

# *The electrosorption of phenol onto activated carbon*

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The electrosorption isotherms of phenol on an activated carbon were measured over a concentration range of 0 to 100 mg<sup>-1</sup>l<sup>-1</sup> at 25°C and pH = 7.7, 6.5, 4.1 and 1.9. Cathodic polarizations relative to the open circuit potential decreased the amount of phenol adsorbed while anodic polarizations apparently increased the amount adsorbed; however, electro-oxidation of phenol masked adsorption at anodic polarizations. Electro-regeneration of spent activated carbon beds was studied. Within defined potential limits, the electro-regenerated bed maintains its virgin capacity. Application of a cathodic polarization to the bed enhanced the degree to which it was regenerated relative to that in a nonpolarized bed; the effect is, however, modest.

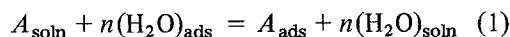
## 1. Introduction

The sorbate-sorbent interaction of an aqueous organic species at the surface of an activated carbon may be physical or chemical in nature. The relative importance of the two mechanisms depends upon the particular organic species and carbon surface involved. The strength of the adsorption bond is a function of the local physical-chemical environment at the sorption site. It is well known that the oxide structure of the surface strongly affects sorbate binding as does the pH and ionic strength of the solution. The electrical potential at the interface will obviously influence the sorption of ionic species from the solution. However, it is not widely recognized that the adsorption of nonionic species may be strongly influenced by the electrical nature of the interface. Sorption in the presence of an applied voltage is called electrosorption. It is relatively simple to polarize a conductive carbon to manipulate the interfacial potential, and hence, the surface adsorptive capacity.

The equilibrium and dynamic characteristics of phenol electrosorption from dilute aqueous solutions (less than 100 ppm) onto an activated carbon are reported here. Equilibrium isotherms at four pH values and under both anodic and cathodic polarizations are presented. Cathodic regeneration of spent carbon and limitations of the electrosorption process are discussed.

## 2. Electrosorption

The influence of an applied electric field on the adsorption of noncharged species at an electrode-solution interface has been well studied. Monographs and review articles are available which discuss the electrosorption of organics [1-3]. On Hg the adsorption isotherms typically go through a maximum with the potential which occurs near the potential of zero charge (PZC). At this potential the interface has a zero charge density and, consequently, the coulombic attraction of the surface for species in solution with charges or permanent dipole moments is minimal. Bockris *et al.* [4] have developed a model to explain the electrosorption isotherms of non-ionic species using competitive adsorption as the basis. The adsorption process may be viewed as a competition reaction between water and sorbate for available adsorption sites; the free energy change for this reaction should be greatest at the PZC since water is highly polar.



At a solid-solution interface the PZC is not as easily measured as at liquid Hg; nevertheless, the electrosorption isotherms are potential-sensitive, although the adsorption maximum may be obscured by the onset of Faradaic processes or by chemical interactions with the more inherently complex solid interface.

