyethylene piping proved to be resistant to the adsorption of OCP. Table 15 shows the amount of OCP adsorbed by the polyethylene tubing in terms of both an increase in the weight of the tubing and a reduction in the OCP concentration. As it can be seen from the data the dynamic study is more sensitive in indicating adsorption of OCP on the piping.

Table 15 Dynamic and static studies to measure OCP adsorption on piping

	DYNAMIC		STATIC	
	BEFORE	AFTER	BEFORE	AFTER
OCP[mg/L]	94.58	91.23	98.95	98.64
Weight [g]			0.2704	0.2705

4. PRELIMINARY ADSORPTION COLUMN STUDIES

The column was loaded in a downflow mode. Before starting the experiment, the air packet had to be removed from the lower part of the column. Therefore, the column was turned upside down, and the OCP solution was directed through the column, until the air was completely driven out and the solution left the column at the top. Then the column was turned back into the position of the experimental run, a part of solution was removed through the outflow of the column to make a place for the carbon bed and then the loading of the carbon was commenced in downflow mode.

The untraditional column design resulted in an unusual loading pattern. As opposed to the classical S - shaped loading curve, the effluent concentration initially equals the influent concentration, then decreases for short time period (Figure 23), later it starts to increase slowly and close to the end of the run it approaches the influent concentration. The equal influent and initial effluent concentration is due to the fact that the OCP solution, which is in the bottom prior to the experiment, does not flow through the carbon layer. Assuming perfect laminar flow, the exact residence time was calculated to be 5.38 min. by using the volume of the lower part of the column (161.5 ml) at 30 ml/min flowrate. In Figure 23, the flowrate was 29 ml/min, which gives 5.57 min as the residence time, this is slightly lower than the 6 min that can be seen on the graph.

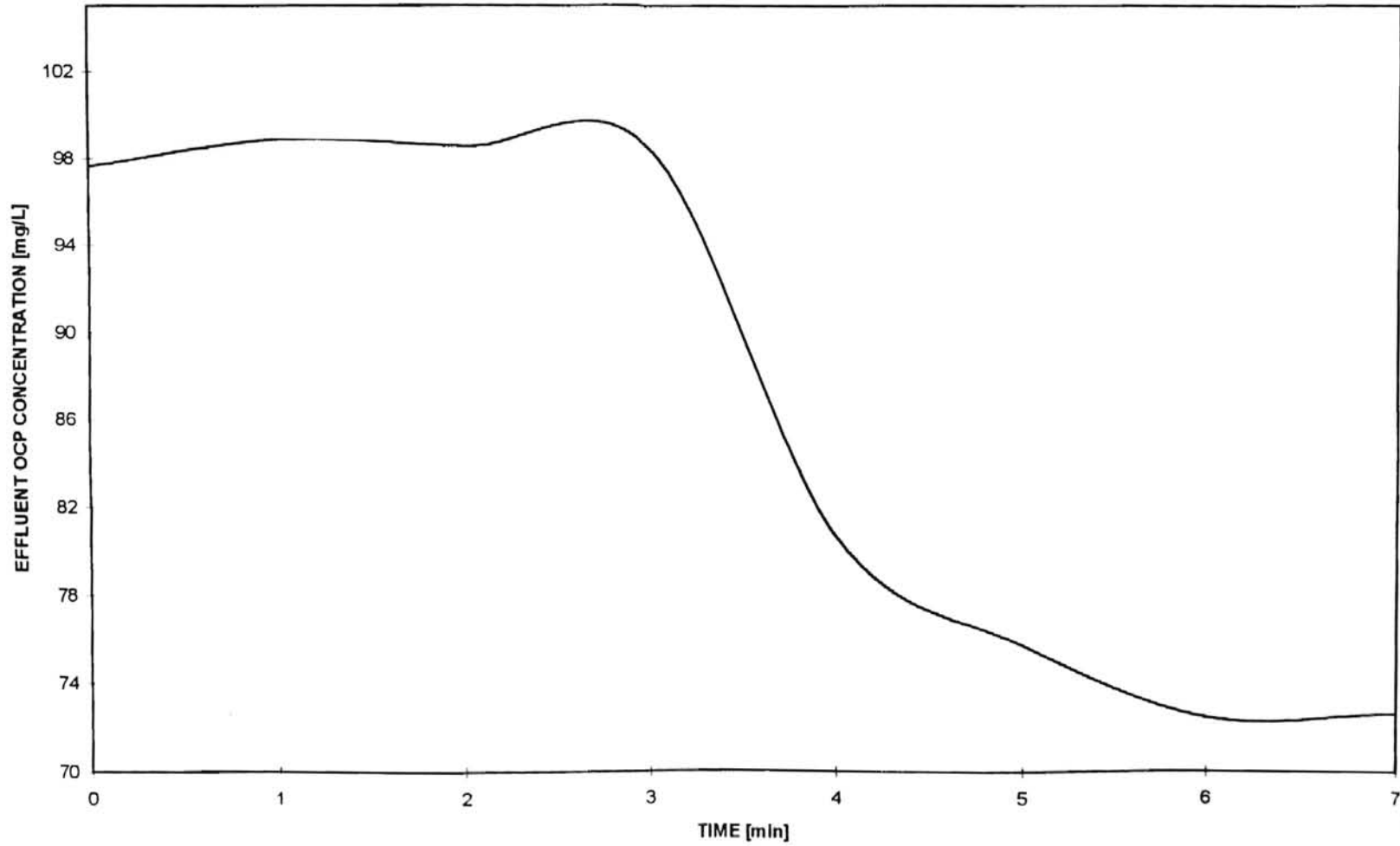


Figure 23 Start - up of loading phase

5. BACKGROUND EXPERIMENTS FOR THE REGENERATION STUDIES

5.1. EQUILIBRIUM STUDY FOR GC MEASUREMENTS

The OCP concentration in the glass bottle vs time is not stable in the first 30 min and the last 15 min. (Figure 24), thus samples prepared for calibration were injected in the time frame extending from the 30 -50 min.

5.2. REGENERATION COLUMN STUDIES

Regeneration was carried out in a direction opposite to that of the adsorption to prevent OCP from passing through the column, and to maintain a high concentration gradient throughout the column. The influent gas temperature was maintained between 110 - 160 °C. The influent and effluent temperature sensors were located at the natural gas entry and exit points of the column. The effluent temperature from the column was often 40 °C lower than the influent temperature, even after the hot gas dried the bed out. This is a significant drop in temperature, which may be caused partly by the imperfect insulation, which is supported by the fact there is a 20 - 30 °C temperature difference between influent and effluent temperatures, when the column is connected without the carbon bed.

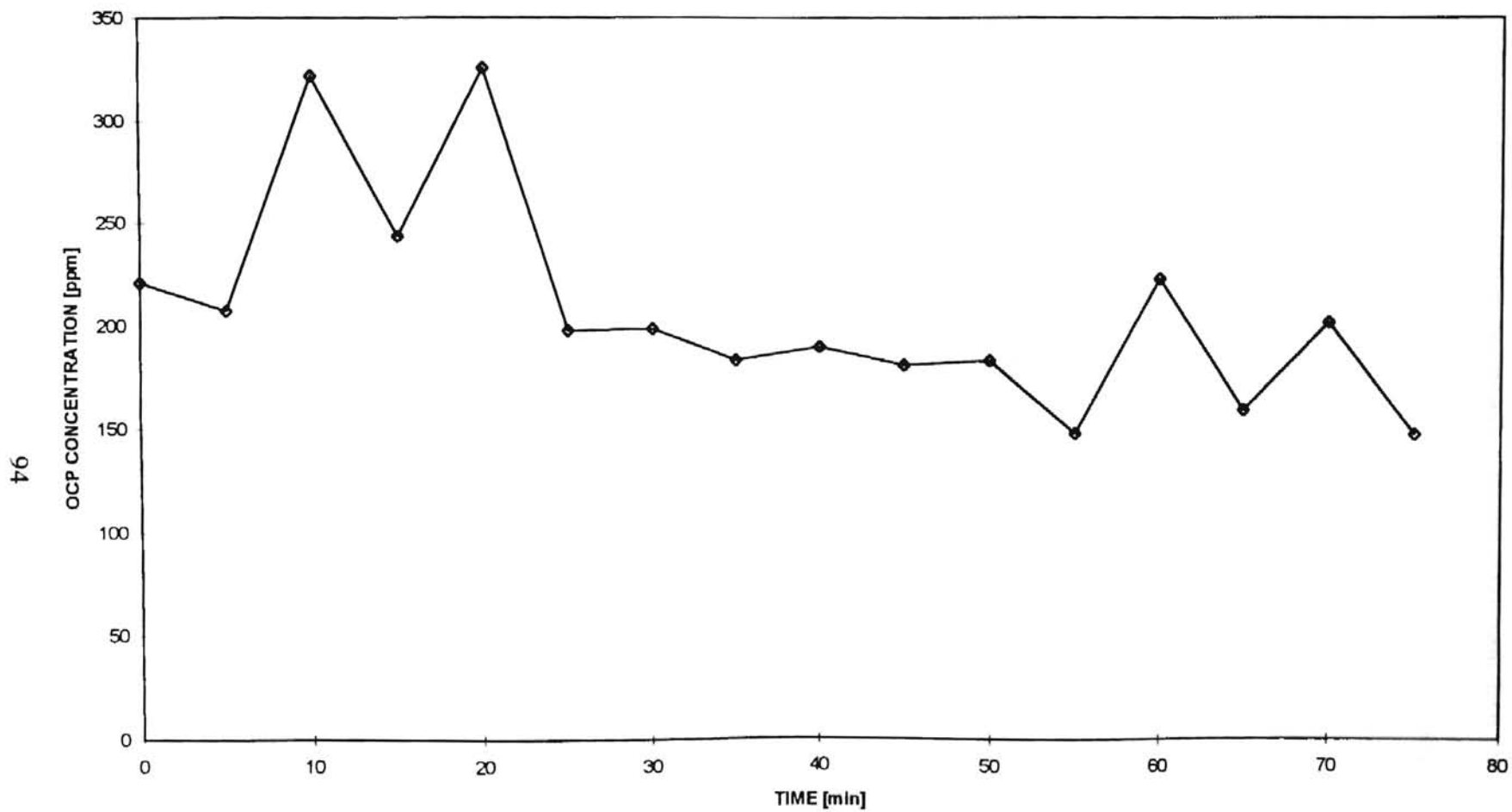


Figure 24 Concentration of OCP vs time in the glass bottle used to calibrate GC

Another fraction of the heat may be consumed by the endotherm desorption process. The natural gas inflow was found to be fluctuating between 6.40 - 8.33 L/min, therefore it was monitored at each sampling time during the run.

