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**Adsorption of Free
and Complexed Metals
from Solution
by Activated Carbon**

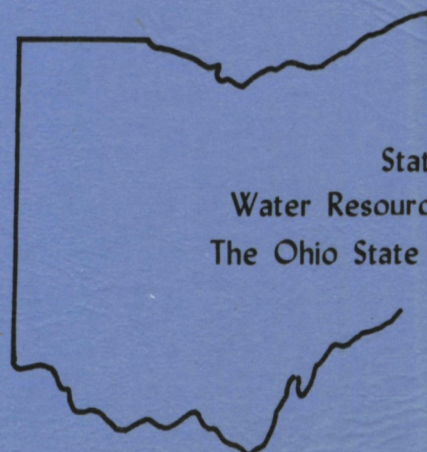
**Alan J. Rubin
and
Danny L. Mercer**

Department of Civil Engineering
The Ohio State University

August 1979

This study was supported in part
by the Office of Water Research
and Technology, U.S. Department
of the Interior under

Project A-044-Ohio



State of Ohio
Water Resources Center
The Ohio State University

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Alan J. Rubin

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Danny L. Mercer

Department of Civil Engineering
The Ohio State University
Columbus, Ohio 43210

WATER RESOURCES CENTER
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INTRODUCTION

Background

Expanding industrial and domestic consumption is rapidly depleting existing sources of unpolluted water. As a result, extensive water reuse is inevitable in the not too distant future. To meet this demand, innovative treatment technology will be required. Activated carbon adsorption, which has been developed as a highly effective yet economical method for removing trace organics from water and wastewater, is a good example of the type of process that will be employed (1).

For public health reasons, the removal of trace metals is certain to be of high priority in the future of wastewater renovation. Maruyama, Cohen and Hannah (2), in citing a 1973 Environmental Protection Agency study, reported that the principal sources of metals to wastewaters are industrial discharges, leaching of metal-bearing minerals and storm runoff. The report states that street runoff to combined sewers may produce metals concentrations in the wastewater on the order of ten to one hundred times greater than normal. The alkali and alkaline earth metals are highly soluble and thus ubiquitous in natural waters. In general, they exert little toxicity even in high concentrations and, therefore, are only of secondary concern. However, many of the so-called heavy metals appear to be quite toxic. Their occurrence in natural waters is largely the result of man's activities. Frequently cited in relation to metal toxicity problems are lead, zinc, mercury and, to an increasing extent, cadmium (3).

The toxicity of cadmium to aquatic organisms is well documented (4-7). A review of the literature citing cadmium as a human health threat is given

by Flick, Kraybill and Domitrof (8). Such effects as renal dysfunction, growth inhibition, arteriosclerosis and nervous disorders are discussed. Accute cadmium poisoning was reported by Kobayashi (9) as a result of mine leaching of heavy metals into the Jintsu River of Japan. Clinical diagnosis of a condition termed 'itai-itai' disease was shown to be caused by ingestion of high concentrations of cadmium. A heavy accumulation of cadmium and other metals was found in the patients' bones and internal organs. Laboratory studies with rats showed that a high intake of cadmium results in excess excretion of the metal.

Zinc, an essential element for humans, is found in low concentrations in such aquatic organisms as marine shellfish and in the United States has been observed in both oysters and clams (10). Studies with rats involving continued administration of zinc salts have shown effects only on digestion. Because of adsorption and/or precipitation onto river silt, zinc often is not recorded at high values in watercourses. At pH 8.4 only $1 \mu\text{M}$ zinc is soluble and since natural waters often range in pH from 7 to 9 a significant portion of the zinc present may be precipitated (11).

Lead is found to be an accumulative poison for mussels at concentrations as low as 0.05 mg/l. Lead is also dangerous to humans since it acts as an inhibitor of several enzymes required in the biosynthesis of the iron-containing heme group which is a critical part of hemoglobin, the oxygen transporter, and the electron carrying cytochromes. Anemia may result at high lead concentrations due to enzyme inhibition. Another problem with lead is that it is attracted to the bones where it interferes with calcium metabolism. The central nervous system may be damaged by lead as well.

In recognition of the heavy metals problem, federal regulatory agencies

have proposed stringent effluent and drinking water standards to help control the aqueous distribution of these substances (12-14). These guidelines have set the maximum allowable concentration of cadmium in drinking water at 0.01 mg/l (approximately 0.09 μM) and the effluent concentration limit of 0.04 mg/l when the receiving stream low flow equals or exceeds ten times the waste flow. Lead and zinc have drinking water limits of 0.05 mg/l and 5 mg/l, respectively (15). In addition, zinc is exceptionally toxic to aquatic life and, like lead and cadmium, has stringent effluent discharge limitations.

Aqueous Chemistry of Cadmium

The solubility of cadmium in most natural waters is governed by carbonate or by hydroxide in systems having very low carbonate concentrations (16). Equations 1 and 2 below show these solubility equilibrium reactions



Aqueous cadmium solubility at any pH and carbonate ion concentration can be calculated from the corresponding solubility product equations

$$K_{\text{sp}} = (\text{Cd}^{2+})(\text{OH}^{-})^2 = 2.2 \times 10^{-14} \quad \dots(3)$$

$$K_{\text{sp}} = (\text{Cd}^{2+})(\text{CO}_3^{2-}) = 5.2 \times 10^{-12} \quad \dots(4)$$

The K_{sp} expression that results in the lower Cd^{2+} ion concentration (under

the specified pH and carbonate conditions) represents the solubility-limiting system. This value is the maximum soluble Cd^{2+} ion concentration theoretically possible under such conditions.

Based upon solubility product calculations, it seems that high-lime precipitation should be very effective for the removal of dissolved cadmium. Pilot plant data reported by Linstedt, Houck and O'Connor (17) in 1971 supports this notion. Using a secondary effluent spiked to a 0.016 mg/l cadmium concentration, they observed a 94% cadmium removal by high-lime precipitation at pH 11. The authors stated that the residual cadmium concentration of less than 0.001 mg/l is consistent with reported solubility data for cadmium hydroxide. In 1975 Maruyama, Cohen and Hannah (2) conducted a similar pilot study using a raw domestic wastewater spiked to 5.0 mg/l cadmium or 300 times greater than the concentration employed by Linstedt and co-workers. High-lime precipitation at pH 11.5 followed by sand filtration resulted in a final cadmium concentration of 0.15 mg/l which is nearly 150 times greater than that obtained in the 1971 study. This value is in gross violation of the recommended effluent standard of 0.04 mg/l cadmium.

The only significant differences between these two studies appear to be the initial metal concentration (0.016 mg/l versus 5.0 mg/l) and the type of test water employed (secondary effluent versus raw wastewater). Since solubility depends only upon the amount of material in the solution phase and not the amount precipitated, the initial metal concentration should have no effect upon the dissolved cadmium concentration after precipitation. The difference between the test waters seems to be more important, however. Gardiner (18) presented data that suggests a significant percentage of cadmium present in sewage and river waters is complexed by organic ligands. This

complexed cadmium is more or less resistant to removal by chemical precipitation. As a result, cadmium solubility calculated from simple solubility product considerations may be greatly exceeded if complexing species are present. The consequence of metal complexation by organic ligands in natural waters and wastewaters is that additional or alternative treatment to chemical precipitation may be necessary to achieve the low metals concentrations often required. Adsorption represents such an alternative treatment process.

Similar considerations also apply to zinc and lead solubility. In addition zinc, and to a greater extent lead, hydrolyze to form soluble hydrolysis products



Adsorption Theory

Adsorption is a surface phenomenon which deals with the unequal partitioning of solute species between a bulk phase and the phase boundary. The species being concentrated or adsorbed is referred to as the adsorbate, and the surface doing the adsorbing is termed the adsorbent. Adsorption is quantified by calculating the amount of material adsorbed per unit of adsorbent surface (mass or moles per unit area). This quantity, referred to as the adsorption density, is often designated by a capital gamma, Γ . For adsorbents having unknown surface areas or surface areas that are difficult to measure precisely the adsorption density is often expressed in terms of the mass of adsorbent (mass or moles per unit mass) and designated by a capital X.

Historically, most theoretical studies have dealt with the adsorption of gases. Herbert Freundlich was one of the first workers to attempt to quantify

the adsorption of gases onto solids. To fit experimental data he used an equation of the form

$$X = kP^{1/n} \quad \dots(6)$$

where P is the equilibrium gas pressure and k and 1/n are constants. Estimation of the constants k and 1/n is possible by plotting the data according to the linearized form of the Freundlich equation

$$\log X = \log k + 1/n \log P \quad \dots(7)$$

and calculating the linear least squares line. The intercept of this line estimates log k, and the slope estimates 1/n. Equation 6 has also been used to quantify adsorption from solution; in which case pressure is usually replaced by the equilibrium concentration of adsorbate.

Langmuir concluded that the Freundlich equation is often quite poor in fitting experimental adsorption data over extended equilibrium pressures (19). Adamson (20) has pointed out the two basic faults of the Freundlich equation. First, it does not express X as a linear function of P at low pressures, a common experimental observation. Second, it does not provide for a maximum value of X. The Freundlich equation predicts infinite surface coverage at infinite pressure, a condition that does not occur; as a result, it gives a good fit to experimental data only over ranges of intermediate pressure.

Most early workers viewed adsorption as a purely physical phenomenon. Irving Langmuir, who laid the foundation for much of present-day understanding of adsorption, presented a theory in 1915 which stated that chemical rather

than physical forces are primarily responsible for adsorption of gas molecules onto the surface of solids. Based on crystal structure investigations and other evidence, Langmuir concluded that unbalanced forces exist on surface atoms and that they are unsaturated chemically. As a result, gas molecules that impinge on the surface of a solid or liquid do not rebound elastically but will condense. The rate of subsequent evaporation from the surface depends only upon the strength of the binding forces and the surface concentration of the adsorbed molecules. Langmuir developed a quantitative model which has been widely applied to describe experimental adsorption data (19). He predicted that under equilibrium conditions and constant temperature, simple adsorption should obey a function of the form

$$X = \frac{X_m bP}{1 + bP} \quad \dots(8)$$

where X_m is a maximum surface coverage which represents the formation of a monomolecular layer on the surface of the adsorbent, P is the equilibrium gas pressure, and b is a constant related to the energy of adsorption. Substituting $1/K$ for b into Equation 8 and multiplying both the numerator and denominator by K gives Equation 9 which is identical in form to the Michaelis-Menton equation of enzyme kinetics

$$X = \frac{X_m P}{K + P} \quad \dots(9)$$

A plot of X as a function of P passes through the origin and is nearly linear at low pressures. As the pressure increases, adsorption approaches the limiting value X_m . Thus, both weaknesses of the Freundlich equation are

corrected. A small value of K (i.e., $1/b$) means that the adsorbent can effectively adsorb at low gas pressure; a high value of X_m indicates a large adsorbent surface area.

