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In situ electrochemical regeneration of activated carbon

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CHAPTER 1

INTRODUCTION

1.1. Background

Water is needed for all life on earth. It may seem that we have it in abundance with two thirds of the planet covered by oceans, but unfortunately, it is not quantity but quality that counts (Figure 1.1). Especially in densely populated or industrial areas the quality of water can become a problem. These areas have a high demand and produce large amounts of wastewater. Beyond a certain point the natural occurring purification processes are no longer sufficient and ground water quality will start to decrease, causing both environmental and economical problems. With an ever-increasing world population these problems will get bigger in the future. One solution is the installation of wastewater treatment facilities. This is where adsorption comes into play.

Adsorption can be used for the removal of organic pollutants from aqueous streams. The polluting molecules accumulate on the inner surface of a porous solid phase therefore depleting the liquid phase. Adsorption is often the last stage of a water treatment section because it is more effective when concentrations are low. The material most used as adsorbent is activated carbon (AC). It is made from peat, wood, coconut shells, coal or synthetic high polymers by heating them under controlled conditions. Traditionally, activated carbon has been used for removal of odours, tastes and colours from both water and gas. A wide range of carbons with different pore size distributions, surface chemistry and shapes are available commercially. For wastewater applications hydrophobic carbon granules possessing a large mesopore

structure are most convenient. The AC granules are packed inside a column. The liquid enters the column on one side and flows through the packed bed. The pollutants will adsorb onto the carbon and the purified liquid leaves the column at the outlet.

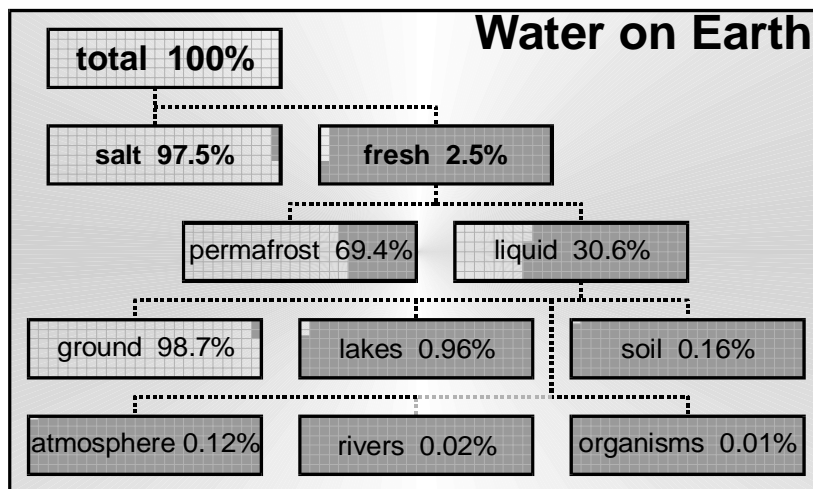


Figure 1.1: Overview of all water on earth. The amount of fresh liquid water is less than 1%.

Activated carbons have a very large surface area due to the presence of micropores, typically in the order of 1000 m^2 per gram of carbon. This is why the uptake of pollutants can be as high as fifty percent of the carbon mass. However, given enough time, the carbon will become saturated. In order to prevent deactivation of the column, the spent carbon must either be replaced by new carbon or regenerated. Replacement is expensive, but can be the cheapest solution if pollutant concentrations are low, hence ensuring a long operational life. Regeneration of the carbon allows it to be re-used a number of times; this can be done in situ as well as off site.

Off site regeneration consists of a number of steps. First the column is emptied. Then the deactivated carbon is transported to a thermal regeneration facility. There the carbon is heated to $1000 \text{ }^\circ\text{C}$ in a hydrogen atmosphere to boil off or pyrolyse the adsorbed load together with about 10% of the carbon matrix. Transporting the carbon back to the site and refilling the column completes the operation. The disadvantage of the method is the relatively high

cost that is in the same order as that for buying new carbon. Reducing costs is difficult, as the biggest contribution comes from transporting the carbon. Thermal regeneration cannot be used to treat all spent carbons. Norit N.V. does generally not accept carbons with loads higher than 10% (Rexwinkel, 1998). Lower loads might not be accepted if they can lead to production of dioxins in the furnace.