6. COMPARISON OF ADSORPTION CAPACITY DETERMINED FROM THE ISOTHERM STUDIES AND COLUMN EXPERIMENTS

The parameters of the carbon loading experiments were selected to ensure that the carbon was exhausted with a similar amount of OCP. Since the individual loadings were within the statistical bounds (Table 16) it can be stated that the particular loadings were reasonably close. Although the role of the adsorption capacity experiments was to define the maximum amount of OCP that can be placed on the carbon, the adsorption capacity obtained from these experiments was lower than the ones gained from the column studies. By comparing the system parameters of the adsorption studies and the column loadings it can be concluded that the pH is slightly higher in the column studies than the adsorption studies, so it would decrease loading instead of increasing it. Temperature was very similar in the two experiments, and it is known that at the temperature of the study, the variation in adsorption is insignificant [92]. The adsorption capacities determined by isotherms and column studies are often not the same as it has been pointed out in literature by many researchers [93]. In this study, the amount of OCP loaded on the carbon in the individual runs are very close, therefore complete exhaustion of the carbon is very probable.

Table 16 Experimental parameters of the adsorption runs

	Run No 1	Run No 2	Run No 3	Run No 4	Run No 5
Total loaded volume[L]	87.2	87.6	94.4	89.2	83.4
OCP loaded [mg]	987 ± 180.33	960 ± 84.41	861 ± 79.50	1023 ± 107.52	255 ± 98.73
OCP from isotherm [mg]	890 ± 6.36	889 ± 6.36	889 ± 6.36	889 ± 6.36	-
Temperature [°C]	21.0 - 22.0	20.0 - 21.5	21.0 - 23.0	21.5 - 23.5	20.5 - 22.0
pH	3.0 - 6.2	6.1 - 6.2	5.9 - 6.4	6.0 - 6.6	6.1 - 6.6
Flowrate [ml/min]	40	30.44	32.22	32.68	28.65
Average infl. OCP conc. [mg/L]	96.99	91.74	93.96	98.56	92.78

96

Table 17 Experimental parameters of the regeneration runs

	Run No 1	Run No 2	Run No 3	Run No 4	Run No 5
Regenerated OCP [mg]	145 ± 8.77	254 ± 46.51	248 ± 4.21 (269 ± 5.70)	337 ± 8.46	410 ± 102.36
RE [%]	15 ± 3.69	26 ± 7.17	29 ± 3.16 (31 ± 3.55)	30 ± 4.28	174 ± 99.58
Average regeneration temperature [°C]	110.4	125.5	157.3	136.9	136.6
Accumulated RE [%]	-	-	-	-	58 ± 2.15
100 * $\frac{\text{OCP load in run No 4.}}{\text{OCP load in run No 3.}}$	-	-	-	25 ± 11.79	-

In the loading phase of the experiments, the influent concentration changed rapidly when switching over from one influent bottle to another. It can be hypothesized that as an effect of the drop in the influent concentration some of the already adsorbed OCP might have desorbed. However, this principle does not falsify the results obtained for the loaded OCP, because the desorbed OCP is shown in column effluent as an increase in the OCP concentration. When finishing the loading experiments the carbon was drained quickly. The OCP solution wetting the carbon surface may stay on the carbon surface after draining, but this amount of OCP as compared to the amount loaded is not considerable.

7. DESCRIPTION OF THE REGENERATION PROCESS

In the majority of the regeneration runs, the OCP did not start to desorb in considerable amount in the first 10 - 15 minutes. Probably, in this time period the heating of the carbon to the boiling point of the water takes place. Also, the fog on the glass sampling port started to develop only after this time period. Besides, the effluent temperature remained low for the first 15 min. of the regeneration cycle. The time of significant OCP removal corresponds to the vigorous evaporation of the water between the 25 - 45 min., therefore the average influent temperature in this time - period was chosen to be the regenerating temperature.

The extent of the regeneration was defined by the fraction of OCP desorbed in the last third of a regeneration cycle (from 85 - 115 min.) per the OCP desorbed in the whole regeneration period (115 min) at the highest regeneration temperature (157 °C, Figure 33,

figures and tables of the experimental runs can be seen in Appendix C). Due the technical failure (the tubing melted) the regenerated OCP concentration in the effluent stream was assumed to be the lowest OCP concentration obtained before the failure occurred. The amount of the regenerated OCP calculated for 115 min regeneration including the amount of OCP assumed to be removed in the last 30 min. is bracketed in Table 17. The fraction of the OCP released in the last 30 min of the regeneration was calculated to be 7.67 %. Consequently, 92.33 % is desorbed in the first 85 min. This ratio seemed to be acceptably high, therefore 115 min was chosen as the duration of regenerating.

8. PERFORMANCE OF THE NATURAL GAS REGENERATION PROCESS

Regeneration experiments were run to explore the maximum regeneration efficiency that can be achieved in the temperature range that can be ensured with natural gas regeneration. Regenerations were run at four different temperatures: 110.4, 125.5, 157.3 and 136.9 C°. As it can be seen from Figure 25 the REs yielded by the natural gas regeneration extend from 15 % at the lowest to 31 % at the highest regeneration temperature. The RE vs regeneration temperature curve flattens at higher regeneration temperatures and the RE does not increase above 32 % by increasing the temperature up to almost 160 C°. Therefore the gain in RE when greater regeneration temperatures are

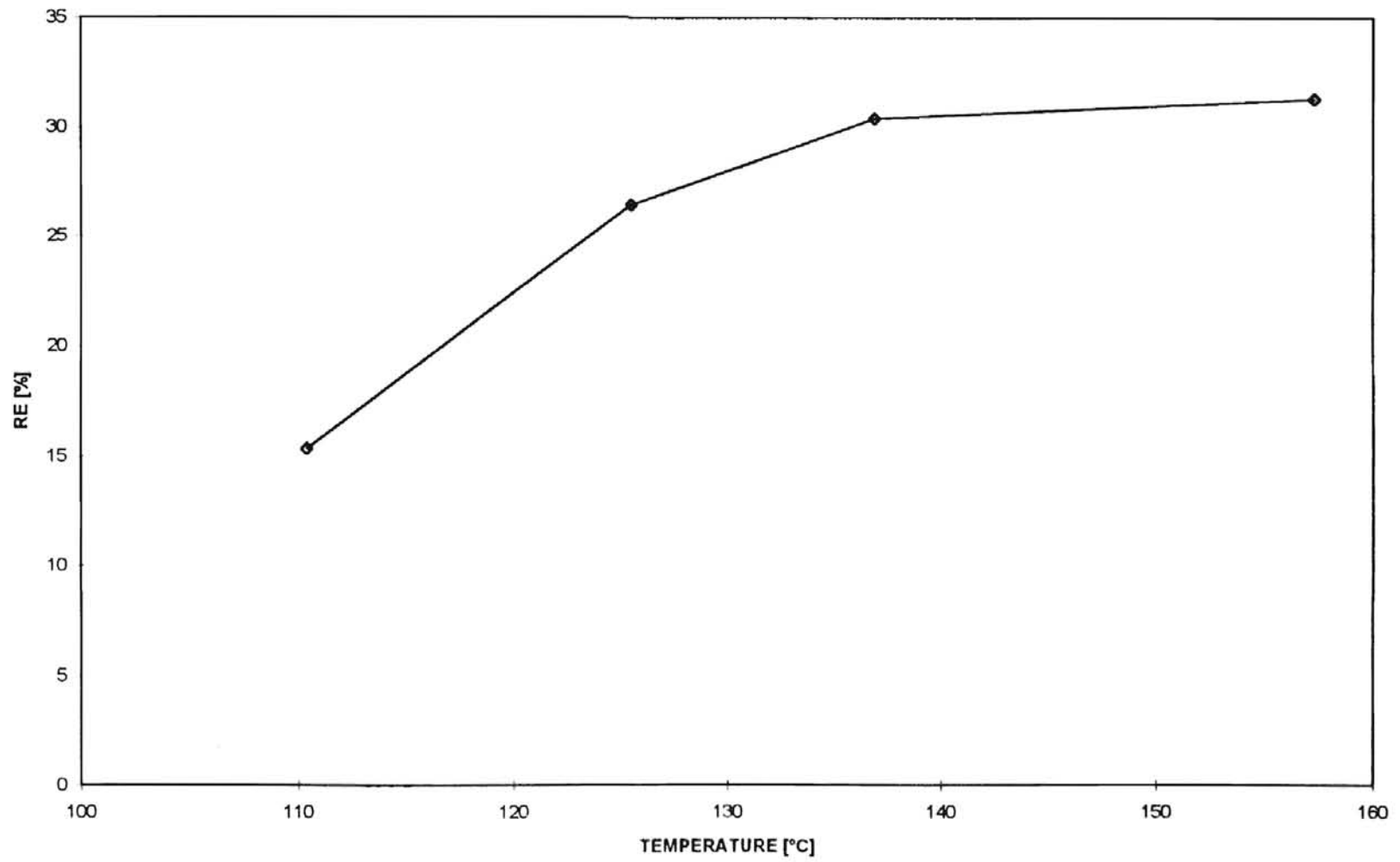


Figure 25 Regeneration efficiency vs regeneration temperature

applied is anticipated to be low. Higher temperatures were not selected for experimental work on regeneration due to the concern with ignition of the natural gas at higher temperatures (ignition temperature of natural gas ~ 538 C°). Although the REs obtained in the experiments are low, a successive regeneration was also carried out to gain insight into how the adsorption capacity varies with regeneration cycles. For the successive run all the parameters (loaded OCP, regeneration temperature, duration of regeneration) were maintained as close to those of the initial run as possible. However due to a drop in the flowrate of loading, the throughput volume was lower in the consecutive regeneration as compared to the initial run. The lower OCP load could partly contribute to the high RE obtained in the consecutive regeneration. Nevertheless, the 174 % RE, and the 58 % accumulated RE (based on the total OCP loaded and the added amount of removed OCP in the two cycles together) cannot be explained by the incomplete saturation of the carbon alone.

The RE was also calculated on the basis of the loaded amount of OCP to compare the REs computed by different methodologies. As it can be seen in Table 17 the RE computed from the OCP loaded in the consecutive runs is 25 % as compared to 30 % obtained by calculating the RE. Since the absolute error of the loaded OCP ratio is greater than the error of the computed RE (± 11.79 as opposed to ± 4.28 with RE), the 30 % RE may be more accurate than the loaded OCP ratio.

9. COMPARISON TO ALTERNATIVE REGENERATION

METHODS

Table 18 provides a detailed overview on researches carried out to regenerate carbon saturated by OCP and Figure 26 presents the lowest, the highest and the averaged REs, (left-, middle- and right column respectively) for identical type of regeneration methods. The observed REs lie in a wide range (from 1.2 % when oxidized by permanganate to 87 % using SCD), with the majority in the 45 -55 % range achieved by rinsing the carbon with organic solvents. The 32 % RE of the natural gas regeneration method is comparable to the less efficient solvent regeneration methods and it is higher than the efficiencies yielded by chemical oxidation methods.