Langmuir was quick to point out that Equations 8 and 9 are strictly applicable only to the adsorption of gas molecules by simple crystalline materials with homogeneous surfaces such as mica and platinum. According to the theory, these simple adsorbents have only one elementary type of adsorption site with a single adsorption energy potential. Langmuir conceded that most adsorbent surfaces are substantially less homogeneous. He stated that the adsorption of gas molecules onto solids which contain more than one elementary type of adsorption site should follow a related, but more complex function than given by Equation 9

$$X = \left(\frac{B_1}{K_1 + P} + \frac{B_2}{K_2 + P} + \dots + \frac{B_n}{K_n + P} \right) X_m P \quad \dots(10)$$

where n is the number of different types of elementary adsorption sites, B_n is the fraction of the surface composed of type 'n' adsorption sites, and K_n is the value of K for type 'n' adsorption site such that $K_1 < K_2 < K_3 < \dots < K_n$. For a completely heterogeneous solid such as glass, the functional relationship between X and P should be of the nature

$$X = \int_0^1 \frac{P X_m dB}{K + P} \quad \dots(11)$$

In this equation K is no longer a constant but rather a function of B .

Equation 11 can also be represented by an infinite series expansion of Equation 10. The implication of adsorbent heterogeneity is that if the equilibrium gas

pressure is varied over several orders of magnitude, X can show a continuous increase. This is perhaps most easily understood by viewing the infinite series expansion of Equation 10. As the equilibrium pressure is increased more terms in the series become significant in magnitude, and the value of X shows a corresponding increase. The exact shape of the adsorption isotherm for a heterogeneous adsorbent will depend upon the distribution of the K values or, more specifically, upon the frequency distribution of the adsorption energy sites on the adsorbent. Adsorption onto activated carbon which is a highly heterogeneous solid should follow this type of function.

Morris and Weber (21) studied the adsorption of phenol from aqueous solution by activated carbon. They observed that over two widely different ranges of equilibrium phenol concentration the calculated adsorption densities (values of X) varied by several hundred percent. This observation is accounted for by Langmuir's theory. Morris and Weber, however, fit their data to the Brunauer, Emmett and Teller (BET) adsorption isotherm

$$X = \frac{ACX_m}{(C_s - C)} \left(1 + (A-1)\frac{C}{S} \right) \quad \dots(12)$$

The BET isotherm which was developed in 1938 is an extension of the simple Langmuir equation. It assumes localized patches of multi-layer adsorption with each layer exhibiting Langmuir adsorption behavior. The BET equation has been widely used to determine surface areas of amorphous solids, usually with nitrogen at 77°K as the adsorbate. Adamson points out, however, that the range of pressures over which the BET equation will adequately fit experimental adsorption data is often quite limited. Furthermore, the assumptions of the model are tenuous indeed (20). It seems, therefore, that a more direct

approach to studying adsorption by heterogeneous adsorbents is to consider the energy distribution of the adsorption sites on the adsorbent as discussed by Langmuir.

Several attempts have been made to incorporate an adsorption energy distribution function into a quantitative model for the adsorption of gases by heterogeneous solids. Most of these start with a function similar to that shown in Equation 13

$$\theta(P,T) = \int_0^{\infty} \underline{\theta}(Q,P,T)f(Q)dQ \quad \dots(13)$$

where $\theta(P,T)$ is the fractional surface coverage (X/X_m) as a function of pressure and temperature; $\underline{\theta}(Q,P,T)$ is the fractional surface coverage as a function of adsorption energy, pressure and temperature; and $f(Q)dQ$ is the adsorption energy distribution function. It should be noticed that Equation 13 is just a generalization of Equation 11. According to Adamson (20), Tempkin took all adsorption sites to vary in energy according to the relationship

$$Q = Q_0(1-\alpha\theta) \quad \dots(14)$$

such that Q_0 is the adsorption energy of the bare surface, Q is the adsorption energy as a function of the surface coverage, and α is a constant. Equation 14 states that as the surface coverage increases, the energy released on adsorption, Q , decreases. Substitution of Equation 14 into the integral form of the Langmuir equation, followed by integration, gives

$$\ln P = -\ln(b_0 \exp Q_0/RT) + \ln \left(\frac{\theta}{1-\theta} \right) + Q_0 \alpha \theta / RT \quad \dots(15)$$

Experimental verification of an equation such as the one given above is extremely difficult because it requires the simultaneous evaluation of both the adsorption model, $\theta(Q,P,T)$, and the energy distribution function, $f(Q)dQ$.

In conclusion, the Freundlich equation seems to be more empirical than theoretical. Its application is limited to ranges of intermediate surface coverage and, hence, intermediate equilibrium gas pressure. The simple Langmuir equation is one of the most widely used models for quantifying adsorption data. The theoretical basis of the equation, its success with fitting data from a wide variety of adsorption systems, and the simplicity of evaluating the parameters from experimental data are the reasons for the Langmuir equation's popularity. However, the use of such a simple model to describe a complex process like adsorption is not without its limitations, especially when employing heterogeneous adsorbents. The BET equation has some practical applications although it is based on rather unrealistic assumptions. Sophisticated adsorption models such as the Temkin equation are of more theoretical than practical interest at the present time, often requiring complicated techniques to evaluate the parameters.

So far this discussion of adsorption theory has focused on the adsorption of gases by solids. When considering adsorption from aqueous solution, additional variables such as pH, ionic strength and adsorbate solubility must be considered. These parameters have no counterparts in gaseous systems and thus are not directly considered in gas adsorption theories. As a result, any quantitative study of adsorption from solution must consider these additional variables.

J. Willard Gibbs advanced a theory in 1878 that explained the relationship between the bulk and surface distribution of a solute and the surface tension

of the solution (22). The conclusion of his theory is that solutes which lower the surface tension of a liquid exist in higher concentration in the surface film than in the bulk liquid. An extension of this notion is given by Traube's rule which states that the adsorption of related organic substances from aqueous solution increases regularly as one ascends the homologous series. The correlation is not between the extent of adsorption and the molecular weight, however, but between the extent of adsorption and the solubility of the adsorbate as illustrated by studies with non-aqueous solvents (20).

Adsorption from aqueous solution invariably is affected by the pH of the system. Morris and Weber (21) found that even the adsorption of highly surface active detergents by activated carbon was slightly dependent upon solution pH over the range 5 to 8. Under proper pH conditions extensive adsorption of inorganic ions by clays and metal oxides and hydroxides has been demonstrated (23-29). These reactions are very pH dependent. James and Healy (30) and subsequently Malotky and Anderson (31) developed quantitative models for the adsorption of ions by metal oxides. Both of these models assume that ion adsorption proceeds by an electrostatic mechanism. Nelson, Phillips and Kraus (32) have discussed the cation exchange properties of activated carbon. They presented data that showed the strong effect of pH upon cation and anion adsorption by activated carbon; cation adsorption being enhanced at high pH and anion adsorption at low pH.

Linearized Langmuir Equation

In spite of the limitations just discussed, the simple Langmuir equation is often used to describe adsorption from solution by heterogeneous solids. Replacement of the equilibrium gas pressure in Equation 9 with the equilibrium

adsorbate concentration gives

$$X = \frac{X_m C}{K + C} \quad \dots(16)$$

Provided the temperature, pH and ionic strength are held constant and the range of equilibrium adsorbate concentration is limited, Equation 16 often gives a reasonably good fit to experimental adsorption data.

Quantifying an adsorption system using Equation 16 requires experimental evaluation of the parameters K and X_m . The most common technique employs batch adsorption studies in which various ratios of adsorbate and adsorbent concentrations are equilibrated under similar conditions of temperature, pH and ionic strength. Following reaction the concentration of adsorbate remaining in solution is measured and X is calculated by

$$X = \frac{(C_0 - C)V}{m} \quad \dots(17)$$

where C_0 is the initial concentration of adsorbate, V is the volume of the solution, and m is the mass of adsorbent.

Mathematical procedures for fitting non-linear functions such as Equation 16 to experimental data are laborious and time consuming, and they are frequently carried out by digital computers. However, various transformations of Equation 16 allow evaluation of K and X_m using the relatively simple graphical or linear least-squares technique. A linear form of Equation 16 is obtained by taking the reciprocal of both sides. This results in an equation of the form $Y = ax + b$

$$\frac{1}{X} = \frac{K}{X_m} \left(\frac{1}{C} \right) + \frac{1}{X_m} \quad \dots(18)$$

Upon multiplication of Equation 18 by C and rearrangement, a second linear form results

$$\frac{C}{X} = \frac{1}{X_m} (C) + \frac{K}{X_m} \quad \dots(19)$$

Multiplication of Equation 18 by $X \cdot X_m$, followed by rearrangement, yields a third linear form

$$X = -K \left(\frac{X}{C} \right) + X_m \quad \dots(20)$$

Three additional linear forms of the Langmuir equation can be generated by interchanging the variables

$$\frac{1}{C} = \frac{X_m}{K} \left(\frac{1}{X} \right) - \frac{1}{K} \quad \dots(21)$$

$$C = X_m \left(\frac{C}{X} \right) - K \quad \dots(22)$$

$$\frac{X}{C} = -\frac{1}{K} (X) + \frac{X_m}{K} \quad \dots(23)$$

Any of these may be used to evaluate K and X_m from experimental data using graphical or linear least-squares analysis. As pointed out by Dowd and Riggs (33) the ability of these equations to accurately predict the true least-squares values of K and X_m are not the same. Equation 18, because it contains two reciprocal quantities subject to experimental error, is less reliable

than either Equation 19 or 20 which should have similar predictive values. Equation 20 possesses the added advantage that K and X_m are obtained directly from the slope and intercept of the least squares line, eliminating the need for further calculations. Equations 21 through 23, though analogous to 18 through 20, should not be expected to predict the same values of K and X_m from experimental data. In fact, for experimental isotherm data all six regression equations calculate different values of X_m and K . This will be demonstrated in the Discussion and Conclusions section.