For the in situ regeneration the carbon remains inside the column. The process is divided into two cycles. In the adsorption cycle the column removes pollutants from the waste stream. It is followed by the desorption cycle where the column is regenerated. Desorption of adsorbed molecules can be achieved by changing process conditions. For instance increasing the temperature, or reducing the pressure, shifts the adsorption equilibrium towards desorption. The desorbing pollutants are collected in a washing stream. The concentrations in the washing fluid are much higher than in the process stream. As a result the waste is reduced to a much smaller volume. This is an important outcome as waste disposal costs depend on volume only, not on the concentration of pollutant dissolved.

As outlined by Suzuki (1990, chapter 9) there are five processes available for the in situ regeneration of spent carbon:

- 1) desorption by an inert stream or low pressure stream,
- 2) desorption at high temperature,
- 3) desorption due to a changing affinity between adsorbate and adsorbent,
- 4) desorption by extraction using strong solvents, and
- 5) removal of adsorbates by decomposition.

Methods 1) and 2) are used for gas phase operation only. The other three methods are applicable for liquids. Some examples: Adsorbed organic acids can be removed with an alkaline solution because the dissociated acids adsorb far worse than the non-dissociated (method 3). An organic solvent can be used to extract or displace adsorbed hydrophobic molecules (method 4). The fifth method can be used if the adsorbed molecules can be converted into smaller or less harmful molecules that tend to desorb better. All methods can restore

only part of the adsorption capacity because they are not ‘powerful’ enough to change the adsorption equilibrium much. The regenerative performance gets worse for multi-component systems. Furthermore elution of the column is slow due to the unfavourable desorption kinetics when compared to adsorption. This means that a lot of effluent is produced. For better results two methods can be combined as is done in steam regeneration where a high temperature and an oxidising environment are applied.

1.2. Problem statement

The previous section indicates that regenerating spent adsorbents is the most troublesome and expensive part of adsorption technology. According to Leng and Pinto (1996) regeneration accounted for about 75% of the total operating and maintenance costs needed for running a granular packed bed AC plant. It seems there is no ideal solution that can be applied generally and probably there will not be one soon. The various regeneration methods in use today have limited applicability and are bound to their various niches by economic restraints. This situation creates a large drive for investigating new ways to regenerate spent adsorbents. One of these is called electrosorption and it is the subject of this thesis.

Electrosorption is short for electrochemically influenced sorption. It basically deals with the effects that an applied electrical potential has on the sorption behaviour. Two effects can be identified. For low potentials the adsorption equilibrium of molecules is a function of the solid-liquid potential drop, even if they are not charged. This rules out simple coulombic interactions as mechanism. By changing the applied potential one is able to change the adsorption equilibrium similar to a type 3 method of Suzuki.

When the applied potentials are higher, electrochemical Faraday reactions occur in addition to equilibrium changes. By exchanging electrons with the electrode, adsorbed molecules can be oxidised or reduced, converting them to less absorbable components or even to carbon dioxide and water (the type 5 method of Suzuki).

Electrosorption is a hybrid process that combines elements from adsorption and electrochemistry. Electrochemical principles dictate that the system must contain at least two electrodes that are connected via an external electrical circuit. Both must be in contact with an electrolyte. The electrodes used in this work are packed beds of carbon particles with liquid flowing through. Inside these electrodes both charge- and mass transfer limitations will occur. In order to avoid limitations an optimal design must be found.

1.3. Literature survey

1.3.1. The discovery of electrosorption

The phenomenon of electrosorption was discovered in 1875 by the electrochemist Lippmann (Gouy, 1903). He carried out experiments using a capillary electrometer, an instrument that consists mainly of a capillary tube filled with mercury serving as electrode. The object was to measure the surface tension γ of the mercury at various conditions. Applying an electrical potential causes the mercury to become polarised. This results in a reduction of its surface tension, due to coulombic repulsion of charges on the surface. Lippmann added surface active compounds to the electrolyte and he found an excess reduction of the interfacial tension when these molecules adsorbed on the mercury interface.