The efficacy of natural gas regeneration in light of the other raised temperature methods can be positioned between that of the oven heated technique and the processes performed at high temperatures with or without oxidation. The RE of the method directed with dry nitrogen is 54 - 58 %, so that the natural gas regeneration has a comparative advantage, since lifting the temperature only to the fraction of that of the nitrogen gas regeneration will effect in the removal of more than half of the OCP, which was observed with the nitrogen gas regeneration.

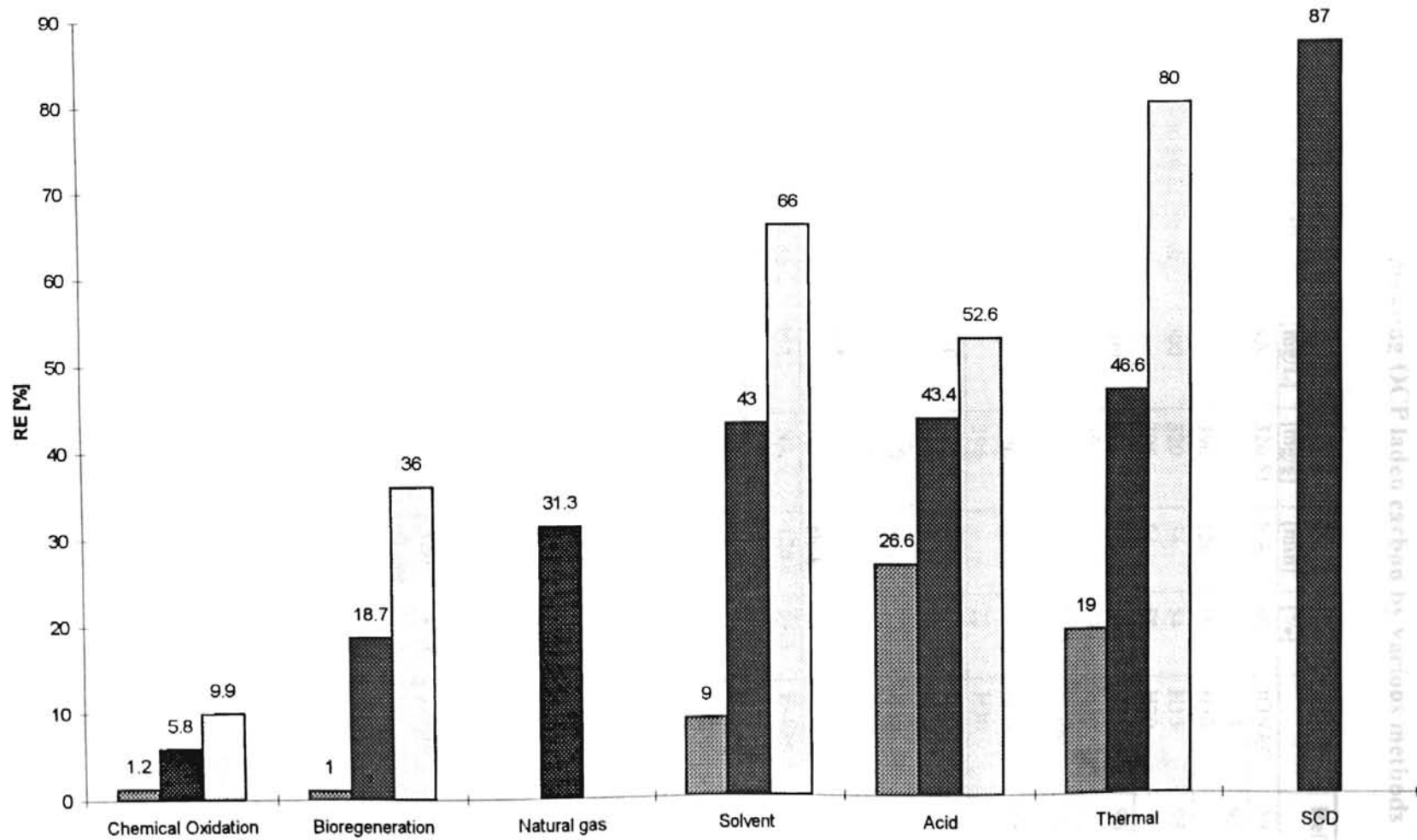


Figure 26 OCP regeneration efficiencies achieved by various regeneration methods

Table 18 Efficiencies of regenerating OCP laden carbon by various methods.

Method	Conditions, regenerants	C_{initial} [mg/L]	Load [mg/g]	τ [min]	RE [%]	AC type	Reference
Thermal	at 800 - 900 C°	NA	326.51	NA	80	IONAC	39
Thermal	in oven, at 120 C°	500	320 396	120 120	22 19	H13 H30	95
Thermal	to 800 C° in dry N ₂ at 20 C°/min	500	320 396	54 54	54 58	H13 H30	95
Solvent	Acetone	500	320 396	NA	13 37	H13 H30	95
Solvent	Acetone	NA	NA	120 + shake	55.7	F-400	16
Solvent	Benzene	500	320 396	NA	9 22	H13 H30	95
Solvent	Ethanol	500	320 396	NA	14 38	H13 H30	95
Solvent	Methanol	500	320 396	NA	13 32	H13 H30	95
Solvent	Ethanolamine	NA	NA	120 + shake	55.6	F-400	53
Solvent	n-Propylamine	NA	NA	120 + shake	54.3	F-400	53
Solvent	Boiling water	NA	NA	90	55	F-400	53
Solvent	n-Butylamine	NA	NA	120 + shake	53.1	F-400	53
Solvent	Triethylamine	NA	NA	120 + shake	45.1	F-400	53
Solvent	Dichloromethane	NA	NA	120 + shake	55.3	F-400	53
Solvent	Chloroform	NA	NA	120 + shake	48.4	F-400	53
Solvent	Carbon tetrachloride	NA	NA	120 + shake	31.7	F-400	53
Solvent	Benzene	NA	NA	120 + shake	41.8	F-400	53
Solvent	Methanol	NA	NA	120 + shake	50.6	F-400	53
Solvent	Ethanol	NA	NA	120 + shake	52.8	F-400	53
Solvent	Ethanol				52.14	IONAC D-50	39
Solvent	2-Propanol	NA	NA	120 + shake	53.7	F-400	53
Solvent	1-Butanol	NA	NA	120 + shake	56.2	F-400	53
Solvent	2-Butanol	NA	NA	120 + shake	66.0	F-400	53

Table 18. Efficiencies of regenerating OCP laden carbon by various methods.

Cont'd.

Method	Conditions, regenerants	C _{initial} [mg/L]	Load [mg/g]	τ [min]	RE [%]	AC type	Reference
Acid	Acetic acid	NA	NA	120 + shake	51.6	F-400	53
Acid	n-Butyric acid	NA	NA	120 + shake	52.6	F-400	53
Acid	iso-Butyric acid	NA	NA	120 + shake	50.9	F-400	53
Acid	Formic acid	NA	NA	120 + shake	47.9	F-400	53
Acid	n-Hexanoic acid	NA	NA	120 + shake	26.6	F-400	53
Acid	10% HCl	NA	NA	120 + shake	28.4	F-400	53
Acid	Propionic acid	NA	NA	120 + shake	51.1	F-400	53
Acid	n-Valeric acid	NA	NA	120 + shake	47.2	F-400	53
Acid	iso-Valeric acid	NA	NA	120 + shake	41.8	F-400	53
Alkali	6M NaOH	NA	NA	120 + shake	36.4	F-400	53
SCF	SCD	NA	530	NA	87	F-400	63
Oxidation	10% K ₂ Cr ₂ O ₇	NA	NA	120 + shake	9.9	F-400	53
Oxidation	10% KMnO ₄	NA	NA	120 + shake	1.2	F-400	53
Oxidation	0.35% NaOCl	NA	NA	120 + shake	6.2	F-400	53
Bioregeneration	-	100	NA	NA	1-36	NA	96

10. GUIDELINES TO IMPROVE REGENERATION EFFICIENCY

BY PROPER SELECTION OF A CANDIDATE

OCP has been chosen as the subject of the experiments to investigate whether the concern with the other thermally activated regeneration methods holds true for the natural gas

regeneration. The results supported the assumption that substance with low volatility are not good candidates for the natural gas regeneration. In order to evaluate the possibilities of improving the efficacy of the method, assumptions must be made on the mechanism of natural gas regeneration.

The process mechanism is most probably a combination of volatilization and displacement. Highly volatile substances exhibit low molecular weight. On the contrary, displacement is the most efficient when the relative ratio between the molecular weight of the adsorbate and the methane in the natural gas is the largest (assumed that the results obtained in liquid phase regeneration (section 2.3.4.2.) can be used in gas phase regeneration), consequently high molecular weight adsorbates are desirable. These factors cannot be satisfied at the same time perfectly, therefore other factors such as dipolar moments, and molar refractions should also be considered. It is suggested to choose another semivolatile compound such as bromoform, and volatile compounds such as benzene and toluene and compare the results to the ones that can be obtained with the equilibrium model described by Crittenden *et. al* [94]. If the results produced by the model provide a good correlation with the regeneration data obtained from the experiments, the best candidates for natural gas regeneration can be selected in a fraction of the time of the lengthy experiments.

CHAPTER IV

SUMMARY

- (i) In the currently available literature, there is no reference for employing natural gas for regeneration at temperatures below its ignition point.
- (ii) Natural gas regeneration of OCP loaded activated carbon with natural gas exhibited a low efficiency (32 %), therefore it is not suitable for the regeneration of OCP saturated carbon.
- (iii) Assuming that the mechanism of natural gas regeneration does not differ significantly from other thermal regeneration processes, it is expected that other non - or semivolatile compounds are also difficult to regenerate with hot natural gas, and natural gas has a potential in desorbing volatile organic compounds.
- (iv) An increase in temperature raises the RE, however the improvement of RE gradually decreases as the regeneration temperature approaches 157 ° C.

CHAPTER V

RECOMMENDATIONS

- (i) In order to measure the temperature more accurately, the temperature sensors have to be built directly into the column on both sides of the screen wire.
- (ii) An inconsistency may be derived from the difference between the temperatures of the gas samples prepared for the calibration, and the samples taken from the column run. To eliminate this potential error, the temperature has to be measured at the sampling port, and if it is necessary, the concentration has to be corrected to this temperature by using the relationships between the universal gas coefficient and the physical conditions of the system.
- (iii) The optimal regenerating conditions (temperature, flowrate) of the process have to be assessed for volatile compounds to be able to make estimations on the cost of the method.
- (iv) Successive regeneration cycles have to be performed with volatile adsorbates to obtain an understanding of the long term regenerating abilities of the process.

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APPENDICES

...and to analyze the adsorptive properties of the

medium. The adsorption process

is related to adsorption

is based on the theory of

the adsorption process

APPENDIX A

METHODS FOR THE EVALUATION OF REGENERATION PERFORMANCE

Regeneration performance can be determined by analyzing the adsorptive properties of the regenerated carbon as it compares to that of the virgin carbon. The adsorption property can be assessed indirectly, by measuring another parameter in relation to adsorption capacity or it can be determined directly. Indirect methods are based on the measurement of apparent density, mean particle diameter, ash content, surface area, iodine number, molasses number, direct techniques involve the determination of the regeneration efficiency, and the adsorption performance.