Literature Review

In order to make quantitative comparisons between adsorption systems using the simple Langmuir equation it is necessary to have an idea of the ranges of values of K and X_m that constitute effective adsorption processes. The following review of the literature dealing with adsorption from aqueous solution is by no means exhaustive, but rather is intended only to point out some of the more important factors that influence adsorption from aqueous solution. Also, the problems associated with using the simple Langmuir equation to describe adsorption by heterogeneous solids are briefly illustrated.

As stated previously, activated carbon is highly effective for the adsorption of large organic compounds from water. Therefore, the data reported by Morris and Weber (21) for the adsorption of alkyl benzenesulfonate (ABS) detergents by activated carbon serves well as a starting point. Using carbon doses of 50 mg/l and equilibrium adsorbate concentrations ranging from approximately 0.5 to 50 μM , Morris and Weber fit their data to the Langmuir equation. X_m values between 160 and 400 $\mu\text{mol/g}$ were calculated for various benzenesulfonate and substituted benzenesulfonate surfactants. The reported

K values were quite small, ranging from 0.5 to 4 μM . Such small values reflect the ability of carbon to adsorb low levels of these materials. For the adsorption of phenol onto activated carbon, they calculated an X_m equal to 1090 $\mu\text{mol/g}$ and a K equal to 9.3 μM at equilibrium phenol concentrations between 5 and 210 μM . For equilibrium phenol concentrations ranging from 1000 to 140,000 μM , they calculated X_m equal to 4500 $\mu\text{mol/g}$ and K equal to 5000 μM . These values illustrate two important points. First, when using the simple Langmuir equation to model adsorption by a heterogeneous solid the calculated X_m value may increase significantly as the equilibrium adsorbate concentration is increased over several orders of magnitude. Second, since K is nothing more than the equilibrium adsorbate concentration at which X is equal to one half X_m , the calculated value of K also depends upon the range of concentrations employed in the study. Both of these observations are the result of the inadequacy of the simple Langmuir equation to model adsorption by heterogeneous adsorbents.

O'Connor and Renn (34) reported on the adsorption of zinc(II) by river silt. They noted that the adsorption process is pH dependent, adsorption increasing as the pH is raised. Using silt concentrations of 171 parts per million and equilibrium zinc concentrations between 2.9 and 159 μM at pH 7.3, they fit their adsorption data to the Freundlich equation obtaining X equal to $1.59C^{0.614}$. Fitting their data to the linearized Langmuir model one calculates X_m equal to 109 $\mu\text{mol/g}$ and K equal to 42 μM .

Posselt, Anderson and Weber (28) demonstrated the high adsorptive capacity of colloidal hydrous manganese dioxide (MnO_2) for cations. They noted that the pH of the isoelectric point (IEP) of MnO_2 is quite low, ranging from pH 2.8 to pH 4.5. At higher pH colloidal manganese dioxide

has a net negative charge. These workers demonstrated that the mechanism of adsorption by MnO_2 is primarily electrostatic by comparing the adsorption of cationic, anionic and uncharged organic compounds. Only the organic cation showed any significant adsorption, and it was adsorbed to about the same extent as the metal cations investigated. For metals including calcium, magnesium and silver, X_m values of 1000 to 3000 $\mu\text{mol/g}$ and K values ranging from 35 to 170 μM were reported. These data were collected using equilibrium metal concentrations between 30 and 1500 μM and MnO_2 concentrations of 10^{-3}M (86 mg/l).

In a later study, Posselt and Weber (29) investigated the removal of trace cadmium by adsorption onto hydrous oxides of manganese, iron and aluminum. They stated that the IEP of iron and aluminum hydroxides is much higher than for MnO_2 , ranging from 5 to 8.5. As a result, MnO_2 is a much more effective adsorbent for cations. They reported X_m values ranging from 1370 $\mu\text{mol/g}$ at pH 5 to 2200 $\mu\text{mol/g}$ at pH 8.3 for the adsorption of Cd^{2+} onto MnO_2 . Calculated values of K were on the order of 0.04 μM . In experiments conducted between pH 5 and 7 the initial cadmium concentration was maintained at 10 μM , and the MnO_2 concentration was varied from 0.91 to 12.7 mg/l; above pH 7 the initial cadmium concentration was reduced to 0.8 μM , and MnO_2 concentrations from 9.1 to 63.7 mg/l were employed. Gadde and Laitinen (25) studied the adsorption of several metals on hydrous manganese oxide and hydrous ferric oxides. In general, adsorption followed the order $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$ and was pH dependent.

Smith et al. (35) reported the use of activated carbon to remove mercury from caustic soda plant effluent. They showed that methyl mercury chloride, an organic mercury compound, is highly adsorbed by activated carbon.

Sigworth and Smith (36) reported that the potential for adsorption of cadmium by activated carbon is slight. In a subsequent paper Smith (37) discussed the various mechanisms by which activated carbon can remove metals from aqueous solution. These include adsorption, precipitation, ion exchange, reduction or oxidation, and filtration. He stated that metal complexes can be strongly adsorbed and cited Leontiadis's (38) work involving adsorption of a chromium-EDTA complex to increase the sensitivity of a radiochemical detector. Nelson et al. (32) showed that enhanced adsorption of Fe(III) by activated carbon occurs when complexed by chloride ion.

Huang and Wu (39) reported the removal of chromate anions from solution by calcinated coke. Their work showed that low pH favors the adsorption of chromate ions by this adsorbent. Interestingly, Huang and Wu observed that the extent of adsorption by 100 to 200 mesh powdered coke to be about double that of 10 to 20 mesh granular coke. The authors seemed to conclude that the difference in adsorption was due to the larger surface area of the powdered adsorbent. Adsorbents such as activated carbon have a relatively large internal surface area and, therefore, the increase in total surface area as a result of grinding to smaller particles is negligible. However, adsorbent particle size can profoundly affect the rate of adsorption; smaller particles adsorbing more quickly than larger ones (21). Huang and Wu reported no details as to the adsorbent surface area or the rate of adsorption. Fitting their adsorption data collected at pH 2 to Equation 20 one calculates X_m equal to $42.8 \mu\text{mol/g}$ and K equal to $345 \mu\text{M}$ for the 10 to 20 mesh calcinated coke. Using the 100 to 200 mesh adsorbent, X_m and K are $99 \mu\text{mol/g}$ and $158 \mu\text{M}$, respectively. Equilibrium chromate concentrations ranged from 100 to $6000 \mu\text{M}$. These results indicate

that chromate ions are only slightly adsorbed by calcinated coke even at high equilibrium concentrations. Table 1 is a summary of the Langmuir adsorption parameters just discussed.

O'Connor, Badorek and Thiem (40) investigated the removal of trace cadmium from water by adsorption onto activated carbon. Their batch studies included the use of various chelating agents to enhance removal. The increased adsorption of cadmium by activated carbon as a result of complexation with EDTA was observed under certain conditions. In these experiments the initial cadmium concentration was maintained at $0.45 \mu\text{M}$ (0.05 mg/l), the calcium bicarbonate concentration at 10^{-3} M and the pH at 7. Several EDTA concentrations were investigated and carbon doses ranging from 10 to 100 mg/l were employed. In the absence of EDTA, only about 50% of the initial Cd^{2+} concentration was removed by 80 mg/l of activated carbon. At an EDTA to Cd^{2+} molar ratio of 0.1, almost 90% of the cadmium was removed by carbon doses of 40 mg/l or larger. Using an EDTA to Cd ratio of 1.0 the removal of cadmium was only about 70% and at a ratio of 10 only 20% of the cadmium was removed, which is less than half the removal that resulted when no EDTA was added. In all these experiments the calculated X values are small, on the order of 5 to 10 μmol s of cadmium per gram of carbon. It is interesting that the greatest removal of cadmium occurred at an EDTA to Cd^{2+} ratio of 0.1 instead of 1.0 which is the stoichiometric ratio of the stable Cd-EDTA complex. This observation, plus the suppression of cadmium adsorption by excess EDTA, suggests that competitive adsorption occurred among the free cadmium ions, the Cd-EDTA complex ions and uncomplexed EDTA. Furthermore, it suggests that the adsorbability of EDTA and the Cd-EDTA complex was not significantly greater than that of free Cd^{2+} ions. The slight adsorbability

Table 1. REPRESENTATIVE LANGMUIR ADSORPTION PARAMETERS

K μM	X_m $\mu\text{mol/g}$	pH	Adsorbate		Adsorbent	
			solute	equil conc. range, μM	solid	conc., mg/l
0.5-4.0	160-400		ABS detergents	0.5-50	activated carbon	50
9.3	1090		phenol	5-210	" "	50
5000	4500		phenol	1000-140,000	" "	50
42	109	7.3	Zn^{2+}	2.9-159	river silt	171
35-170	1000-3000		Ca^{2+} , Mg^{2+} , Ag^+	35-170	MnO_2	86
0.04	1370	5	Cd^{2+}	10	MnO_2	.91-12.7
0.04	2200	8.3	Cd^{2+}	0.8	MnO_2	.0091-.0637
345	42.8	2	CrO_4^{2-}	100-6000	10-20 mesh calcinated coke	5000
158	99	2	CrO_4^{2-}	100-6000	100-200 mesh calcinated coke	5000

of EDTA seems reasonable based upon its high solubility which Welcher (41) reported as being 11.1 g per 100 grams of solution, or approximately 0.3 M, at 21°C.