The effect of applied polarizations on the

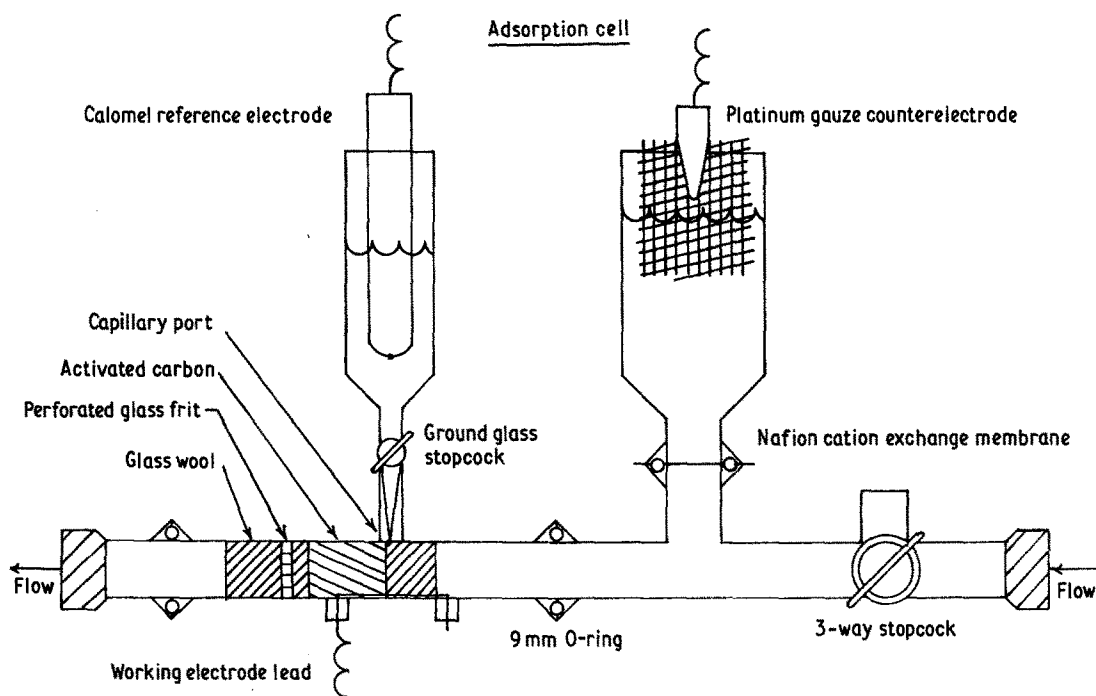


Fig. 1. Adsorption cell for isotherm measurements.

adsorption of nonionic species on an activated carbon has not been reported; however, previous work is available describing electrosorption at a graphite-solution interface. Strohl and Dunlop [5] studied the dynamic electrosorption characteristics of quinone solutions. They found that the adsorptive capacity of a bed of graphite particles could be greatly enhanced by applying a voltage. Specific quinones were separated from a mixture of quinones with the proper polarization and desorbed from the carbon at sufficiently negative potentials. Eisinger and Alkire [6-8] have published a series of articles describing the equilibrium and dynamic characteristics of  $\beta$ -naphthol electrosorption on graphite and is a ground-breaking effort in applying electrosorption phenomena to solid adsorbents. Their adsorption data was correlated with a modified Langmuir isotherm with a potential-dependent equilibrium constant. A mathematical model was developed for a fixed-bed electrosorber and was used to correlate their measured breakthrough curves.

### 3. Experimental details

The carbon used in this work was from Barneby

Cheny (Columbus, Ohio), Type UU, activated coconut charcoal of 50-200 mesh. Pretreatment consisted of washing repeatedly with warm 4.4 M HCl followed by rinsing with deionized water. Prior to use, the carbon was dried and sieved to a fraction between 60 and 115 mesh. The solutions were buffered with phosphate salts at pH = 7.7 and 6.5, and unbuffered at pH = 4.1 and 1.9. All solutions contained 0.5 M  $\text{Na}_2\text{SO}_4$ .

The cell used in the isotherm measurements is shown in Fig. 1 and is made of 9 mm i.d. glass tubing. Platinum gauze was used as the counter electrode (CE) and was separated from the carbon working electrode by a Nafion membrane. The bed was typically packed to a 1.3 cm length and contained 0.5 g of carbon. Electrical contact was made with the carbon by a platinum wire which ran along the inside wall of the cell. A perforated glass disc served as a support for the carbon and glass wool and was placed on both sides of the bed. A saturated calomel reference electrode was used. All experiments were carried out at 25°C.

The cell was placed in the flow loop shown in Fig. 2. The deoxygenated solution was pumped from a 100 ml reservoir through the cell and UV spectrophotometer and back to the reservoir.