Apparent density

In thermal reactivation, the duration of the regeneration is one of the most important aspects. The proper residence time can be easily estimated by measuring the apparent density (the weight per unit volume of the activated carbon homogenized by a vibrating trough before measurement). In the laboratory analysis, the exhausted carbon is heated in a small scale furnace under conditions equal to the ones in the actual reactivation chamber, and a calibration is made on the apparent density as it relates to the residence time and indirectly the adsorption capacity.

Mean Particle Diameter

Oxidation of the carbon may lead to a decline in the diameter of the carbon particle.

As a result, after each regeneration the headloss across the bed increases, causing undue operating expenses. In order to follow changes in mean particle diameter, the bulk of carbon is separated into fractions of various particle sizes. Then the fractions are weighted and their weight are multiplied by their diameter. Finally, the products are averaged. The average diameter of a fraction can be obtained as the midvalue of the sieve opening which retains the fraction and the one which is passed through by the fraction.

Ash - content

The ash-content represents the weight fraction of the adsorbate not removed by regeneration, and the residuals derived from the regeneration method (solvent from eluent regeneration, etc.). An ash-content of lower than 5 - 8 % is usual for the higher quality bitumenous virgin carbon. Lignite - based carbons can be characterized by higher ash-contents: 12 -18 %.

Surface Area (cumulative surface area)

One of the most important properties of the adsorbent is the accumulated internal surface area. The Brunauer - Emmett - Teller (BET) method is very often used to measure the total surface area based on the adsorption and desorption of nitrogen gas at its boiling point - 197 C° under different pressures. The total surface area includes the area of the pore walls of diameters up to 100 - 200 Å. A substance can only enter a pore if it is

smaller than the pore size. Thus, the selectivity of the carbon for a specific compound can be defined as the fraction of the total surface, represented by the pores which have the appropriate size. The surface area of the micropores can be analyzed by the iodine number, and the area of larger pores can be obtained by the molasses number.

Iodine Number

Iodine number can be expressed as the milligrams of iodine adsorbed by one gram of carbon, when the iodine concentration in the residual filtrate is 0.02 normal. The iodine number represents the amount of the iodine adsorbed and due to the low molecular weight of the iodine molecules, this property is in relation to the pores of small size.

Molasses Number

Measurement of molasses number involves making a number of molasses solution prepared in different concentrations, which are standardized against known pore distribution. Since the molasses molecules are large in size, the degree of decolorization of the molasses solution by the carbon will indicate the pore volume available for larger adsorbates. The molasses number of a given carbon sample is determined by filtering a molasses solution through both standard activated carbon and regenerated carbon, and the ratio between the optical densities of the two filtrates is determined. This ratio is termed as

Decolorizing Index Unit (DIU), which indicates the capability of the carbon to adsorb the high molecular weight compounds.

Regeneration efficiency

The regeneration efficiency (RE) is the dividend of the amount of solute adsorbed by an identical weight of new (A_0) and regenerated carbon (A_R) calculated as follows:

$$RE = A_0 / A_R * 100 \quad (eq - 6)$$

Since RE is directly dependent on regeneration performance, it is frequently encountered in regeneration studies.

Adsorption Performance

The previously described methods may estimate well the efficacy of the regeneration, nevertheless the most reliable results for a specific water or wastewater type can only be obtained from experiments carried out, in the actual treatment unit. In the experiments, two adsorbers are joined in parallel in the treatment line, one loaded with virgin carbon, the other with spent carbon and they are fed with the same influent stream. In the two columns identical operational conditions are maintained and the time required for the breakthrough of the column is recorded. The disadvantage of the method is the relatively

long time, required to collect the data (running time of adsorbers is 6 months in average in drinking water treatment).

APPENDIX B

COST CALCULATIONS FOR STEAM REGENERATION

Table 19 Cost calculations for steam regeneration

	Steam regeneration for groundwater treatment ^a [\$/1000 gal]	Steam regeneration for wastewater treatment ^b [\$/1000 gal]
Carbon purchase	0.026	0.009
Shipping of carbon	0.002	0.001
Disposal of carbon	0.003	0.001
Cost of steam	0.030	0.006

Notes:

- a. adsorption capacity loss: 3 %, steam-carbon ratio: 5 lb/lb [46], and
- b. calculated based on the research of Parmele and Allan [46] by using 1 % adsorption capacity loss, and 1 lb/lb steam-carbon ratio, which was observed when regenerating carbon exhausted in wastewater

APPENDIX C

EXPERIMENTAL RESULTS AND GRAPHS

Table 20 Experimental data for the Freundlich isotherm

Cr [mg/L]	x/m [mg/g]	log Cr	log x/m
89.73	289.59	1.953	2.462
70.24	285.29	1.847	2.455
51.50	275.82	1.712	2.441
47.49	268.48	1.677	2.429
32.21	254.81	1.508	2.406
23.79	246.76	1.376	2.392
109.42			

Note: c_r - remaining OCP concentration after equilibrium reached

Table 21 Experimental data for the Langmuir isotherm

Cf[mg/L]	C/x
19.69	0.068
39.18	0.137
48.69	0.185
57.92	0.210
61.93	0.231
77.21	0.303
85.63	0.347

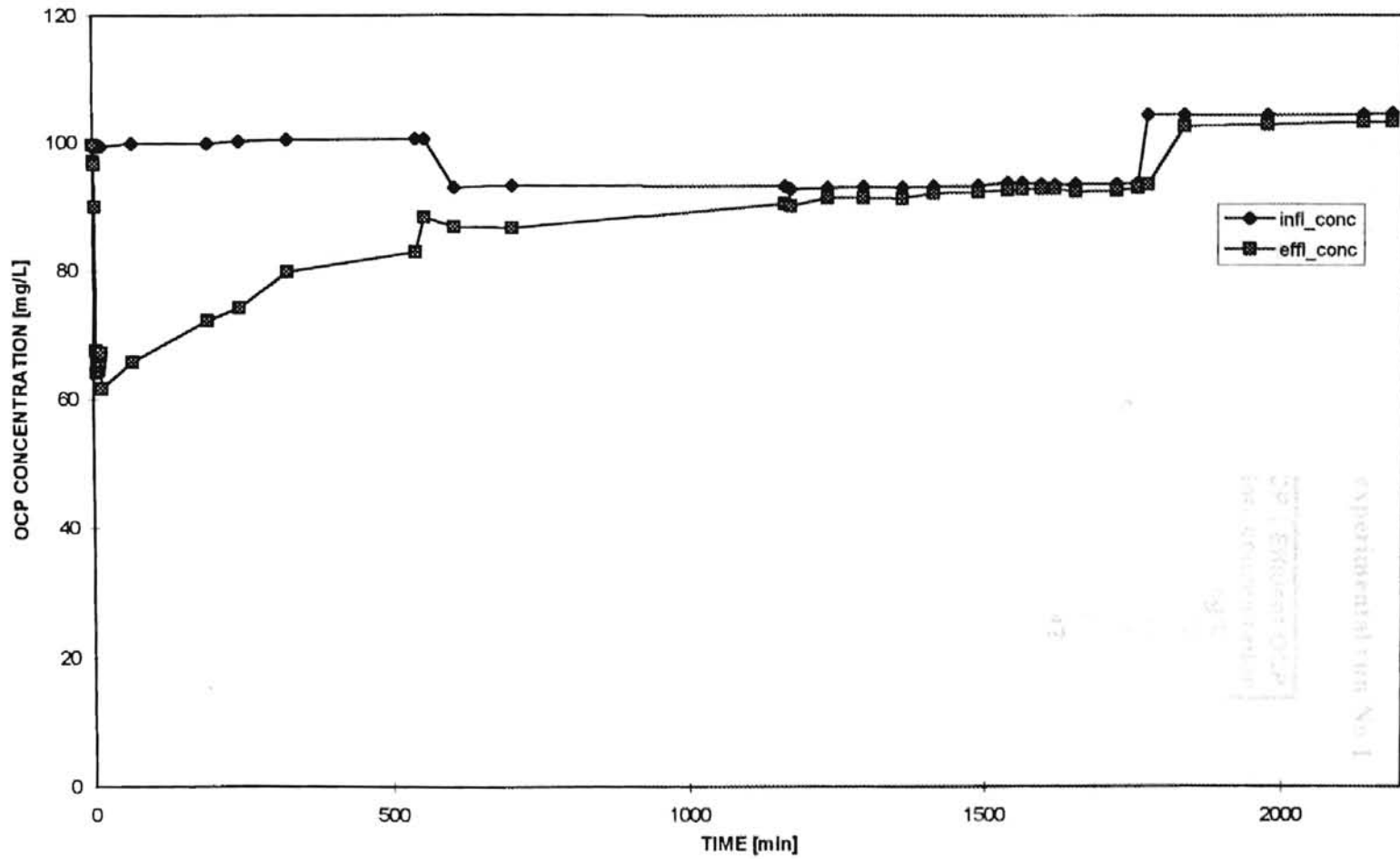


Figure 27. Run No 1. Loading phase

Table 22 Adsorption data for experimental run No 1

for experimental run No 1, Cont

Time [min]	Influent OCP concentration [mg/L]	Effluent OCP concentration [mg/L]
0	99.41	99.67
1	99.41	97.01
2	99.41	96.55
3	99.41	89.87
4	99.41	67.42
5	99.41	64.05
6	99.41	66.26
7	99.41	65.61
8	99.41	66.78
9	99.41	64.38
10	99.41	65.02
11	99.41	65.67
12	99.41	66.78
13	99.41	67.04
14	99.41	61.52
65	99.86	65.74
190	99.86	72.1
243	100.25	74.11
323	100.45	79.69
538	100.58	82.74
553	100.58	88.25
603	92.99	86.69
700	93.25	86.5
1160	93.25	90.46
1170	92.79	90.13
1233	92.92	91.36
1293	93.12	91.36
1360	92.99	91.23
1413	93.12	92.01
1490	93.25	92.21
1540	93.64	92.53
1565	93.7	92.66
1597	93.38	92.79
1620	93.31	92.73
2180	104.6	103.37

Table 20 Adsorption data for experimental run No 1. Cont.