O'Connor and co-workers reported that citric acid shows little tendency to increase the adsorption of cadmium by activated carbon. In fact, their data shows that a ratio of citric acid to Cd^{2+} of 0.1 resulted in a suppressed cadmium removal of only 18%. As the citric acid to Cd^{2+} ratio was increased to 1 and then to 10, the removal of cadmium increased. At the ratio of 10, however, the removal of cadmium was only about the same as that in the absence of chelating agent. These observations can also be explained in terms of competitive adsorption and the high solubility of the chelating agent.

More recently, Thieu, Badorek and O'Connor (42) described the adsorption of Hg^{2+} by activated carbon, using "tannic acid" as a chelating agent. As before, the extent of adsorption was dependent upon the ratio of chelating agent to metal ion concentration, and even under the conditions where the most extensive adsorption was observed, the surface coverage was only about 10 to 15 $\mu\text{mol/g}$ using an initial Hg^{2+} concentration of 0.05 μM . The authors expressed surprise that Ca^{2+} ions did not interfere with the adsorption of Hg^{2+} by activated carbon. Actually, this is not surprising at all since calcium is more soluble than mercury and has a much lesser tendency to form complex ions with organic ligands.

Purpose and Scope

Based upon studies reported in the literature it seems to be generally true that adsorption of metal ions from aqueous solution is controlled by an electrostatic mechanism. These adsorption reactions are quite sensitive to

pH; high pH favors the adsorption of cations and low pH favors the adsorption of anions. The adsorbability of uncharged molecular species seems to be more dependent upon the aqueous solubility of the material than the pH of solution; slightly soluble materials tend to be highly adsorbed.

Activated carbon is a readily available, inexpensive adsorbent. Unfortunately, carbon has little net surface charge and is thus ineffective for adsorbing dissolved metals. It seems possible, however, that effective adsorption of metals by activated carbon might be obtained by complexing the metal with a relatively insoluble organic molecule prior to contacting the carbon. The complexing agent of choice must be highly adsorbable by activated carbon and able to complex strongly with the metal. It is hoped that the resultant metal-organic complex would display adsorption properties more closely related to those of the organic molecule than of the free metal ion. This could allow the effective removal of low concentrations of metals by operation of carbon columns similar to those now employed for the removal of trace organics. In fact, it seems feasible that the simultaneous removal of organics and chelated metals could be carried out. Furthermore, the adsorption of the metal complex should be less sensitive to pH than the adsorption of the free metal ion because of partial charge shielding by the organic ligand.

To test these hypotheses, the following research objectives were established:

1. To study the adsorption of Cd(II), Pb(II) and Zn(II) by several different activated carbons as a function of pH.
2. To examine the extent of adsorption by activated carbon of
 - a) EDTA, a highly soluble chelating agent, and
 - b) 1,10-phenanthroline, a slightly soluble chelating agent.

3. To investigate the effect of complexation by these organic ligands upon the adsorptive removal of cadmium from aqueous solution by activated carbon.
4. To test the ability of the simple Langmuir and Freundlich equations to fit the experimental adsorption data.
5. To compare the ability of the various linear plotting forms of the Langmuir equation to predict the least-squares values of K and X_m from experimental data.

EXPERIMENTAL METHODS AND MATERIALS

Solutions and Suspensions

Demineralized, double-distilled water with a specific conductance equivalent to less than 1.0 part per million as NaCl was used for the preparation of all solutions and activated carbon suspensions. Reagent grade chemicals were used throughout, and polypropylene bottles were used as reaction vessels and to store all solutions.

Four activated carbons were examined. Three were manufactured by Westvaco Chemical Division in Covington, Virginia, including Nuchar WV-L, Aqua Nuchar, and Nuchar S-A. The fourth was Darco HDC manufactured by ICI United States, Inc., of Wilmington, Delaware. The Darco carbon was a lignite base material while the WV-L and Aqua Nuchar carbons had bituminous coal matrices. The remaining carbon was wood based. All of these carbons were produced by a high temperature activation process (1800 to 2000°F) under reducing conditions. The carbons were obtained in powdered form with the exception of Nuchar WV-L which was an 8x30-mesh granular material. A 50 to 200-mesh powdered activated carbon was produced from the granular WV-L by grinding in an electric blender followed by careful sizing through U.S. Standard sieves. This particular carbon was used for most of the studies. Suspensions of the powdered carbons were prepared each day of use by mixing a weighed amount with distilled water in a volumetric flask.

0.01 M stock solutions were prepared from the hydrated nitrate salts of cadmium, zinc and lead. Metal ion solutions for atomic adsorption spectrophotometry standards were prepared according to the Perkin-Elmer analytical methods guide. Disodium ethylenediaminetetraacetate (EDTA)

solutions were prepared by drying the dihydrate at 80° for four days and cooling in a desiccator, after which 37.21 g/l were dissolved. Three replicates of EDTA solution standardized against standard calcium solution had an average concentration of 0.0994 M or 0.0995 M with standard deviations of ± 0.0002 M. 1,10-phenanthroline 0.001 M stock solution was prepared by dissolving 0.180 g/l of the solid reagent (G. Frederick Smith Chemical Co.). The addition of 5 to 10 ml of concentrated HCl and moderate heating were required for dissolution. Just prior to the start of an experiment, metal ion and/or chelating agent working solutions were prepared by volumetric dilution of the appropriate stock solutions. Sodium chloride or lithium perchlorate solutions were used for ionic strength adjustment. Acetate and phosphate buffer solutions were each prepared at two concentrations. 1.0 M buffer solution was used in adsorption experiments in which the carbon dose was 5000 mg/l. With doses of 500 mg/l or less, 0.1 M buffer was used.

Experimental Procedures

All test mixtures were prepared as follows, except where otherwise noted. To a 100-ml volumetric flask were added:

1. An aliquot of cadmium nitrate (or other metal salt) working solution using a 25-ml automatic zero buret,
2. 1 ml of 1.0 M LiClO_4 solution using an Eppendorf auto-pipet,
3. 1 ml of the appropriate buffer solution from an Eppendorf auto-pipet,
4. A quantitative volume of working chelating agent solution (if required) from a 25-ml automatic zero buret, and
5. 25 ml of well mixed activated carbon suspension from a 25-ml pyrex volumetric delivery flask, or an equivalent amount of granular carbon.

Dilution to the mark with distilled water produced a mixture that was well defined in terms of metal ion, chelating agent and activated carbon concentrations, ionic strength and pH. Modifications of this procedure were required in the kinetic and chelating agent adsorption studies.

For the kinetic study initial volumes were 1000 ml so as to minimize the effect of volume depletion due to sampling. For these experiments both the granular and powdered carbon were weighed on an analytical balance and added to one-liter volumes of test solution at the start of experimentation. A 5-ml sample was withdrawn from each of the two reactors with a Mohr pipet at each sampling time. Test mixtures for the chelating agent adsorption studies were prepared as previously described but with no cadmium added. Prior to analysis these test mixtures were filtered through Whatman No. 1 paper to remove the powdered carbon. Corrections for adsorption by the paper filter were made.

Blank solutions were prepared the same way as the test mixtures but omitting the activated carbon. Analysis of these blanks repeatedly confirmed the accuracy of this procedure for the quantitative preparation of test mixtures. Initially, blanks were prepared to correspond to each test mixture so that the effects of container wall adsorption and precipitation as well as the precision of the analytical methods could be assessed. Later, blanks were run only for selected samples. Whenever experimental conditions were changed (e.g., different pH or chelating agent) extensive blanks were run to check for wall adsorption and precipitation.

During equilibration, samples were shaken on an Eberbach variable speed laboratory shaker. The shaker box was insulated with 1 inch of fiberglass wool to prevent excessive heat transfer from the shaker motor to the test

mixtures. The temperature of the samples at the conclusion of each experiment did not vary by more than $\pm 3^{\circ}\text{C}$ from 24°C . Prior to analysis for residual metal, all test mixtures containing powdered carbon were centrifuged to ensure good separation of the test solution from the adsorbent. Gravity settling was adequate to separate the granular carbon from the test solutions.

Analytical and Calculation Procedures

A Sargent-Welch model NX digital pH meter and combustion electrode were used to measure the final pH of the solutions. Metal ion concentrations in the experimental solutions were determined with a Perkin-Elmer model 403 atomic adsorption spectrophotometer using flame atomization. Signal output was recorded by a Sargent model SRG strip recorder.

The analytical scheme was as follows. Thirty minutes or more prior to the start of an analysis the main power to the instrument was turned on. This warm up period improved signal stability and detection, especially at sub-milligram per liter concentrations. After the flame was ignited, distilled water was aspirated through the burner until a stable baseline signal was obtained. Standard solutions bracketing the range of concentrations to be analyzed were aspirated and the pen deflections were adjusted to correspond to the calibration curve. Samples were aspirated until a stable recorder signal was obtained. Following each experimental sample, a distilled water blank was aspirated to check for baseline drift. After every five or six samples a standard solution was aspirated to check for signal stability. Any baseline or signal drift greater than 1% was cause for restandardization of the instrument and reanalysis of the affected sample. Recorder deflections were converted to concentration units using the calibration curve.

EDTA and 1,10-phenanthroline concentrations were determined by complexometric titration with a standard Cd^{2+} solution. The course of the reaction was monitored potentiometrically using an Orion (model 94-48A) cadmium ion electrode coupled with an Orion model 90-01 single junction reference electrode and Orion model 801A "Ionalyzer". The Gran's plotting procedure which facilitates potentiometric endpoint determination using only four or five values from the titration curve was employed (43). All concentrations were calculated to the nearest $0.1 \mu\text{mol/l}$. Lead was determined by a similar procedure using a Lazaar (model IS-146) ion selective electrode. Zinc was determined with a procedure involving an Orion (model 94-29) cupric ion electrode. Since the ion sensed by the electrode (cupric ion) was absent from the sample, an indicator was prepared by titrating an 0.01 M copper solution with tetraethylenepentamine (TEPA) exactly to the endpoint. One ml of this 0.01 M CuTEPA solution was added to a 100-ml zinc sample and subsequently titrated with TEPA solution.