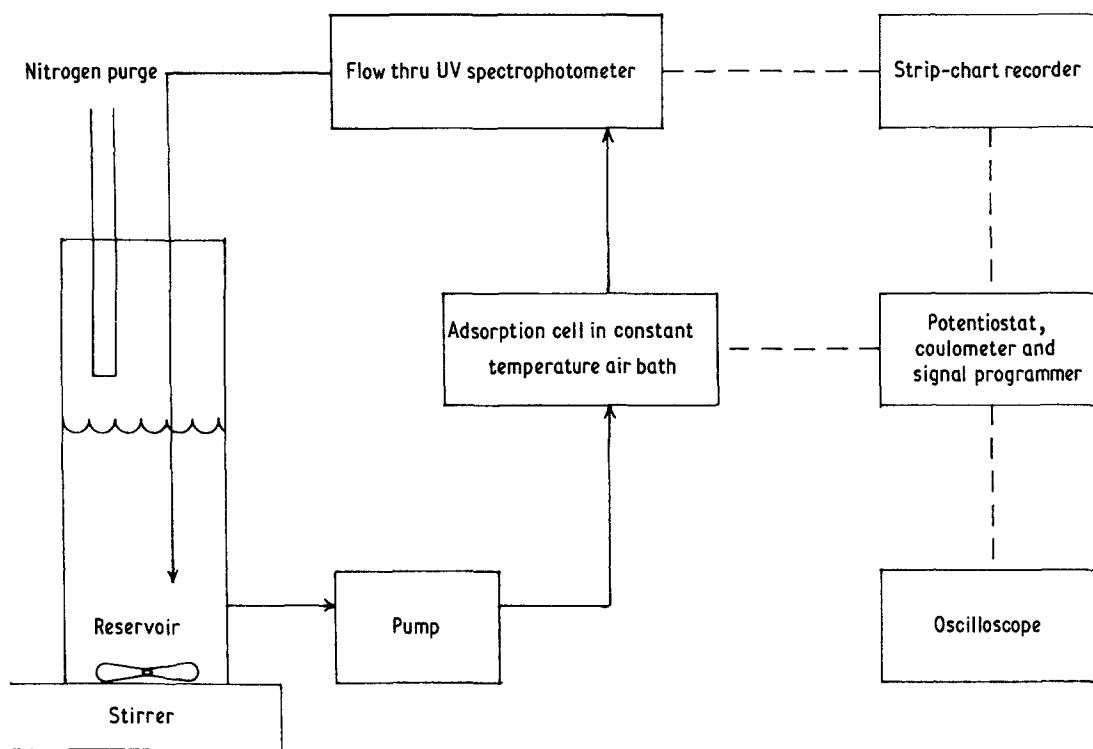


Fig. 2. Schematic of experimental apparatus for isotherm measurements.

An ordinary isotherm was measured by adding an aliquot of a stock phenol solution to the reservoir and recording the final phenol concentration. This procedure was repeated 5–7 times for each packing. Electrosorption isotherms were measured in the same manner with the bed polarization set by the potential difference between the reference and working electrodes. A potentiostat was used to maintain the desired polarization [9].

A different cell was used in the regeneration studies and is shown in Fig. 3. The working electrode contained 0.6 g of carbon and was 2.5 cm (in length)  $\times$  0.65 cm  $\times$  0.65 cm. This cell was used in both an equilibrium and dynamic flow scheme as shown in Fig. 4. The reversibility of the electrosorption process was studied in the equilibrium mode. In the dynamic mode of operation, solute breakthrough curves were recorded. After breakthrough, the column was rearranged to operate in the equilibrium mode with clean solvent recirculating. The bed was cathodically polarized during this recirculation. Buffered solution was pumped through the CE compartment.

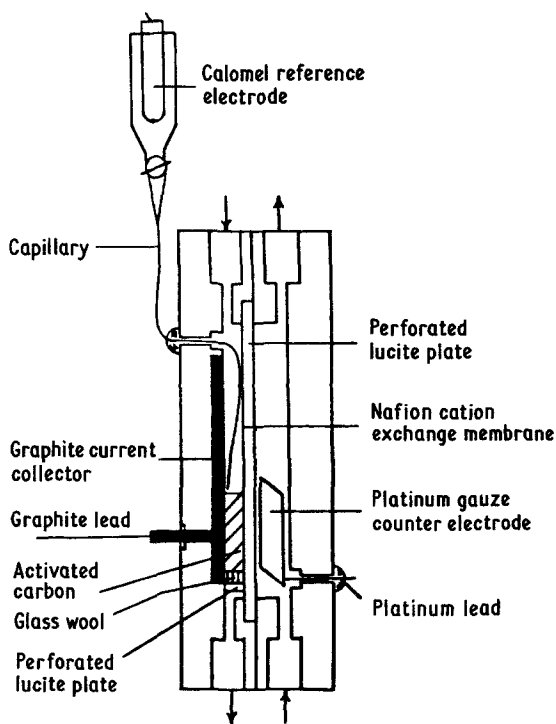


Fig. 3. Flow cell used in regeneration studies.

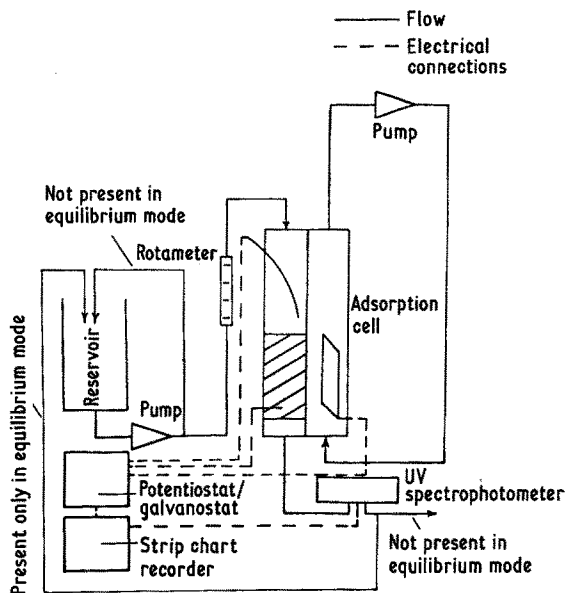


Fig. 4. Schematic diagram of flow scheme for regeneration studies: dynamic and equilibria mode.