Time [min]	Influent OCP concentration [mg/L]	Effluent OCP concentration [mg/L]
1655	93.51	92.27
1724	93.51	92.53
1759	93.7	92.99
1776	104.47	93.51
1837	104.47	102.65
1974	104.34	102.85
2132	104.47	103.24

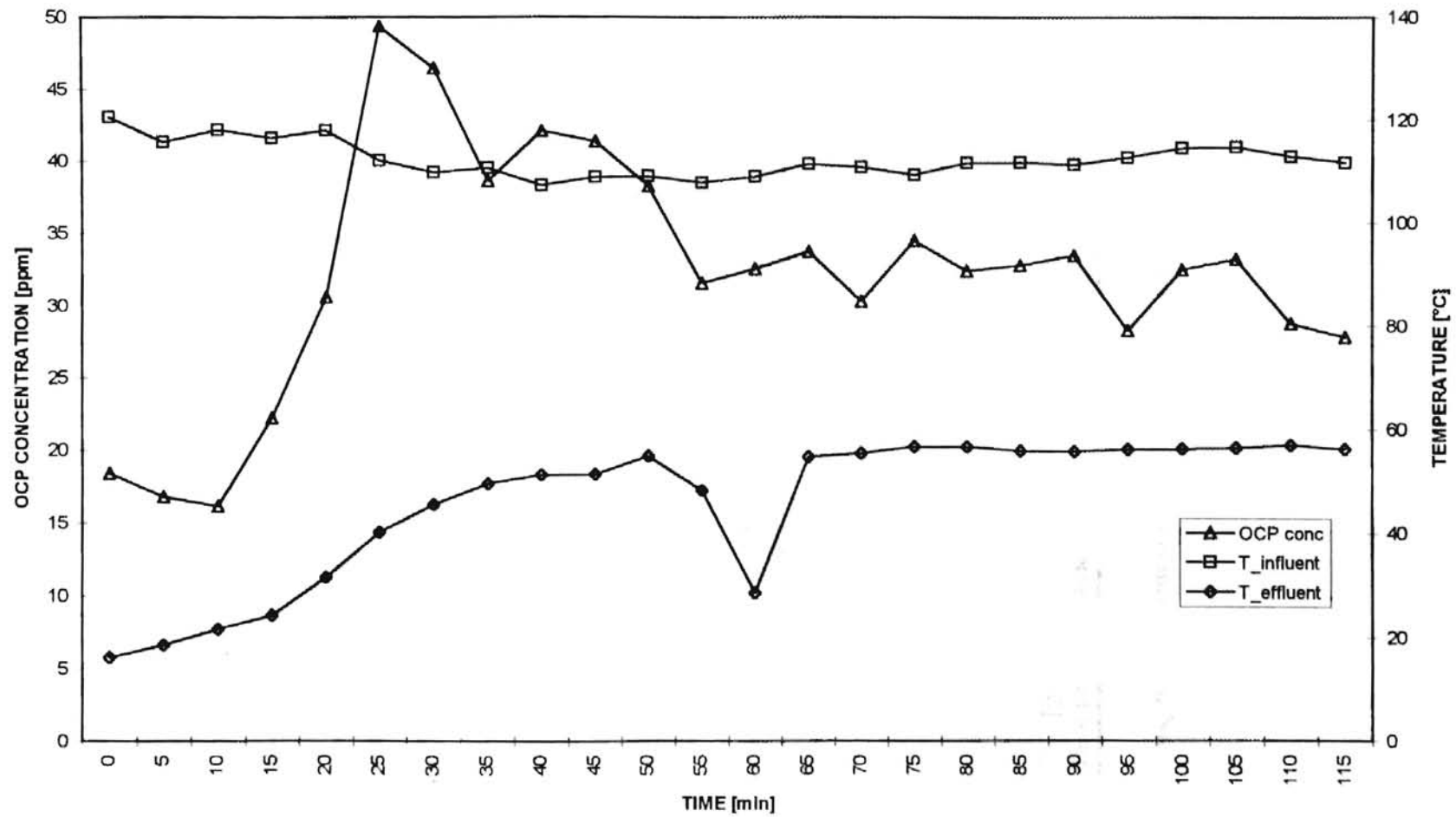


Figure 28 Run No 1, Regeneration phase

Table 23 Regeneration data for experimental run No 1

Time [min]	OCP conc. [mg/L]	Influent temp [°C]	Effluent temp [°C]
0	18.41	120.6	16.2
5	16.79	115.7	18.6
10	16.12	118.1	21.6
15	22.2	116.4	24.2
20	30.51	117.9	31.5
25	49.37	112.1	40.2
30	46.47	109.8	45.5
35	38.62	110.7	49.5
40	42.14	107.3	51.3
45	41.4	108.9	51.4
50	38.29	109.2	54.9
55	31.53	107.9	48.2
60	32.54	109.1	28.6
65	33.76	111.5	54.7
70	30.31	110.9	55.4
75	34.5	109.4	56.6
80	32.34	111.7	56.5
85	32.74	111.8	55.7
90	33.42	111.3	55.6
95	28.22	112.7	56
100	32.47	114.6	56.1
105	33.22	114.8	56.4
110	28.76	113	56.9
115	27.81	111.8	56.1

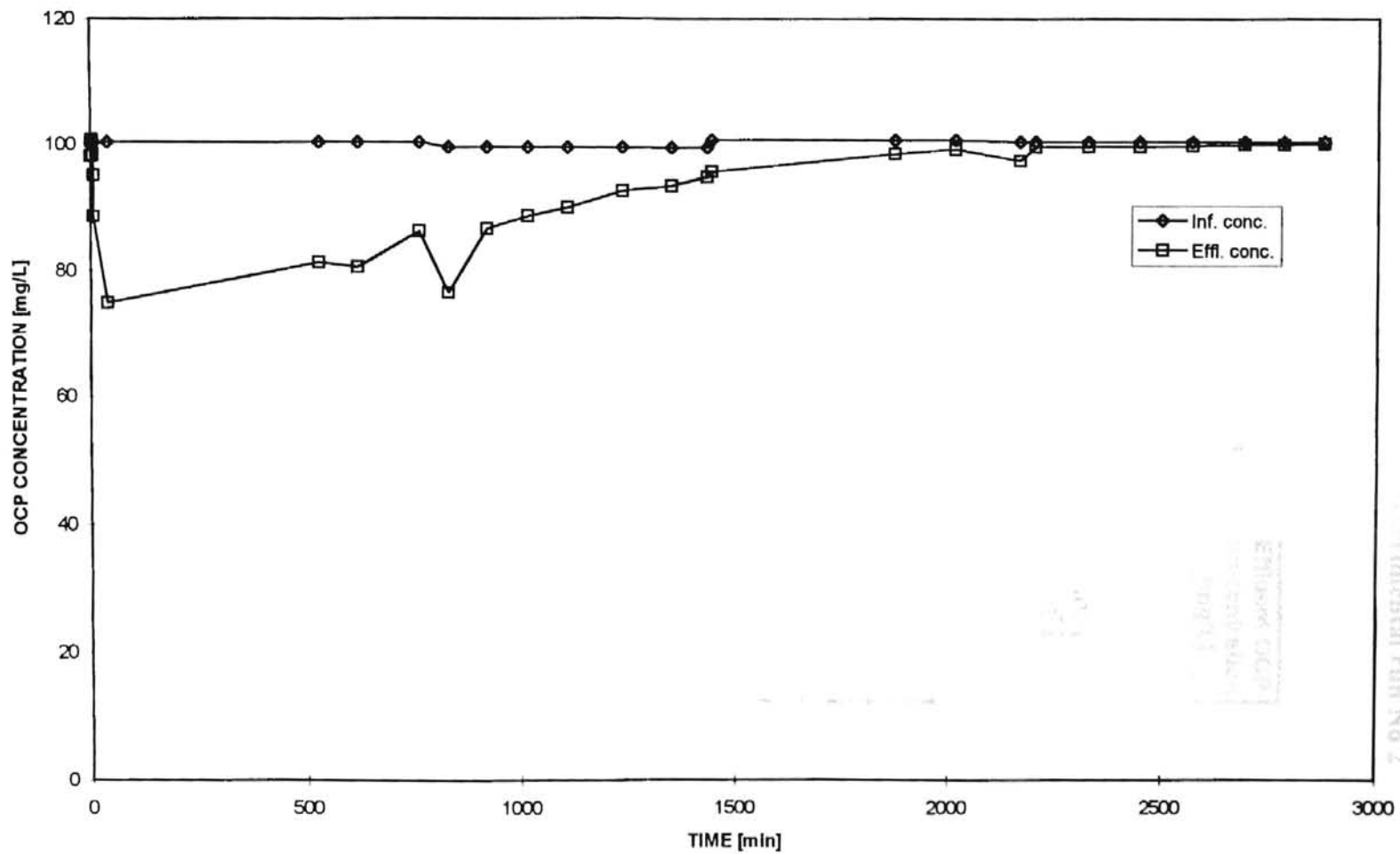


Figure 29 Run No 2, Loading phase

Table 24 Adsorption data for experimental run No 2

Time [min]	Influent OCP concentration [mg/L]	Effluent OCP concentration [mg/L]
0	100.34	98.08
1	100.34	100.47
2	100.34	100.74
3	100.34	100.6
4	100.34	100.47
5	100.34	98.21
6	100.34	95.03
7	100.34	88.53
38	100.34	74.86
527	100.34	81.29
618	100.34	80.56
761	100.34	86.14
829	99.54	76.45
919	99.54	86.54
1014	99.54	88.59
1107	99.54	89.92
1236	99.54	92.57
1352	99.54	93.44
1435	99.54	94.83
1446	100.74	95.69
1877	100.74	98.48
2019	100.74	99.21
2170	100.47	97.42
2206	100.47	99.61
2329	100.47	99.67
2449	100.47	99.67
2571	100.47	99.81
2692	100.47	99.94
2784	100.47	100.01
2877	100.47	100.21