A Fortran program was used to calculate the adsorption variables from raw data that are needed to plot Langmuir and Freundlich isotherms. Computer analysis using the "Statistical Analysis System" developed at North Carolina State University (44) was carried out to investigate the ability of the various linearized forms of the Langmuir equation to predict the least squares values of the Langmuir parameters K and X_m for fitting isotherms to experimental data points. The Biomedical Computer Program X85, "Nonlinear Least Squares" (45), was used to obtain the best "unbiased" estimates of the Langmuir parameters. All computing was done at The Ohio State University Instruction and Research Computer Center.

The isoelectric points for each of the activated carbons were determined

by titration with acid or base solutions adjusted to different ionic strengths with sodium chloride. A sample of activated carbon was washed prior to titration with double distilled water and dried at 105°C. The washing was repeated five times to assure removal of impurities. One-half gram of carbon in 100 ml of solution was then titrated while passing nitrogen gas through the solution to purge the CO₂. The titrant was 0.01 N HCl with three titrations performed, each at a different ionic strength. Equilibrium was attained before recording the pH. This procedure was repeated using 0.01 N NaOH as the titrant. From the data generated, the hydrogen ions or hydroxide ions adsorbed by the carbon was calculated. The excess of one over the other adsorbed is determined by the difference between total added base or acid and the equilibrium OH⁻ and H⁺ concentrations in solution.

EXPERIMENTAL RESULTS

Preliminary Studies

Initial experiments were run to evaluate analytical procedures and to assess the loss of cadmium from solution by precipitation or as a result of adsorption onto the walls of the polypropylene reaction vessels. Studies were then performed to compare the rate of cadmium ion adsorption by granular and powdered activated carbons.

From the preliminary experiments it was concluded that atomic adsorption spectrophotometry is well suited to trace metal studies of this type because of ease of operation, speed, analytical precision and sensitivity and its freedom from interferences by the organic chelating agents and carbon-leachable organics. The titrimetric procedure adapted for analysis of residual chelating agents, however, was less reproducible. This lack of analytical precision is reflected in the scatter of EDTA and 1,10-phenanthroline adsorption data presented in subsequent sections. Analysis of $9.8 \mu\text{M}$ cadmium solutions without chelating agent or activated carbon showed that below about pH 8 less than 2% was lost due to container wall adsorption and precipitation during the 24-hour reaction period. Above about pH 8.5 there was significant loss of cadmium, however. In contrast, solutions which also contained chelating agents showed much less cadmium loss at high pH.

Figure 1 shows the uptake of cadmium as a function of time from a $9.8 \mu\text{M}$ (1.1 mg/l) solution at pH 6.6 by 5000 mg/l Nuchar WV-L activated carbon. Comparison is made between 8 to 10 mesh granular carbon (circles) and 50 to 200 mesh powdered carbon (squares). The granular activated carbon required more than 95 hours to reach equilibrium adsorption whereas adsorption by the

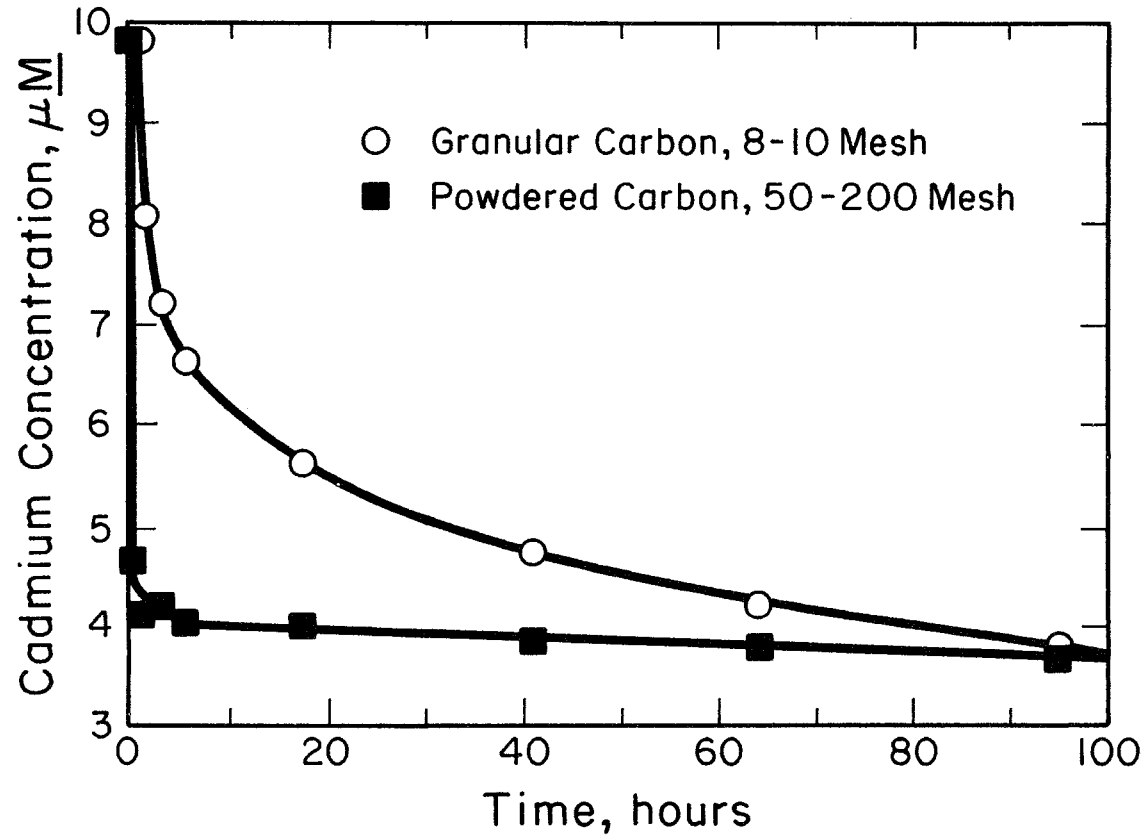


Figure 1. RATE OF CADMIUM ADSORPTION BY POWDERED AND GRANULAR NUCHAR WV-L ACTIVATED CARBON AT pH 6.6. Carbon Dose 5000 mg/l.

powdered carbon was virtually complete in less than six hours. A slight additional uptake of cadmium by the powdered carbon (approximately $0.1 \mu\text{mol/g-day}$) continued throughout the remainder of the testing period, but was negligible compared to the initial adsorption. It should be noted that the "equilibrium" adsorptive capacities of the granular and powdered carbon are nearly equal. The rapid adsorption rate of powdered carbon, its similar adsorptive capacity to granular forms and the ease of quantitative carbon dosing using a well-mixed slurry make powdered carbon ideally suited for batch adsorption studies. As a result, all further experiments were conducted using 50 to 200 mesh powdered carbon. Samples were shaken for 24 hours to provide adequate reaction time for the attainment of equilibrium in all samples.

Effect of pH, EDTA and Adsorbent Dose

As previously discussed, it is a common observation that the adsorption of cations is favored by high pH. Also, adsorptive removal tends to increase as the adsorbent concentration is raised. Figure 2A shows the percent removal of free Cd^{2+} ions by powdered Nuchar WV-L activated carbon as a function of pH. Three carbon doses are compared using an initial cadmium concentration of $9.8 \mu\text{M}$. Open symbols represent acetate buffered samples and blackened symbols are for phosphate buffered samples. The data clearly show that, as expected, increasing the adsorbent dose and pH results in a greater percent removal of cadmium. No significant effect due to the type of buffer was observed. Figure 2B shows the percent cadmium removal from a solution that was initially $9.8 \mu\text{M}$ in both cadmium and EDTA. For a carbon dose of 5000 mg/l (circles) the presence of EDTA enhanced the removal of cadmium over most of the pH range. At 500 (squares) and 50 (triangles) mg/l carbon, however, EDTA