Further experimental details are given by Dwiggins [10] and McGuire [11].

4. Results

A recirculating solution is not commonly used in measuring adsorption isotherms; therefore, preliminary experiments were performed to compare the ordinary (nonpolarized) isotherms measured in the recirculating cell with those obtained by the commonly used batch procedure. A given amount of carbon was added to a flask containing a phenol solution. After 24 h in a thermostated shaker bath, the phenol concentration was measured. No statistically significant difference was observed between the isotherms measured in the batch and recirculating flow cell.

On the Pourbaix diagram shown in Fig. 5, the anodic and cathodic potential limits applied to the carbon at the four pH values studied are shown. The solid points represent the open circuit potential of the ordinary isotherms.

Fig. 6 illustrates the open circuit adsorption isotherms at the four pH values. The solid lines on this figure and all following isotherms are the best-fit Freundlich isotherms

$$m = Kc^n \quad (2)$$

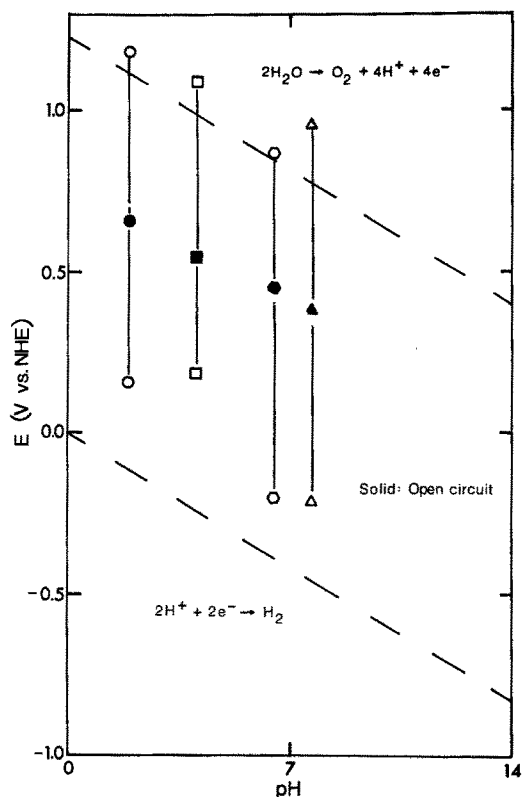


Fig. 5. Applied potential limits in electroadsorption isotherm measurements.

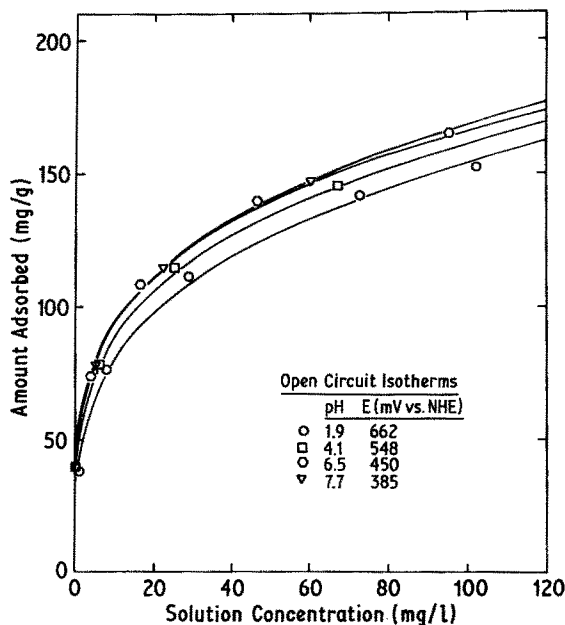


Fig. 6. Ordinary adsorption of phenol at various pH values.