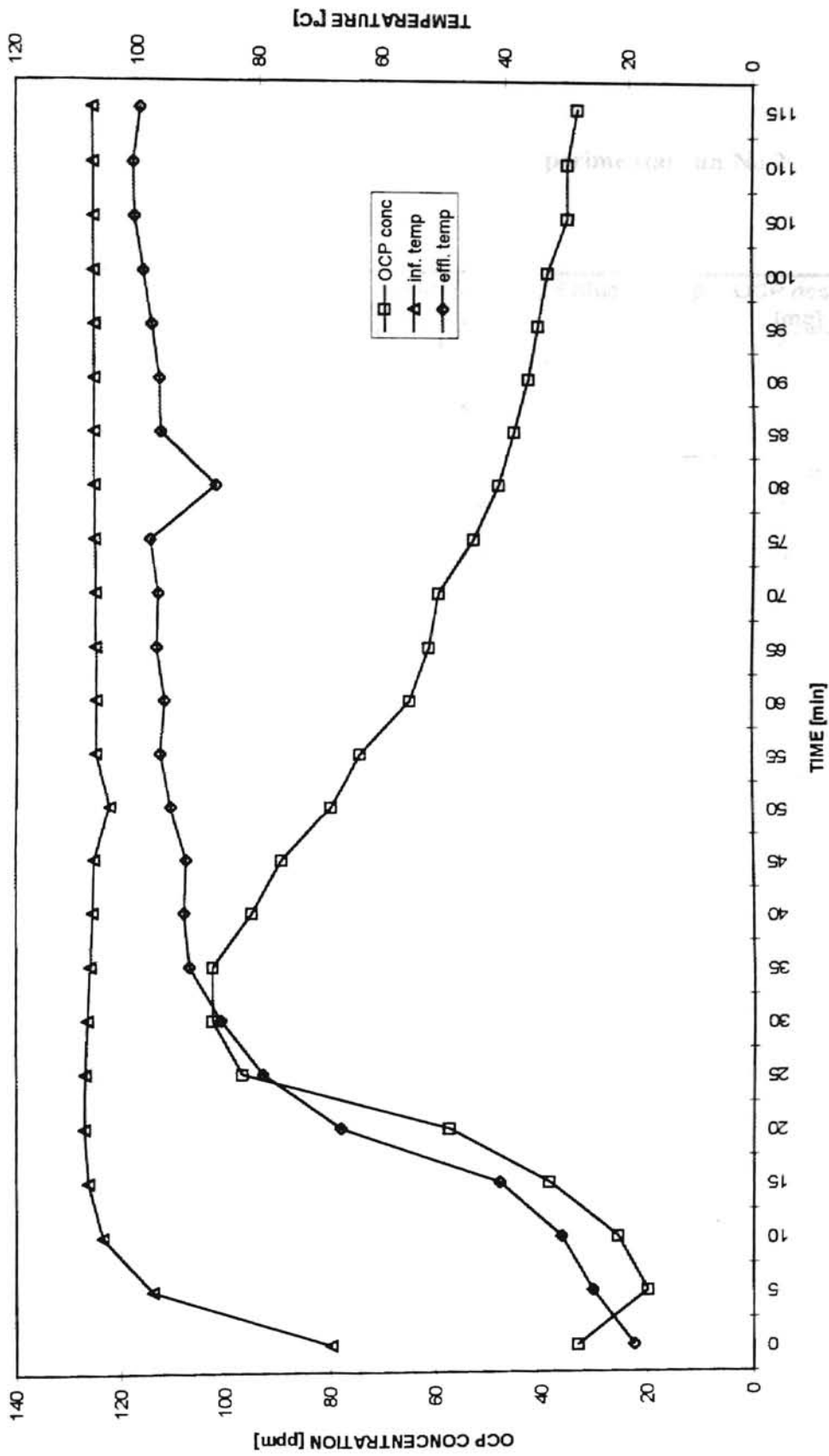


Figure 30 Run No 2, Regeneration phase

Table 25 Regeneration data for experimental run No 2

Time [min]	OCP conc. [mg/L]	Influent temp [°C]	Effluent temp [°C]	OCP des'ed [mg]
0	33.01	175.6	23.9	6.85
5	19.88	237.1	30.2	6.85
10	25.51	254.3	37.7	7.58
15	38.64	259.4	49.2	7.04
20	57.39	260.6	64.4	7.69
25	96.78	260.2	76.6	7.14
30	102.4	259.5	81.2	7.35
35	102.4	258.6	84.5	7.35
40	94.90	257.7	86.5	7.69
45	89.28	257.2	87.8	7.46
50	79.90	252.0	88.2	7.81
55	74.27	256.9	88.9	7.69
60	64.89	256.6	88.9	7.69
65	61.14	256.9	88.9	6.85
70	59.27	256.9	89.1	7.58
75	52.70	257.0	89.5	6.67
80	48.01	257.1	89.5	6.85
85	45.20	257.1	89.5	6.41
90	42.39	257.1	89.4	6.49
95	40.51	257.1	89.6	6.67
100	38.64	257.4	89.8	6.76
105	34.89	257.4	89.9	6.49
110	34.89	257.6	89.9	7.04
115	33.01	257.5	90.1	6.76

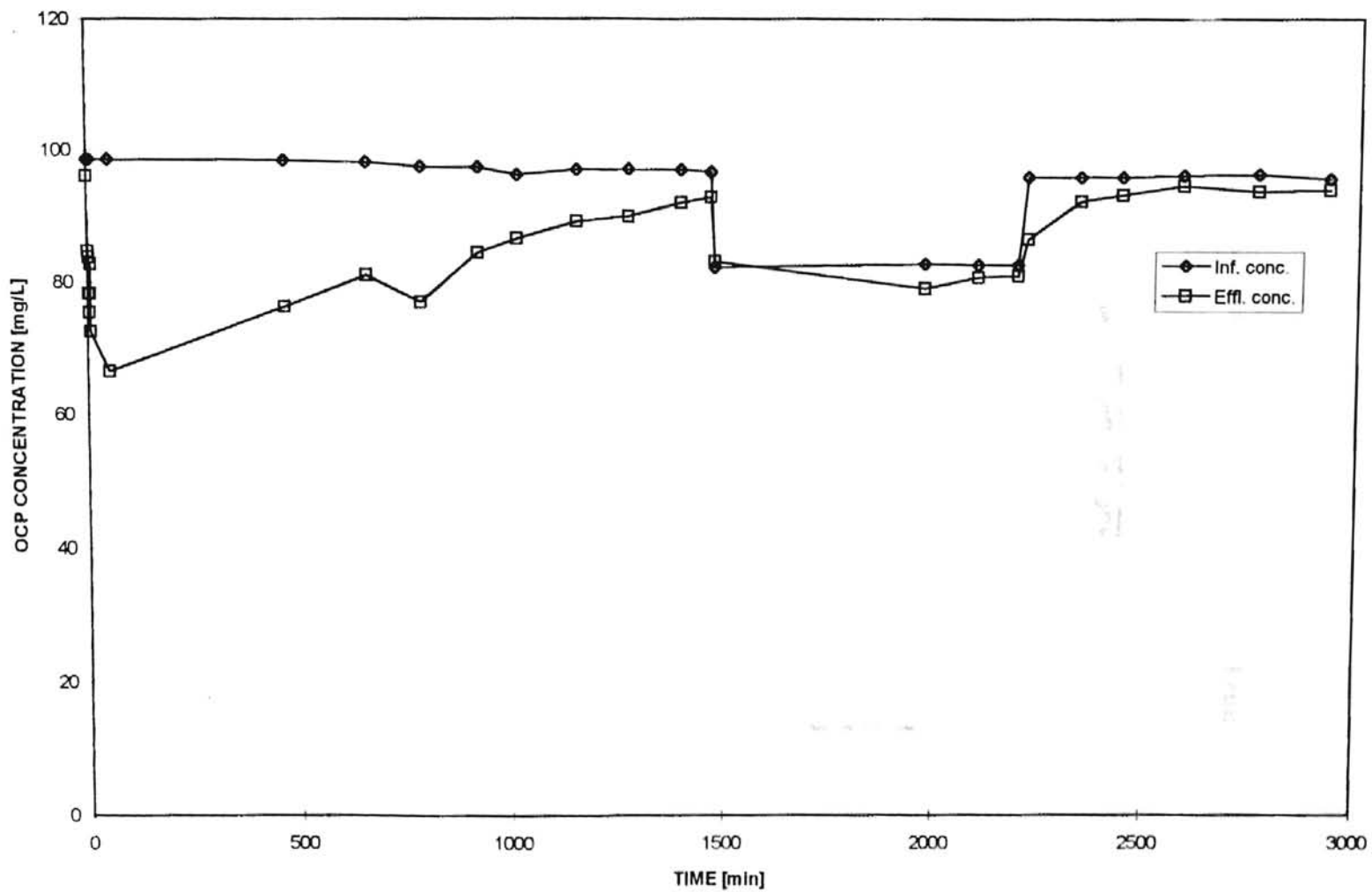


Figure 31 Run No 3, Loading phase

Table 26 Adsorption data for experimental run No 3

Time [min]	Influent OCP concentration [mg/L]	Effluent OCP concentration [mg/L]
0	98.6	96.11
1	98.6	84.65
2	98.6	83.73
3	98.6	78.23
4	98.6	75.35
5	98.6	78.3
6	98.6	82.69
7	98.6	72.53
50	98.6	66.44
460	98.47	76.2
653	98.14	80.92
781	97.49	76.86
916	97.36	84.39
1008	96.24	86.48
1149	97.03	89.1
1273	97.1	89.96
1398	97.03	91.99
1469	96.7	92.84
1479	82.16	83.08
1981	82.62	78.89
2110	82.42	80.52
2204	82.29	80.79
2227	95.85	86.35
2351	95.85	92.18
2449	95.85	93.17
2591	96.05	94.54
2765	96.24	93.62
2930	95.59	93.95