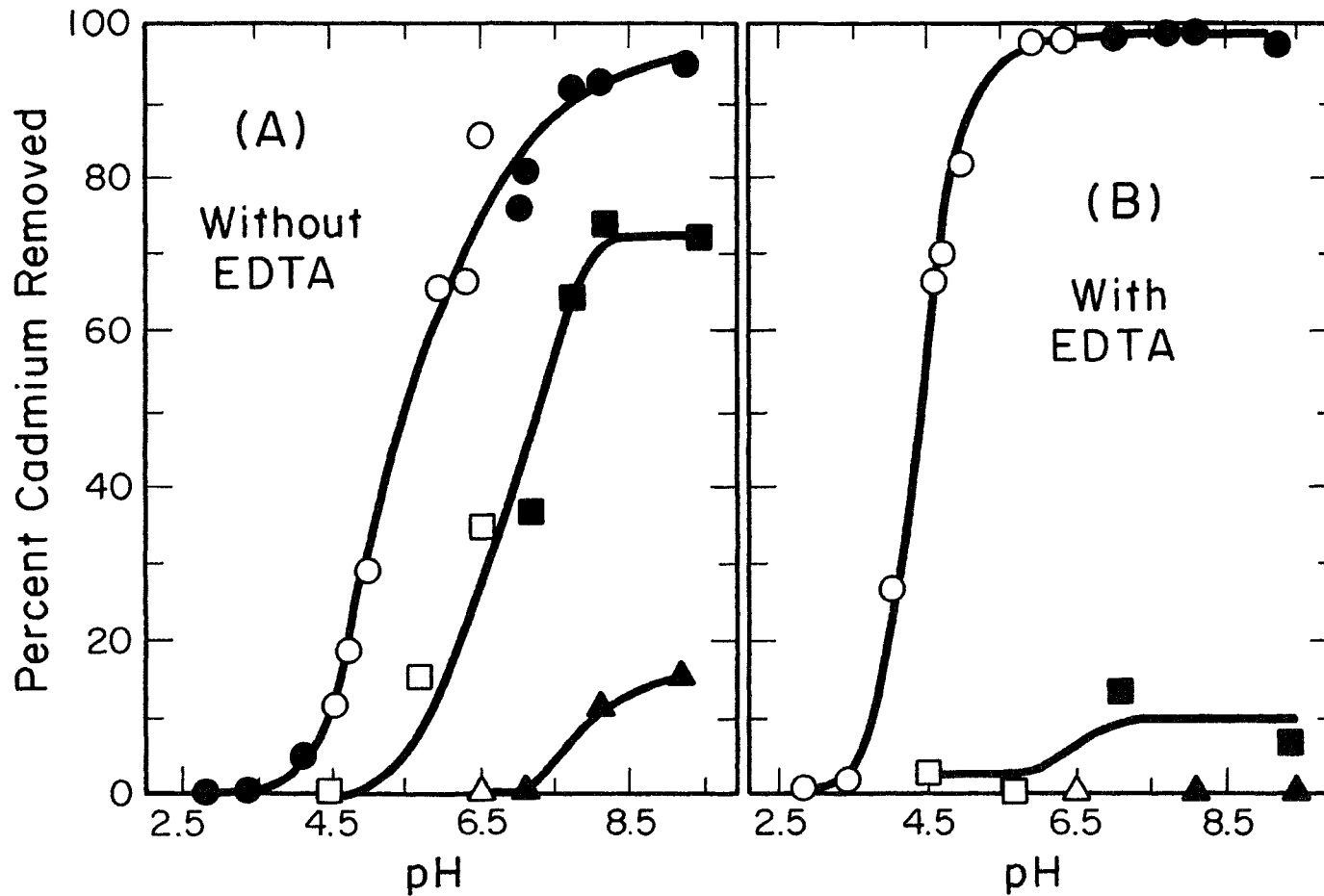


Figure 2. REMOVAL OF CADMIUM AT DIFFERENT CARBON DOSES AS A FUNCTION OF pH IN THE ABSENCE AND PRESENCE OF EDTA. Circles represent 5000, squares represent 500, and triangle represent 50 mg/1 carbon. Initial Cd^{2+} and EDTA concentrations were each $9.8 \mu\text{M}$. Open symbols are acetate and blackened symbols are phosphate buffered systems.

Table 2. SUMMARY OF CADMIUM REMOVAL AS A FUNCTION OF pH

Carbon Dose mg/l	Buffer	pH	Cd ONLY		Cd plus EDTA	
			$[Cd]_f$ μM	Percent Removal	$[Cd]_f$ μM	Percent Removal
5000	Phosph.	2.80	10.18	0	9.73	0.9
5000	Phosph.	3.40	9.91	0	9.64	1.8
5000	Phosph.	4.10	9.28	5.4	7.14	27.3
5000	Acetate	4.60	8.57	12.7	3.21	67.3
5000	Acetate	4.70	7.95	19.1	2.95	70.0
5000	Acetate	4.95	6.96	29.1	1.70	82.7
5000	Acetate	5.90	3.30	66.4	0.18	98.0
5000	Acetate	6.00	3.30	66.4	0.18	98.0
5000	Acetate	6.30	3.21	67.3	0.18	98.0
5000	Acetate	6.55	1.34	86.4	--	--
5000	Phosph.	6.95	2.32	76.4	0.09	99.0
5000	Phosph.	7.10	1.79	81.8	0.09	99.0
5000	Phosph.	7.70	0.80	92.7	0.09	99.0
5000	Phosph.	7.75	0.80	92.7	0.09	99.0
5000	Phosph.	8.10	0.80	92.7	0.09	99.0
5000	Phosph.	9.20	0.45	95.0	0.27	97.3
500	Acetate	4.50	9.82	0	9.56	3.0
500	Acetate	5.70	8.30	15.0	9.80	0
500	Phosph.	6.50	6.43	35.0	--	--
500	Phosph.	7.10	6.16	37.3	8.48	13.6
500	Phosph.	8.10	2.41	74.7	--	--
500	Phosph.	9.40	2.50	72.0	9.20	6.0
50	Phosph.	5.70	--	--	9.80	0
50	Acetate	6.50	9.90	0	9.80	0
50	Phosph.	7.10	9.90	0	--	--
50	Phosph.	8.10	8.75	11.0	9.80	0
50	Phosph.	9.20	8.30	15.0	--	--
50	Phosph.	9.40	--	--	9.80	0

suppressed the removal of cadmium. The data shown in Figure 2 is also summarized in Table 2.

Comparison of Isotherms and Models

Isotherms for the adsorption of cadmium ion by Nuchar WV-L are presented in Figures 3 through 7. Carbon doses in these experiments were always 500 mg/l or less. In the figures, open symbols are for carbon doses of 500 mg/l; blackened symbols represent lower doses. Unless otherwise specified, the Langmuir parameters X_m and K were determined from the data using the nonlinear least-squares program discussed earlier (45). Freundlich parameters k and $1/n$ were calculated from a linear least-squares analysis of experimental adsorption data transformed according to Equation 7. These adsorption parameters were then used to calculate the Langmuir and Freundlich adsorption isotherms represented in the figures by solid and broken lines, respectively. The calculated parameters are summarized in Table 3.

Figure 3 compares the adsorption of uncomplexed (free) Cd^{2+} at pH 5.7, 7.1 and 8.1 as a function of the equilibrium metal concentration. The importance of solution pH on cadmium adsorption is clearly shown. The calculated Langmuir and Freundlich isotherms for the pH 5.7 data are virtually identical and the solid line in the figure represents both isotherms. The nonlinear least-squares program was unable to successfully fit the pH 7.1 data to the Langmuir equation. This can be understood by close examination of the plotted data. Instead of bending toward the abscissa at higher concentrations, the data appear to be slightly concave upward. This also explains why the calculated pH 7.1 Freundlich isotherm shows such deviation from the experimental points at higher concentrations. For the pH 8.1 data the calculated Langmuir

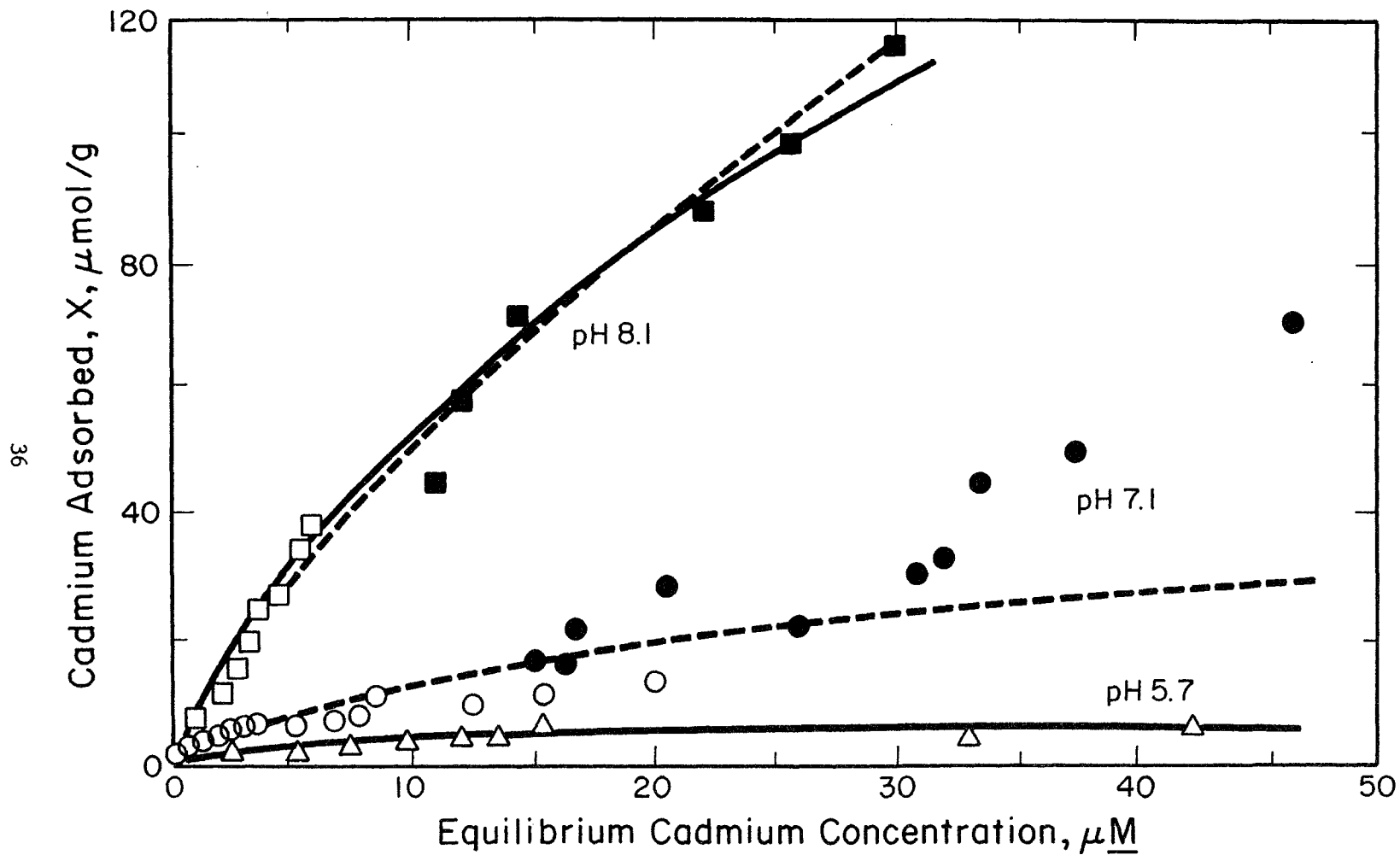


Figure 3. ADSORPTION OF CADMIUM ON NUCHAR WV-L AT pH 5.7, 7.1 and 8.1. Solid Line is calculated Langmuir isotherm; broken lines are calculated Freundlich isotherms. Carbon dose: 500 mg/1 (open symbols) and less than 500 mg/1 (blackened symbols).

parameters are $247 \mu\text{mol/g}$ and $37 \mu\text{M}$ for X_m and K , respectively; which fall beyond the range of the experimental points plotted in the figure. This indicates that the experimental adsorption data are relatively linear, being well below the plateau region of the isotherm. The portion of the Langmuir isotherm corresponding to sub-monolayer surface coverage is precisely the range where the Freundlich equation gives a good fit (20), as evidenced in the figure.