The excess reduction of capillary curves was the first direct proof of the electrosorption phenomenon. In 1903, Gouy published the first part of his extensive capillary curve data collection. Electrocapillary curves recorded in the presence of an organic compound had a very characteristic shape. If no organic compound was present, a plot of γ versus the polarising potential ϕ yielded a parabola. Adding surfactants resulted in a lowering of the curve. This effect was large for small potentials and diminished when the potential was increased (see also Figure 1.2). With increasing $|\phi|$, desorption of organic molecules becomes more pronounced than adsorption. At high potential differences all curves coincide, suggesting that hardly any organic molecules remain on the surface. Gouy (1916, 1917) concluded that there was a definite relation between applied potential and adsorptive behaviour of neutral organic compounds.

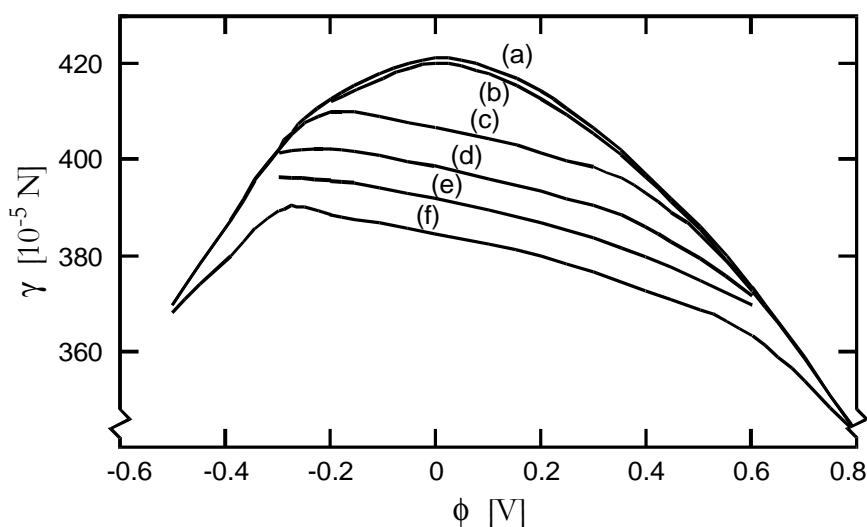


Figure 1.2: Electrocapillary curves for different concentrations tert-butanol in 1 N NaCl solution: (a) 0, (b) 10, (c) 50, (d) 100, (e) 200 and (f) 400 mol/m³. The adsorption of alcohol causes the decrease in γ around $\phi = 0$ (Gouy, 1903).

1.3.2. Theoretical work

Frumkin (1925, 1926) attempted to derive the equations needed to describe Gouy's data. He used the resemblance of a polarised interface to an electrical capacitor in order to calculate and predict changes in adsorption. Butler (1929) followed a similar, but more molecular approach by introducing the molecular polarisability and the dipole moment into the equations. Butler reasoned that electrosorption occurred because these parameters change as molecules move from a region with a low field (bulk) to a region with a high field (interface). Parsons (1959) compared the Frumkin and Butler theories and found that they were essentially the same. He was the first to look at the relation between adsorption and differential electrical capacity (Parsons, 1959; Breiter and Delahay, 1959; Parsons, 1963). Further understanding of the mechanism behind electrosorption came when Bockris *et al.* (1963) published their model for the structure of the electrified interface, now known as the triple layer model. Bockris *et al.* explained the potential dependency of the adsorption of neutral species on polarised electrodes by taking into account the change in energy of orienting water dipoles with a changing electrical field and due to competitive adsorption of organic molecules.

Between 1965 and 1975 workers in the field of electrosorption became polarised themselves into two quarrelling groups: The ‘Russian school’ followed the ideas of Frumkin and the ‘British school’ that of Bockris. Both groups tried to prove the superiority of their own concepts at the expense of the other (Bockris *et al.*, 1967; Damaskin, 1969; Gileadi, 1971; Damaskin, 1971; Frumkin *et al.* 1980). As was to be expected this did not lead to new insights. Only minor improvements were made on both the original Frumkin and Bockris theories (Schuhmann, 1987).