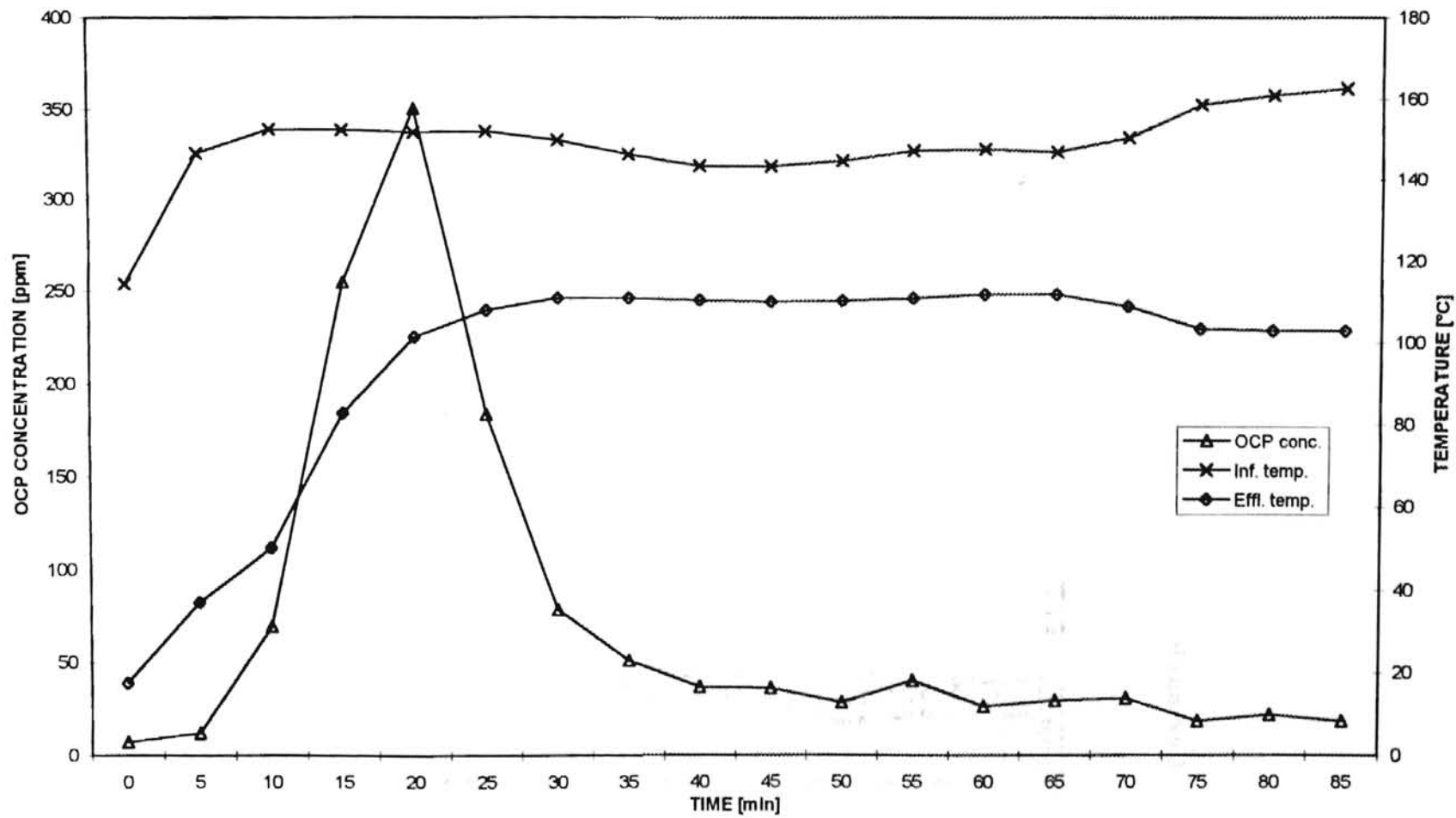


Figure 32 Run No 3, Regeneration phase

Table 27 Regeneration data for experimental run No 3

Time [min]	OCP conc. [mg/L]	Influent temp [°C]	Effluent temp [°C]
0	7.3	114.2	17.5
5	11.73	146.4	36.9
10	69.33	152.6	50.3
15	254.63	152.4	82.9
20	350.1	151.7	101.2
25	183.32	152	107.7
30	78.19	149.8	110.7
35	50.78	146.3	110.6
40	36.52	143.4	110.3
45	35.99	143.3	109.9
50	28.24	144.7	110.1
55	39.71	147.1	110.7
60	26.21	147.6	111.6
65	29.21	146.9	111.6
70	30.35	150.4	108.7
75	18.29	158.6	103.2
80	21.46	161.1	102.8
85	18.11	162.7	102.8

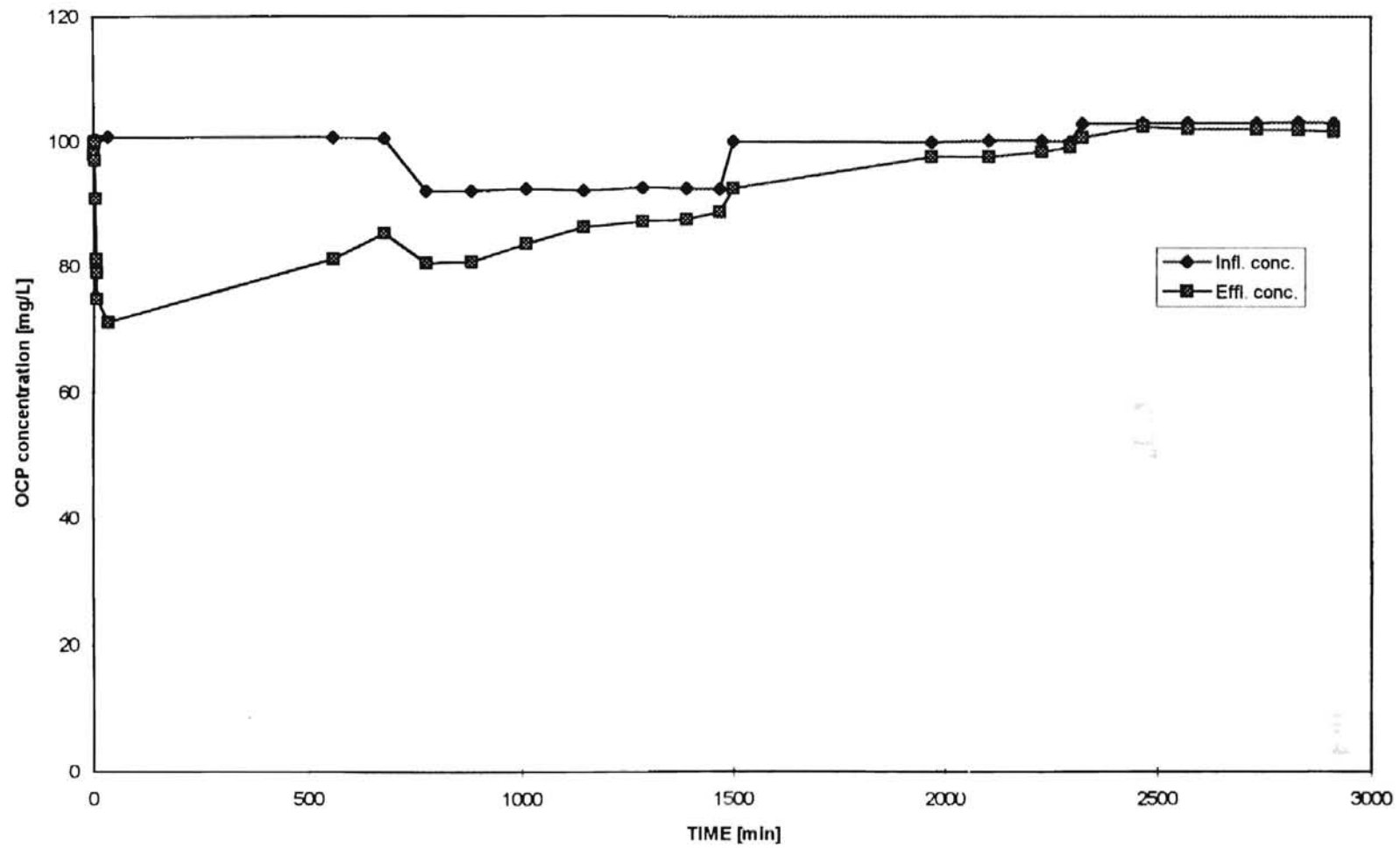


Figure 33 Run No 4, (run preceding the successive one), Loading phase

Table 28 Adsorption data for experimental run No 4

Time [min]	Influent OCP concentration [mg/L]	Effluent OCP concentration [mg/L]
0	100.36	98.03
1	100.36	99.71
2	100.36	100.04
3	100.36	97.06
4	100.36	90.89
5	100.36	81.23
6	100.36	79.03
7	100.36	74.88
33	100.82	71.18
557	100.75	81.23
677	100.56	85.25
775	92.06	80.52
882	92.06	80.65
1011	92.39	83.57
1146	92.13	86.29
1286	92.58	87.13
1391	92.58	87.65
1469	92.52	88.82
1501	100.23	92.58
1971	100.04	97.64
2107	100.3	97.64
2232	100.3	98.48
2298	100.1	99.2
2327	102.96	100.75
2470	103.09	102.5
2574	103.15	102.18
2735	103.09	102.11
2832	103.28	102.05
2915	103.09	101.73

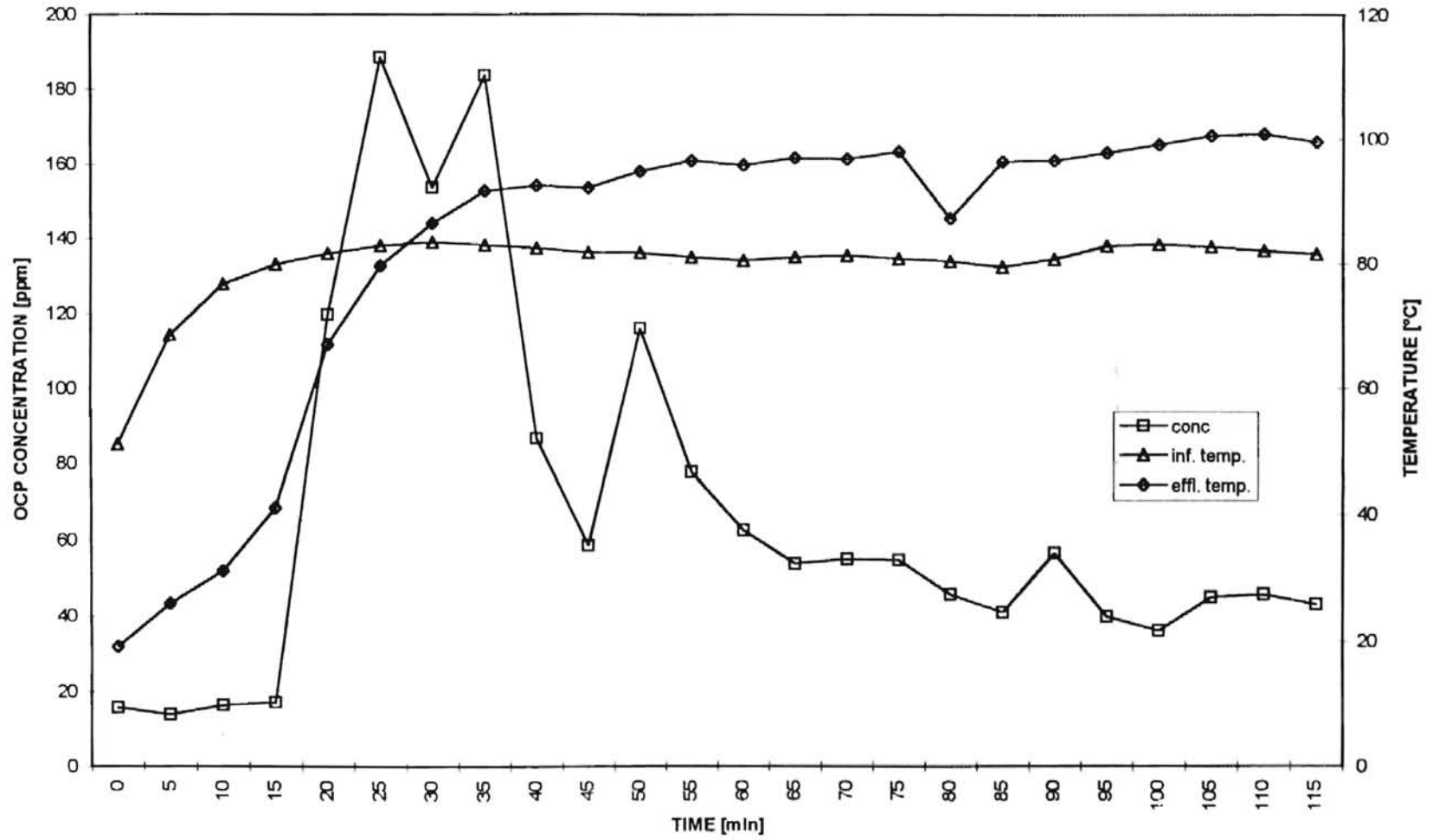


Figure 34 Run No 4, Regeneration phase

Table 29 Regeneration data for experimental run No 4

Time [min]	OCP conc. [mg/L]	Influent temp [°C]	Effluent temp [°C]	OCP desorbed [mg]
0	15.8	85.1	19.2	0.532
5	13.83	114.3	26	0.551
10	16.28	127.7	31.1	0.648
15	17.06	133	41.1	0.65
20	138.82	135.8	66.9	5.612
25	212.24	137.9	79.5	7.855
30	175.03	138.8	86.4	6.571
35	207.17	138.1	91.6	8.125
40	103.72	137.3	92.5	3.894
45	58.49	136.2	92.1	2.196
50	134.94	136.2	94.8	5.455
55	94.23	135	96.5	3.93
60	62.56	134	95.8	2.349
65	53.69	134.9	97	2.276
70	54.84	135.3	96.8	2.119
75	54.53	134.6	98	2.077
80	45.59	133.7	87.2	1.711
85	40.89	132.2	96.3	1.679
90	56.3	134.4	96.5	2.176
95	39.78	138	97.8	1.584
100	35.95	138.4	99.1	1.5
105	44.89	137.7	100.6	1.934
110	45.57	136.7	100.8	1.842
115	42.96	135.8	99.6	1.636