The seemingly contradictory observation indicated by Figure 2, that EDTA enhances cadmium adsorption by activated carbon at high carbon doses and suppresses cadmium adsorption at lower carbon doses, should be explainable by a comparison of the adsorption isotherms for free Cd^{2+} ion and the cadmium-EDTA complex. The pH 7.1 Freundlich adsorption isotherms for free EDTA and for the Cd-EDTA complex (measured as cadmium) are shown in Figure 4. The free Cd^{2+} ion adsorption isotherm at pH 7.1 from Figure 3 is included for comparison. The extensive scatter of the EDTA adsorption data (circles) results from the poor precision of the analytical technique used to measure the residual EDTA. The ordinate of Figure 4 is expanded four times relative to Figure 3. It is apparent from the figure that EDTA is less extensively adsorbed at pH 7.1 by Nuchar WV-L than is Cd^{2+} over most of the range of equilibrium adsorbate concentrations examined. The Cd-EDTA complex is adsorbed to an even lesser extent, being only about as adsorbable as free Cd^{2+} ion at pH 5.7. The isotherms in Figure 4 corroborate the data of Figure 2 (and Table 3) showing, at carbon doses of 50 or 500 mg/1, that free Cd^{2+} ion is more adsorbable than the Cd-EDTA complex over the equilibrium adsorbate concentration range between 5 and $50 \mu\text{M}$.

To further study the suppressive effect of EDTA upon the adsorption

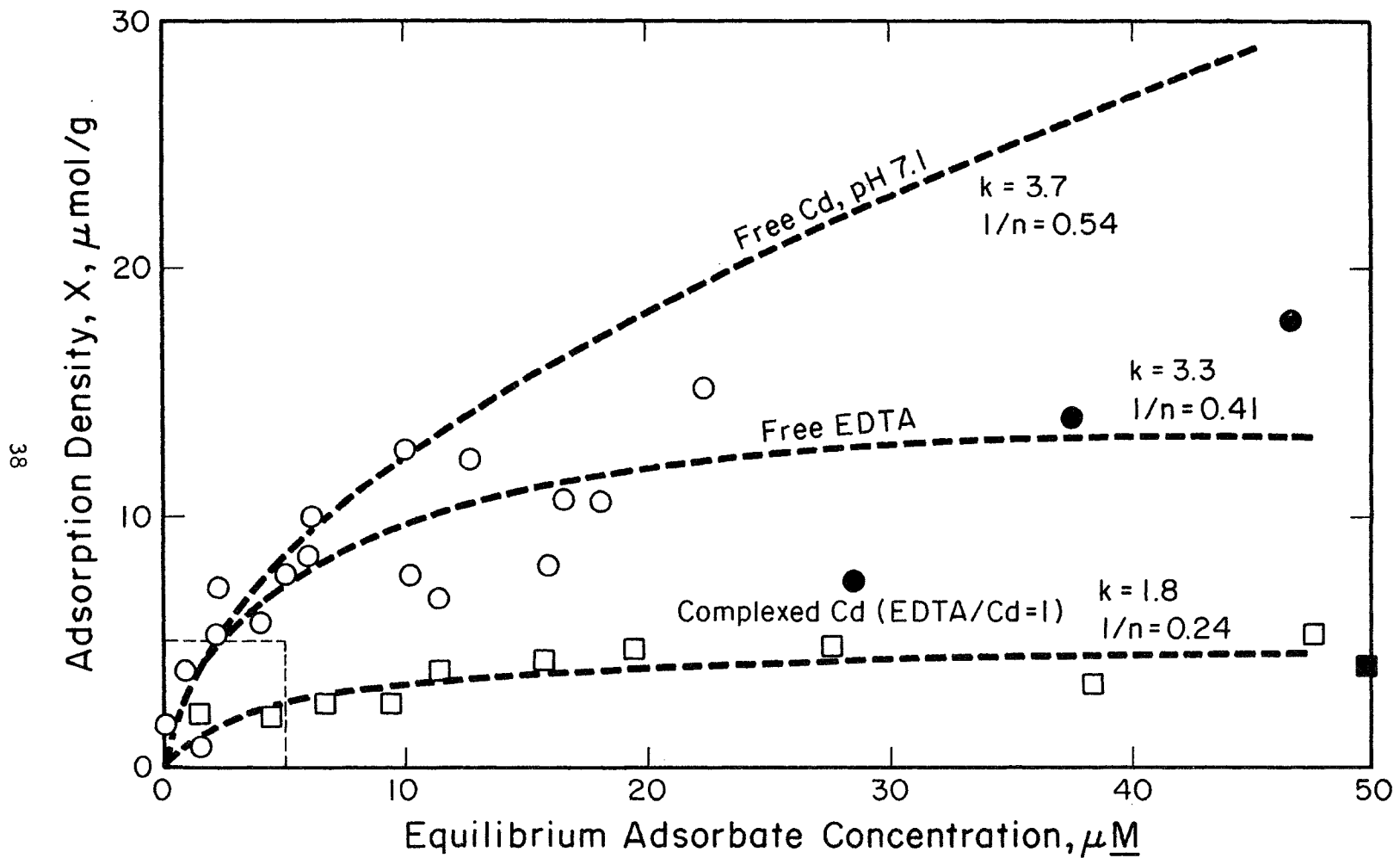


Figure 4. ADSORPTION OF FREE EDTA AND COMPLEXED CADMIUM BY NUCHAR WV-L AT pH 7.1. Circles are EDTA, squares are complexed cadmium. Carbon dose: 500 mg/l (open symbols) and less than 500 mg/l (blackened symbols).

of cadmium by activated carbon, the ratio of EDTA to cadmium in the test solution was varied. The results are shown in Figure 5. The free Cd^{2+} and the complexed cadmium (EDTA to metal ratio of 1.0) isotherms presented in Figure 4 are included for comparison. The circles and squares represent an EDTA to Cd ratio of 0.1 and 0.5, respectively. Figure 5 indicates that the principal effect of EDTA is to suppress the adsorption of cadmium by Nuchar WV-L, and that the extent of suppression is proportional to the EDTA concentration.

Effect of 1,10-phenanthroline

1,10-phenanthroline is relatively insoluble in water and hence should be readily adsorbed from aqueous solution by activated carbon. Figure 6 summarizes the equilibrium adsorption data for experiments at pH 7.1. The scatter in the data points resulted from the poor precision of the analytical technique used to measure residual phenanthroline. The extent of adsorption is similar in magnitude to that reported by Morris and Weber (21) for the adsorption of benzenesulfonate detergents onto activated carbon. The solid line is the calculated Langmuir isotherm with X_m equal to $1131 \mu\text{mol/g}$ and K equal to $12 \mu\text{M}$. The upper dashed line is the calculated Freundlich isotherm. The poor fit of the Freundlich equation to the 1,10-phenanthroline data occurred because adsorption is approaching a maximum value indicating almost complete monolayer coverage of the adsorbent. The Freundlich equation, of course, makes no allowance for a maximum surface coverage and therefore usually gives a poor fit to curvilinear data.

Figure 7 shows the adsorption of cadmium from a solution containing equimolar concentrations of the metal and 1,10-phenanthroline at pH 7.1 (circles) and pH 8.1 (squares). Carbon doses of 50 mg/l were employed in both cases.

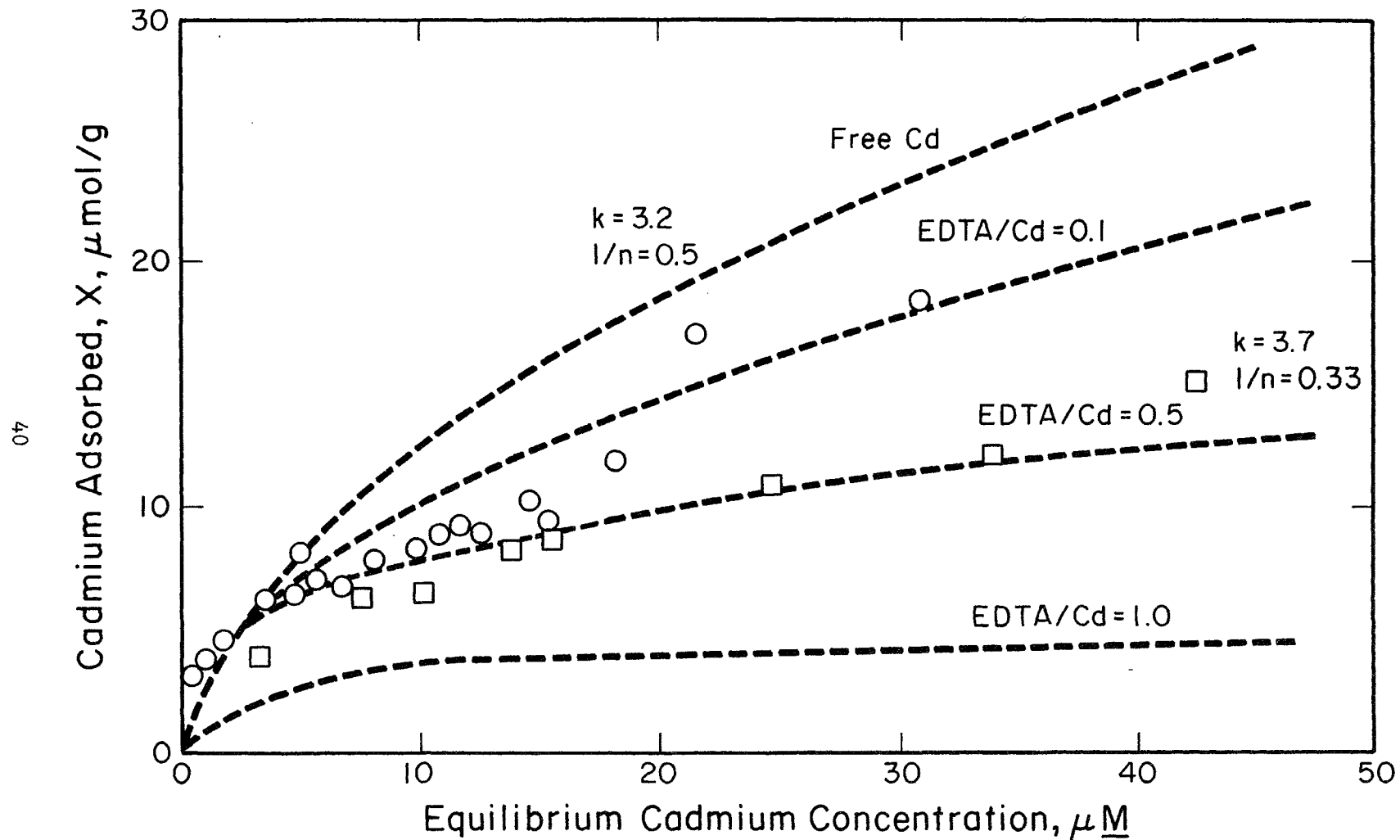


Figure 5. EFFECT OF THE MOLAR RATIO OF EDTA TO CADMIUM UPON ADSORPTION BY NUCHAR WV-L AT pH 7.1. Circles are EDTA/Cd = 0.1, squares are EDTA/Cd = 0.5. Carbon doses are 500 mg/l