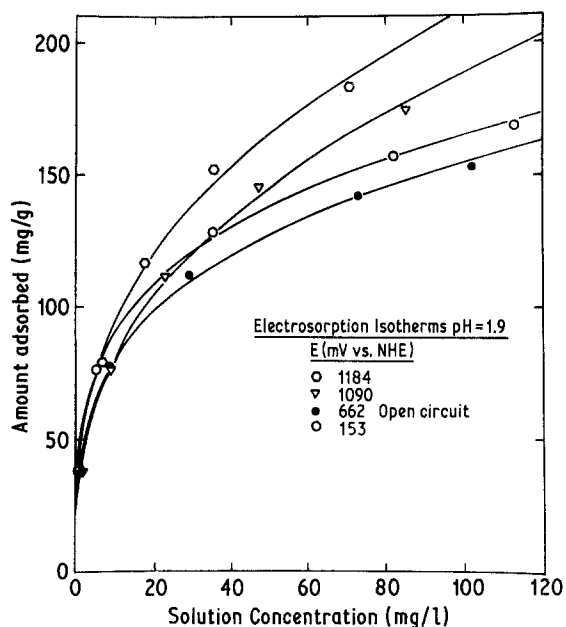


Fig. 7. Representative electrosorption isotherms at pH = 1.9.

where  $m$  is the loading of phenol on the solid ( $\text{mg g}^{-1}$ ) and  $c$  is the solution concentration ( $\text{mg l}^{-1}$ ). Figs. 7–10 illustrate representative electrosorption isotherms. In order not to clutter the graphs, all data collected are not

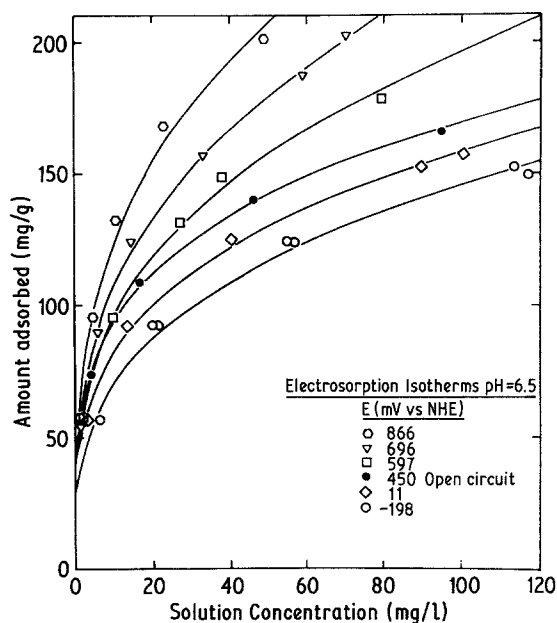


Fig. 9. Representative electrosorption isotherms at pH = 6.5.

reported, but the complete set of results are available [10, 11].

The Freundlich isotherm parameters  $K$  and  $n$  were slightly pH dependent. It was found that  $K$  was more potential-sensitive than the exponent

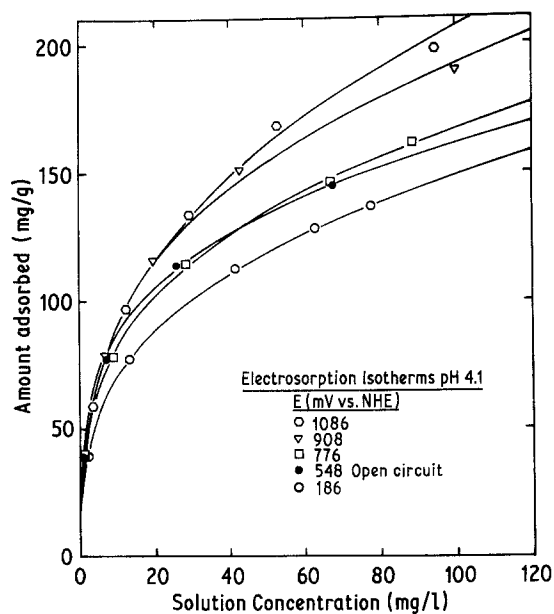


Fig. 8. Representative electrosorption isotherms at pH = 4.1.

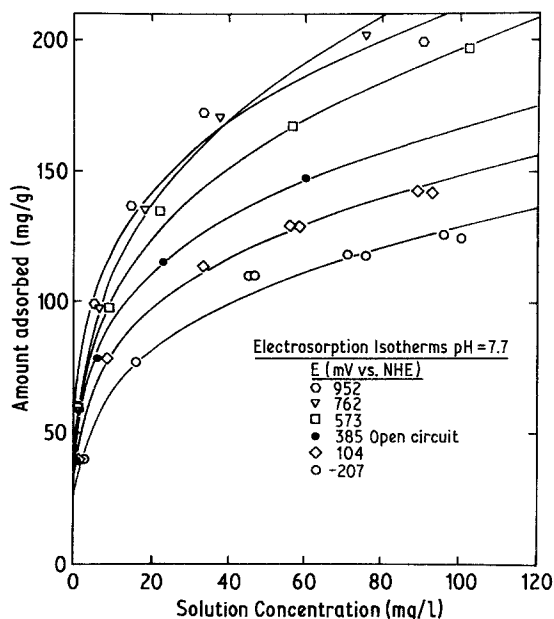


Fig. 10. Representative electrosorption isotherms at pH = 7.7.