Before the early 1970’s all research on electrosorption dealt exclusively with metal electrodes. These can be considered one-dimensional and have small surface areas. A packed bed of carbon granules is at least two-dimensional and possesses a very large surface area. As a result the latter has a huge electrical capacity. This leads to a very sluggish electrical response. Electrical charging of a packed bed can take days if the bed length is too large. The electrical potential inside a packed bed electrode is not constant but a function of time and place.

Posey and Morozumi (1966) studied the ‘Potentiostatic and Galvanostatic Charging of the Double Layer in Porous Electrodes’. They determined analytical solutions to describe potential distributions inside semi-infinite porous electrodes in the absence of Faraday reactions. Their results are mathematically analogous to one-dimensional heat transfer in slabs of material (Carslaw and Jaeger, 1959) as the conducting matrix can be considered to be an infinite number of resistors in series. Charging a packed bed electrode is equivalent to charging a network of resistors and capacitors. Each capacitor represents an infinitesimal part of the surface. Resistors are situated between capacitors and represent carbon and liquid electrical resistances. Understanding the electrical behaviour of large surface materials resulted in attempts to use them for the desalination of salt water (Johnson and Newman, 1971).

Alkire and Eisinger (1983a) performed the first dynamic simulations of a packed bed electrosorption unit. They used a one-dimensional plug flow model with axial dispersion to describe the liquid flow through the bed. Mass transfer resistance was assumed to be external. An analytical potential distribution equation was used and the coupling between isotherm (a modified Langmuir) and applied potential was done by means of an empirical expression. Chue *et al.*

(1992) improved the model by taking intra-particle mass transfer into account together with a potential dependent Freundlich isotherm. Card *et al.* (1990) differentiated between bed porosity and micro-pore porosity. This resulted in a two-dimensional model with the direction of the overall current penetrating the micro-pores perpendicular to the direction of the liquid flow. This flow-by bed configuration is better than a flow-through configuration with current and flow parallel, because for the flow-by configuration it is possible to keep the bed small in the direction of the current and long in the direction of the flow (Xu *et al.*, 1992). They used the results from experimental obtained two-dimensional potential distributions to design an electrochemical packed bed reactor for the electrochemical reduction of nitrobenzene to produce *p*-aminophenol.

1.3.3. Experimental work

All early electrosorption experiments focussed on the dropping mercury electrode because of its smooth and well determined surface area. An additional advantage is the direct relation between the molecular composition at the mercury interface and the surface tension of the metal, resulting in very accurate experimental data. From surface tension measurements a relatively large potential dependency of the adsorption became obvious, as was shown earlier (Figure 1.2).

Wroblowa and Green (1963) were the first to do similar experiments with solid metal electrodes. Their radioactive tracer method was sensitive enough to determine the amount of thiourea adsorbing on their (small surface) gold electrode. A similar technique was used by Gileadi *et al.* (1965) to determine the electrosorption of ethylene gas on platinum electrodes. These results show the same quadratic relation between adsorption and potential although the data seems less smooth compared to the mercury measurements. Both Wroblowa and Gileadi found the difference between minimum and maximum adsorption to be a factor of three to five. It increased for higher concentrations and decreased with electrode age. For both ethylene and thiourea the maximal adsorption occurred at relatively large and positive potentials.

Strohl and Dunlap (1972) considered the possible use of electrosorption as a means of separating mixtures. For separation purposes a large surface is

essential. The authors found that they could alter the adsorptive capacity of a packed bed of graphite particles by changing the applied potential. They could also change the uptake of a specific quinone from a multi-component mixture. Their column breakthrough data reveals a large effect of the applied potential, even exceeding a factor of five.