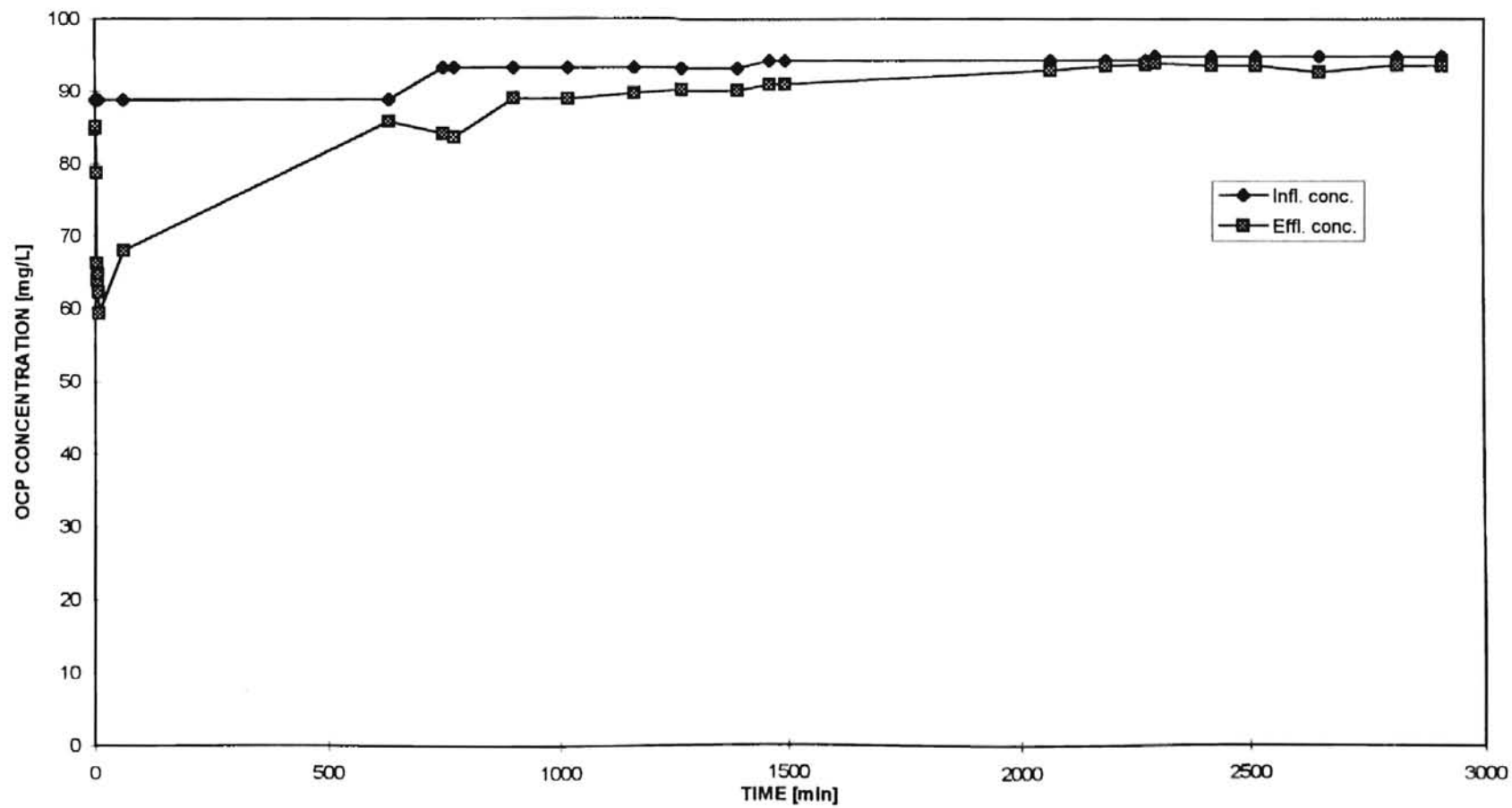


Figure 35 Run No 5 (successive), Loading phase

Table 30 Adsorption data for experimental run No 5

Time [min]	Influent OCP concentration [mg/L]	Effluent OCP concentration [mg/L]
0	88.83	84.79
1	88.83	85.11
2	88.83	78.71
3	88.83	66.22
4	88.83	63.92
5	88.83	64.69
6	88.83	62.25
7	88.83	59.37
60	88.83	68.01
629	88.83	85.75
745	93.24	84.09
770	93.24	83.64
897	93.24	88.95
1016	93.24	88.89
1160	93.24	89.66
1264	93.24	90.17
1387	93.24	90.11
1457	94.27	91
1491	94.27	90.94
2066	94.27	92.86
2187	94.27	93.44
2273	94.27	93.69
2293	94.78	93.82
2416	94.78	93.56
2512	94.78	93.56
2649	94.78	92.67
2815	94.78	93.63
2911	94.78	93.56

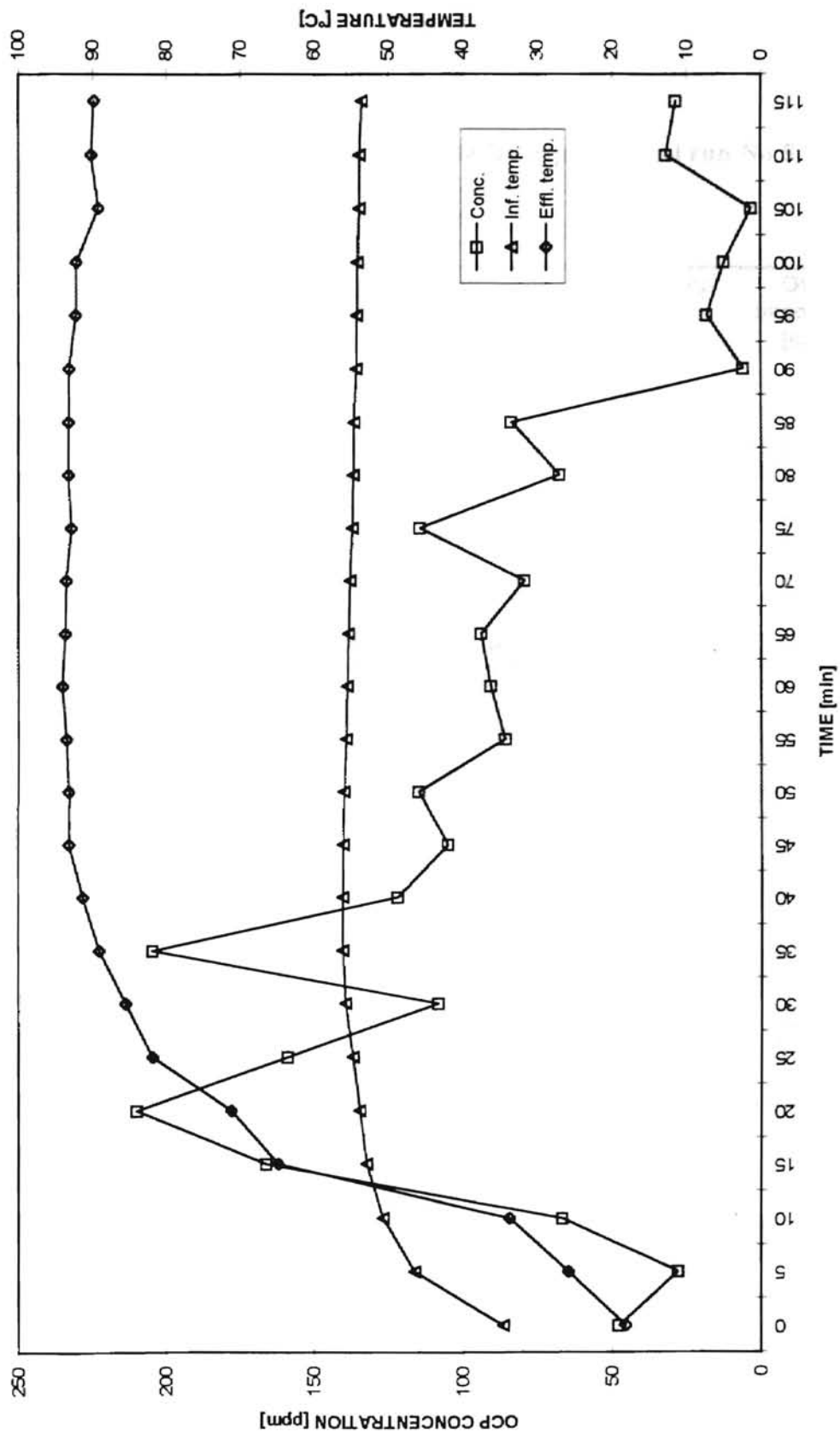


Figure 36 Run No 5 (successive run), Regeneration phase

Table 31 Regeneration data for experimental run No 5

Time [min]	OCP conc. [mg/L]	Influent temp [°C]	Effluent temp [°C]	OCP desorbed [mg]
0	47.66	86.6	18.2	1.957
5	28.03	116.3	25.9	1.151
10	66.75	126.8	33.8	2.973
15	166.01	132.2	64.8	6.711
20	210	134.4	71.1	8.49
25	158.5	136.7	81.8	6.311
30	108.09	139.2	85.5	4.656
35	204.58	140.1	89.1	8.271
40	121.49	140.1	91.3	4.837
45	104.63	139.9	93.2	4.23
50	114.58	139.7	93.3	4.241
55	85.66	139	93.6	3.216
60	90.47	138.6	94.1	3.962
65	93.76	138.2	93.7	3.623
70	79.2	137.6	93.6	3.469
75	114.2	136.8	92.9	4.84
80	67.55	136.5	93.3	2.958
85	83.63	136.2	93.3	3.488
90	5.96	135.6	93.2	0.224
95	18.23	135.3	92.3	0.684
100	12.43	135.1	92.2	0.467
105	3.19	134.7	89.2	0.12
110	31.7	134.7	90.2	1.388
115	28.55	133.9	89.8	1.25

VITA²

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