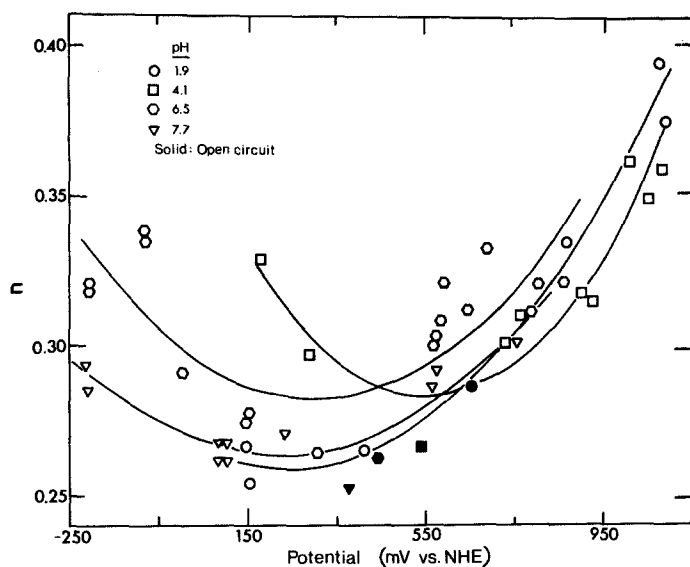


Fig. 11. Freundlich isotherm exponent ( $n$ ) as a function of polarization.

$n$ ; Fig. 11 illustrates the potential dependence of  $n$ . An integral average of  $n$  over the potential span studied was calculated and was used to determine  $K$  at each pH and potential. The results of these calculations are shown on Fig. 12. Statistical tests showed no improvement in the correlation of the results if the data were fitted with an isotherm with a potential dependent  $n$  instead of the averaged  $n$ .

The data in Table 1 demonstrate the reversibility of the electrodesorption process when the bed is cycled from a zero to  $-600$  mV cathodic

polarization relative to the open circuit. Also shown is one cycle in which the bed was first cathodically polarized and then allowed to relax to a new open circuit potential (i.e. the potential was not potentiostatically ramped to the initial open circuit voltage).

The data in Table 2 demonstrate the use of electrodesorption as a means of adsorbent regeneration. A uniformly spent carbon bed was exposed to a given volume of solvent in the presence or absence of a cathodic polarization of  $-600$  or  $-800$  mV relative to open circuit. As

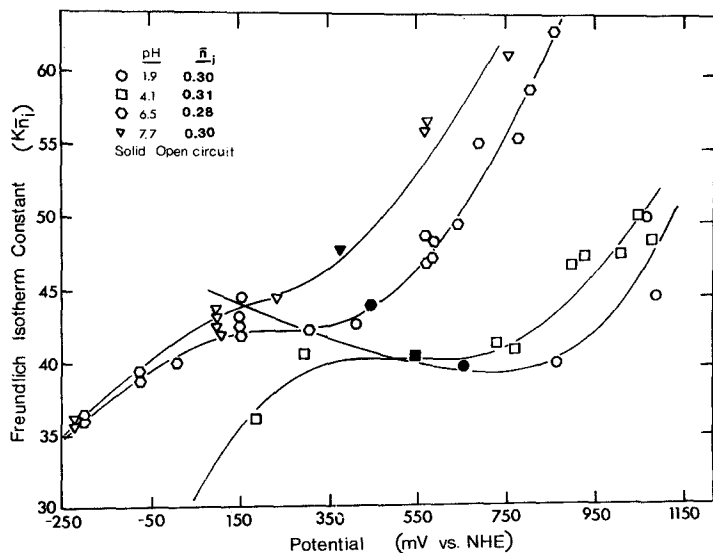


Fig. 12. Potential variation of the Freundlich isotherm constant calculated using the integral average exponent ( $\bar{n}_i$ ) for each pH value.

Table 1. Demonstration of electrosorption reversibility at pH = 6.5.

Open circuit potential (mV vs NHE)	Polarization (mV)	Equilibrium concentration (mg l <sup>-1</sup> )	Surface coverage (mg g <sup>-1</sup> )
434	0	39.2	115
	-600	56.8	112
	0	39.0	115
	-600	55.5	113
458*	0	38.1	115
	-600	61.5	111
438	0	38.1	115
	-600	38.2	112
	0	54.4	109
	-600	38.0	112
	-600	52.3	110
	0	35.2	113

\* Polarization applied before introduction of phenol then allowed to relax upon attaining equilibrium (i.e. no forced return to initial open circuit potential).

a reference point, the first two entries in the table show the regeneration when no cathodic polarization was applied.