In 1985 McGuire *et al.* published potential dependent isotherm data for electrosorption of phenol on activated carbon under various conditions. In 1994 Costarramone *et al.* studied competitive electrosorption using two ternary systems containing chloroform/benzoic acid and chloroform/phenol. Three follow up studies were done by Hazourli *et al.* (1996) for the same system. In 1997 Schäfer and in 1998 Bán *et al.* measured electrosorption isotherms for aromatic substances with positive, negative and no charge. A displacement of the maximum adsorption was found as expected due to coulombic interaction with the charged activated carbon. Janocha *et al.* (1999) measured electrosorption for the substances OPE (1-o-[4-(1,1,3,3-tetramethylbutyl)-phenyl]-decaoxyethylen) and phenol. For OPE a small dependence on potential was found (about a factor of 2) but the adsorption for phenol was found independent of the applied potential for well over a 2 V range, which seems to be in disagreement with earlier work.

Experimental data regarding the electrical behaviour of packed bed electrodes appeared in literature around 1970. Evans (1966), Johnson and Newman (1971) and Oren *et al.* (1984) measured the differential capacity of various activated carbons and graphite electrodes by recording charging currents in response to a step in applied potential. In 1975 Tiedemann and Newman determined differential capacities for medium sized surface areas using the Posey-Morozumi analytical solutions for potential distributions. Zabasajja and Savinell (1989) used the Bockris triple layer model together with the Tiedemann and Newman method to determine the effects of surface coverage on electrical capacity. Actual potential distributions can only be measured directly by small probing electrodes on various positions in the bed (Alkire and Eisinger, 1983b; Card *et al.*, 1990).

Strohl and Dunlap (1972) and Chue *et al.* (1992) looked at the dynamic behaviour of the packed bed electrosorption unit. Chue *et al.* monitored the

outlet concentration while the bed was forced to a different potential. From the resulting change in concentration in time they could determine the ratio between the sorption wave and the potential wave going through the bed. Eisinger and Keller (1990) determined the characteristic times of four processes and used them as their primary design parameters. They also investigated process configurations and power consumption.

Only recently experiments have been conducted in which the applied potentials were much higher, in order to electrochemically oxidise or reduce the adsorbed components. Slavinskii *et al.* (1984) examined the regeneration of a packed bed loaded with nitrotoluene using a constant current density of 20-40 A/m². Narbaitz and Cen (1994) tried to regenerate a carbon loaded with phenol. They found high efficiencies of up to 95% with no apparent carbon losses. Zhang *et al.* (2000) found improvement in the regeneration of activated carbon adsorbed with phenol after applying 2-20 A/m².

1.4. Approach and thesis outline

In this thesis we investigate the electrosorption phenomenon both theoretically and experimentally. Our aim is to see whether electrochemical regeneration of spent activated carbon is technically (and economically) feasible. The first step is to investigate the mechanism behind the influence of the potential on the adsorption equilibrium. This is done in chapter 2. The potentials that can be applied are limited to ± 1.5 V because at higher potentials Faraday reactions occur. These Faradaic reactions are unwanted for they cause a leakage of current, as carbon, ions and water molecules get oxidised or reduced. On the other hand the same Faraday reactions could be useful for regenerating the adsorbent because also the adsorbed pollution will be converted. This high voltage electrodynamic regeneration will not be investigated in this work, however. It is a completely different process and the electrostatic alternative is more attractive from an economic point of view as current is only needed for initial charging of the electrode and after this no current runs during desorption.

The outline of the thesis is discussed in more detail below. The relations between the various chapters are visualised in Figure 1.3.