Table 3 presents the results measured when a nonuniformly spent carbon bed was cathodically regenerated after the bed was used in a dynamic phenol breakthrough study. The feed concentration was 200 mg l<sup>-1</sup> and breakthrough was defined as an exiting phenol concentration of 100 mg l<sup>-1</sup>. Each bed was exposed to a breakthrough-cathodic regeneration-breakthrough cycle.

## 5. Discussion

### 5.1. Supporting electrolyte

The addition of Na<sub>2</sub>SO<sub>4</sub> was necessary to ensure a small variation in the interfacial potential difference across the carbon bed. The salt increases the conductivity of the solution and, hence, lowers the ohmic voltage drop. Preliminary runs were made with buffered solutions in the absence of the salt, but the cell voltage required at moderate polarizations was prohibitively large for the potentiostat used. Ordinary adsorption data were measured for solutions at pH = 6.5 and 1.9 in the presence and absence of the salt. There was a slight increase in the adsorptive capacity at each pH when the salt was present. This may be attributed to the small basic shift of the pH with a consequential slight increase in the adsorption as seen in Fig. 6.

The concentration of the supporting electrolyte can be reduced if an electrosorber is designed to keep the length in the current flow direction small to minimize the ohmic voltage drop. A 'jelly-roll' configuration of the carbon and counter electrode could, for example, be used to pack a large surface area into a small volume and still maintain a small current path length.

### 5.2. Equilibrium isotherms

The Freundlich isotherm constant  $K$  shows the same trend with potential as found by Eisinger and

Table 2. Dependence of activated carbon regeneration on applied potential (constant volume of electrolyte)

	Open circuit potential (mV vs NHE)	Equilibrium concentration (mg l <sup>-1</sup> )	Surface coverage (mg g <sup>-1</sup> )	Regeneration (%)
Adsorption cycle	437	35.6	113	
Flush (at open circuit)		26.0	109	3.5
Adsorption cycle	433	40.4	115	
Flush (at open circuit)		28.6	110	4.0
Adsorption cycle	442	43.9	112	
Flush (at -600 mV)		49.1	103	7.4
Adsorption cycle	436	43.0	114	
Flush (at -600 mV)		48.1	106	7.1
Adsorption cycle	442	36.2	116	
Flush (-800 mV)*		55.7	106	8.2
Adsorption cycle*		26.5	111	

\* Potential forced back to initial open circuit value. Flush volume = 100 ml (i.e. approximately 100 bed volumes). pH = 6.5.

Table 3. Breakthrough characteristics: feed concentration = 200 mg l<sup>-1</sup>

Run	Breakthrough time (min)	Polarization (mV)	Flush volume (ml)	Change in surface coverage (mg g <sup>-1</sup> )
1	326			150
	23.0	0	117	-11.0
2	20.5	0	114	10.0
	379			-10.6
	27.0	0	115	8.6
3	19.0			174
	368			-13.7
	10.0	-600	115	10.8
	72.0	-600	113	-12.7
4	249			8.0
	61.5	-600	115	188
	50.0	-600	115	-19.5
		-600	115	4.0
				-13.9
				27.8
				154
				-20.2
				26.1
				-23.2
				19.7

Effluent concentration at breakthrough time = 100 mg l<sup>-1</sup>, flowrate = 2.0 ml min<sup>-1</sup>, pH = 6.5.

Alkire for the Langmuir constant of  $\beta$ -naphthol on graphite. The water competition model of Bockris may be used to interpret the data; support has been given for the competition between water and sorbent for available adsorption sites [12]. However, since the PZC on the activated carbon is not known and strong chemical interactions at the surface may occur, the data were not interpreted with this theory. The intent of this work was to demonstrate the technological feasibility of manipulating adsorption on activated carbon with an applied polarization. The experiments were not designed to ascertain the mechanism of the phenol-surface interaction; such discussions are available in the literature [12-16].

The open circuit isotherms show a slight increase in adsorption as the pH is increased. As the pH is lowered, more of the surface oxides assume their protonated form. It has been shown that the adsorption of phenol on an activated carbon decreases as the surface becomes more acidic [12, 13, 17, 18]. In all results reported here the phenol was unionized since its  $pK_a = 9.9$  at 20°C. If the pH is increased above the  $pK_a$ , a decrease in adsorption has been reported which may be attributed to coulombic repulsion between the surface and the phenolic anion [19].

A cathodic polarization decreased the electro-

sorption except at pH = 1.9 where an increase in adsorption was observed. Since it has been observed that phenol adsorption goes through a maximum with pH [19], it is possible that the decrease in phenol adsorption at pH = 7.7, 6.5 and 4.1 is caused by a local basic pH shift at the adsorption sites. In the strong acidic solution, however, the basic pH shift is not sufficiently large enough to change the surface pH to the right of the maximum and, hence, would not cause a decrease in adsorption, but rather, increases the adsorption since the pH is still to the left of the maximum.

In all solutions studied, an anodic polarization apparently increased the adsorption of phenol. These results should be interpreted qualitatively, however, since a Faradaic reaction, assumed to be the oxidation of phenol, occurred at these polarizations [20-22]. The oxidation of phenol caused a decrease in the solution concentration which appeared as an increased adsorption. The extent of the electro-oxidation became more pronounced as the polarization increased. Attempts were made to compensate the data for the reaction but lack of knowledge of the kinetics precluded success. However, no Faradaic reaction of the phenol occurred under cathodic polarizations. The only significant Faradaic reaction



which occurred under cathodic polarizations was the consumption of protons, perhaps used in the reduction of adsorbed oxygen or surface oxides. The cathodic potential limit in the unbuffered pH = 4.1 and 1.9 solutions was limited by the unacceptable basic shift of 2 pH units during the course of the run. A pH shift in the buffered solutions was not a problem.

The above discussion illustrates an inherent limit on the potential span that may be applied to an electrosorber. Even if the sorbate was electroinactive (as is phenol under cathodic polarization) the sorbent or solvent may participate in electrochemical reactions. For example, the upper and lower dotted lines on the Pourbaix diagram on Fig. 5 illustrate the *thermodynamic* decomposition potential for the oxidation of water and reduction of protons, respectively. Of course, the oxidation of a substance may be beneficial in removing it from a waste water, but the process should not then be called electrosorption.

The electrosorption process was found to be reversible in the pH = 6.5 solution under cathodic polarizations up to  $-600$  mV as shown by the data in Table 1. A flush cycle of a spent bed at  $-800$  mV was more effective in lowering the phenol loading than at  $-600$  mV. However, the subsequent return to the bed's open circuit potential was found to be cathodic relative to the initial open circuit. This potential shift is indicative of an irreversible change of the carbon surface at the higher polarization.

It is known that the surface oxides on carbon are electroactive and will respond to the applied polarization [23, 24]. Experiments were performed at cathodic polarizations in the absence of phenol to ascertain the background current level. The largest currents were observed under high cathodic polarizations and a basic shift of solution pH was observed. The distribution of oxide-types may, therefore, be changing during the experiment. Work is currently in progress to study the effect of polarizations on the surface oxide distribution using the method of Boehm *et al.* [25].

### 5.3. Electrogeneration

Table 2 illustrates, for a uniformly spent carbon bed, a modest enhancement in removing phenol

from the surface under a cathodic polarization: approximately 7.3% regeneration at  $-600$  mV polarization in comparison to 3.7% at open circuit. The electrochemically regenerated bed maintains its virgin capacity.

A dynamic study of an adsorber operated under cathodic regeneration polarizations also showed an improvement in phenol removal. A feed concentration of  $200$  mg phenol  $l^{-1}$  was used to record the breakthrough time at an exit concentration of  $100$  mg  $l^{-1}$ . These high concentrations were necessary to enable the detection of an electrodeposition effect with the analytical instrumentation available. It was difficult to reproduce the breakthrough time and characteristics from run-to-run as seen in the data given in Table 3. This variation was attributed to channelling around the flexible Nafion membrane and the problem was particularly acute in Run 3. The carbon bed regenerated at  $-600$  mV (Run 4) showed longer breakthrough times than the beds regenerated with no applied polarization (Runs 1 and 2).

## 6. Conclusions

1. The application of a potential to the activated carbon affects its adsorption capacity for phenol. Cathodic polarization decreases the adsorptive capacity while anodic polarization apparently increases the amount adsorbed.
2. The anodic polarization results should be interpreted qualitatively because of uncompensated electro-oxidation of the phenol.
3. Relative to a non-polarized bed, in a solvent flushing operation, a cathodic polarization enhances the degree to which the carbon is regenerated.
4. The electrochemically regenerated carbon maintains its virgin capacity and the effect is reversible to a polarization of  $-600$  mV relative to the open circuit.

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