- In chapter 2 the electrified interface is studied in detail to investigate the mechanism of electrosorption. A number of double layer models is examined. Special attention is paid to the influence of the electrical field on the dielectric constant of the solute and the solvent. Adsorption on a charged electrode is found equivalent to the moving of a slab of dielectric in a parallel plate capacitor. Using thermodynamics, changes in stored energy can be translated to changes in adsorption equilibrium.
- In chapter 3 the potential dependent equilibrium constant is combined with an appropriate isotherm equation. Experimental electrosorption data is compared with theory. Comparing the electrosorption effects to those of an alternative regeneration method provides an initial benchmark. The energy requirements associated with desorption of one mole phenol are estimated. New experimental electrosorption data is presented and compared with theory and literature data.
- Chapter 4 discusses the electrical behaviour of the packed bed electrode subjected to a change in applied potential. First electrodes without physical dimensions are considered. Laplace transformation is used to obtain the current responses for these systems. To include dimensions in the equations, an electrical circuit that behaves analogous to a packed bed electrode is constructed. Simplifying assumptions are made and for three different cases the potential distribution models are presented.
- In chapter 5 transient current experiments are presented. These experiments provide the data for validating the distribution functions. It will be shown that only the external losses model is capable of adequately fitting the data. The influence of mechanical pressure, ionic strength, potential and concentration on the total capacity and the total resistance is also determined.
- Chapter 6 deals with modelling an electrosorption unit. A first estimation of optimal dimensions of the unit is obtained from six characteristic times and their order of magnitude. A theoretical model is presented including differential equations to describe mass and charge

Chapter 1: Introduction

transfer and the coupling between these. The computer program *gPROMS* was used to do dynamic simulations. The results are examined for a number of different input variables and configurations.

- In chapter 7 three miscellaneous subjects are treated. First the phenomenon of streaming current is examined. Secondly, experimental results suggesting a coupling between mass and charge transfer are investigated. The adsorption seems related to current peaks found during experiments. Thirdly, an approximate economic calculation is done comparing electrosorption process costs to three alternative processes.

- In chapter 8 the concluding remarks can be found.

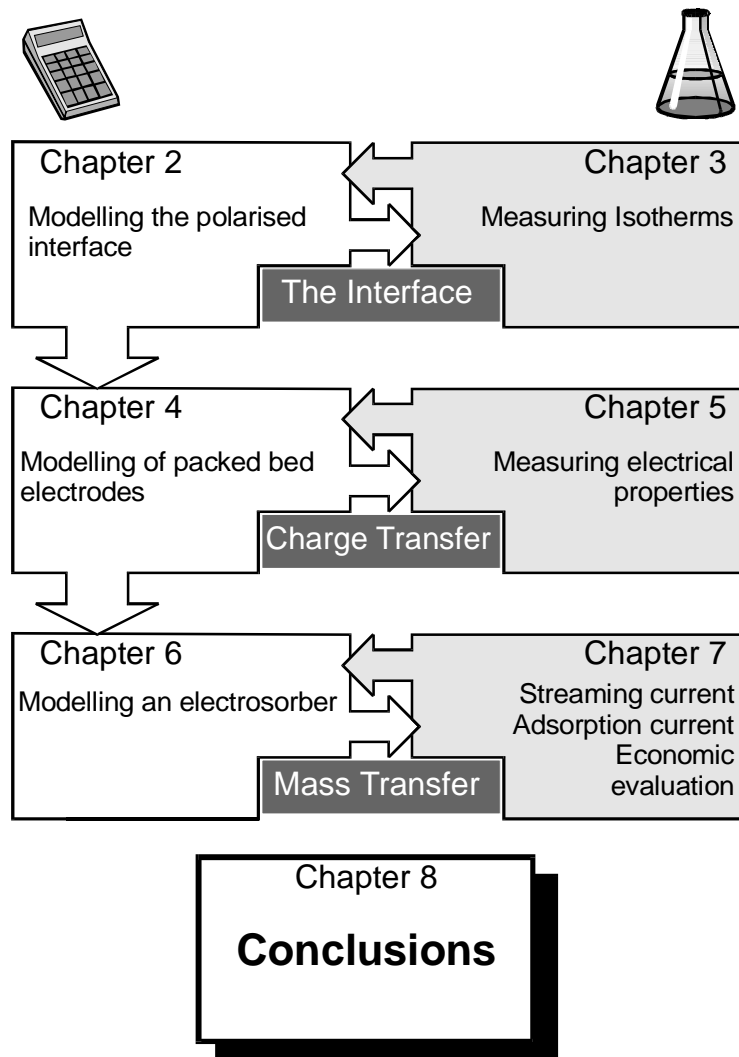


Figure 1.3: Outline of the thesis.