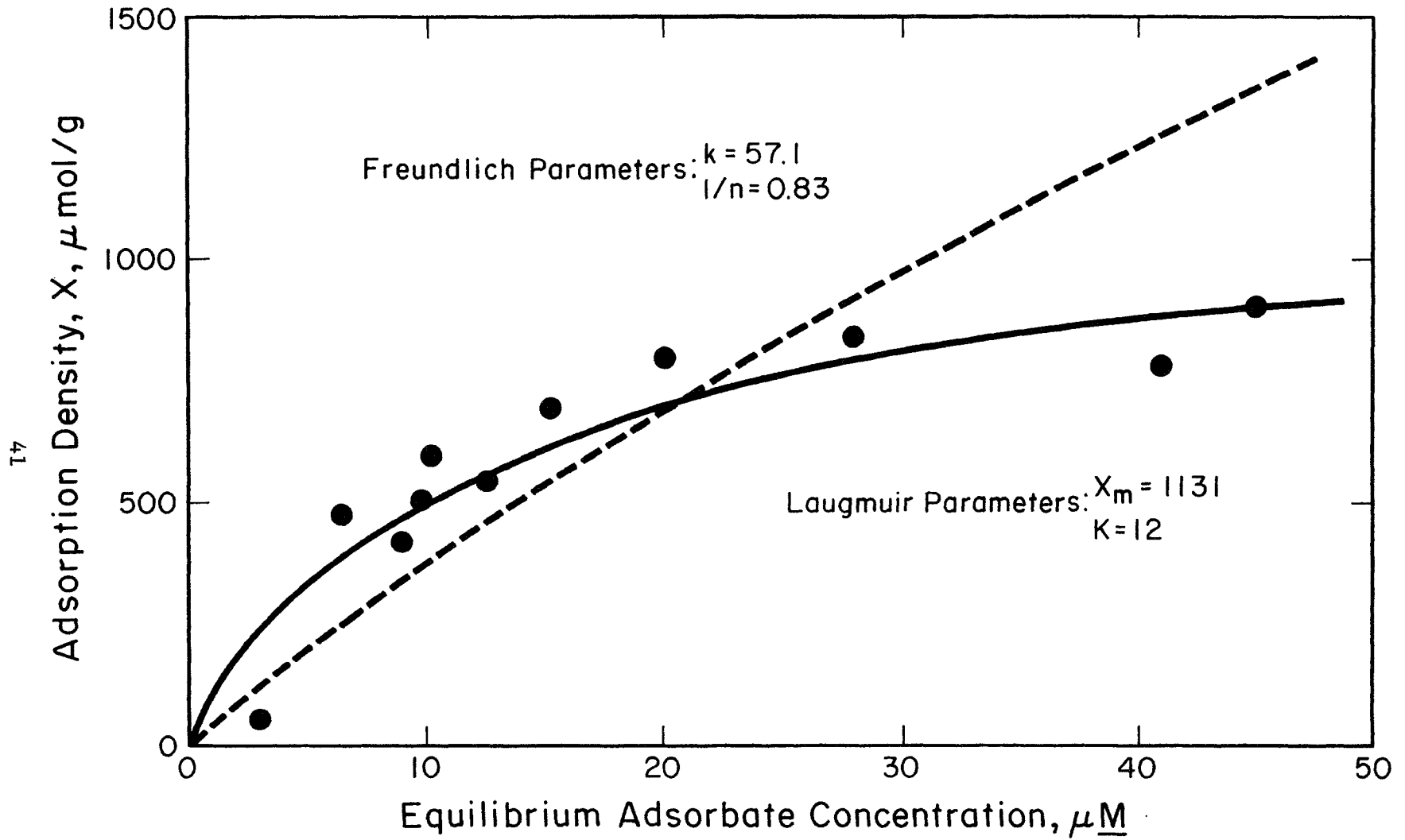


Figure 6. ADSORPTION OF 1,10-PHENANTHROLINE BY 50 mg/l NUCHAR WV-L. Dashed line is Freundlich isotherm; solid line is Langmuir isotherm.

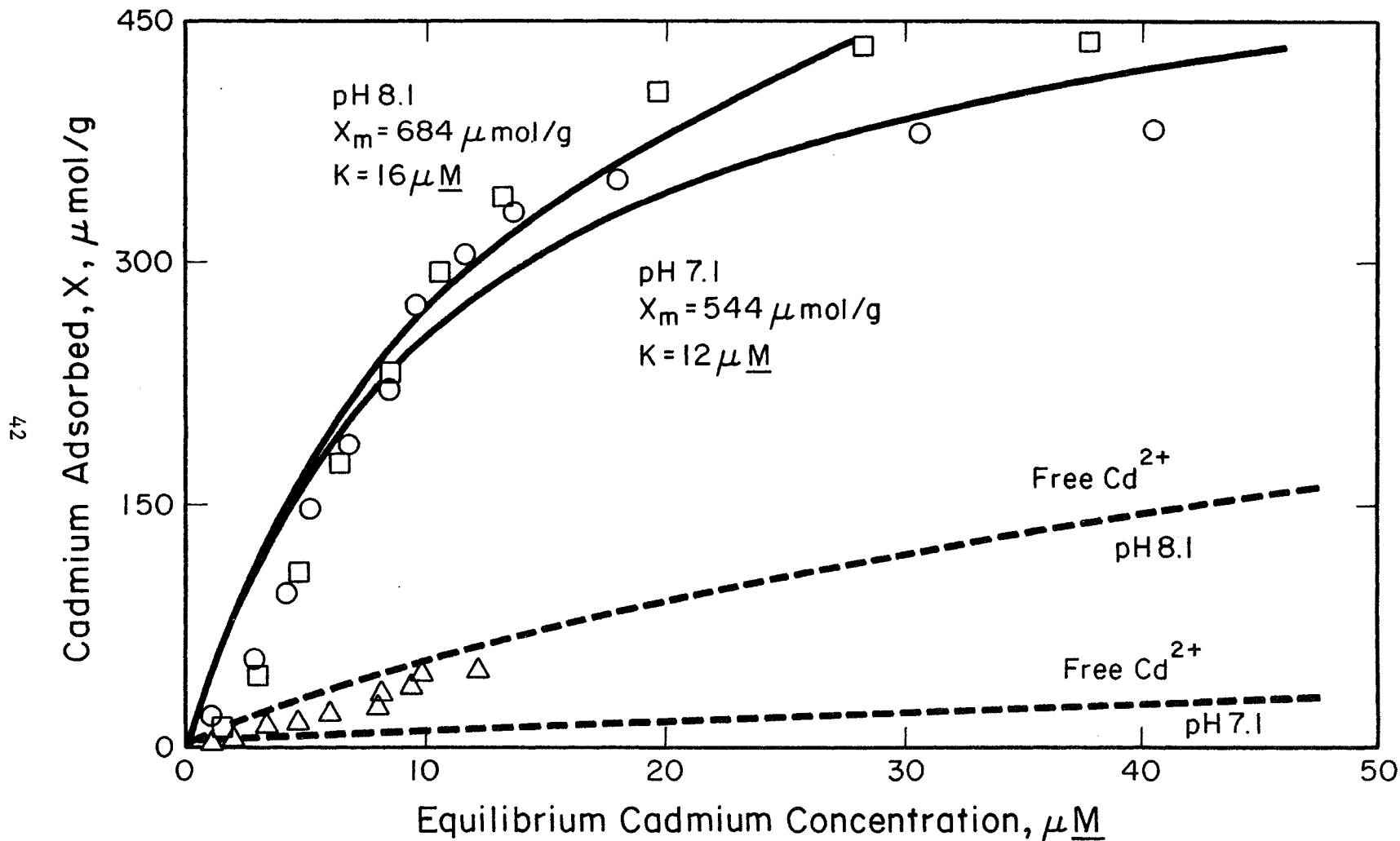


Figure 7. ADSORPTION FROM A 1,10-PHENANTHROLINE-CADMIUM EQUIMOLAR MIXTURE BY NUCHAR WV-L. Triangles are pH 7.1 and 500 mg/1 carbon. Circles are pH 7.1 and 50 mg/1 carbon. Squares are pH 8.1 and 50 mg/1 carbon.

The triangles represent data at pH 7.1 and carbon doses of 500 mg/l. The upper and lower dashed lines are the Freundlich isotherms for the adsorption of Cd^{2+} presented earlier.

Table 3 summarizes the adsorption isotherm parameters calculated from the experimental data. It is apparent that uncomplexed 1,10-phenanthroline is adsorbed to a much greater extent than free cadmium ion or EDTA.

Comparison of Other Carbons and Metals

A few experiments were run using three carbons in addition to Nuchar WV-L and with zinc and lead for comparison with cadmium. Using the procedure described by Parks and DeBruyn (46), the carbons were titrated with acid and base solutions at different ionic strengths to determine their isoelectric points. The results of these studies along with the manufacturer's values for their specific surface areas are summarized in Table 4.

The adsorptive capacity of 1,10-phenanthroline for each of the carbons at pH 7.1 was determined. The initial phenanthroline concentrations ranged from 5 to 1000 $\mu\text{mol/l}$ and 50 mg/l of powdered carbon was used for each experiment. The X_m values correlated directly with the surface area of the respective carbons.

X_m values for Cd, Zn and Pb at pH 6.5 and 8.0 were also determined for the four carbons and included in Table 4. There was no significant adsorption of the metals on Nuchar S-A, the carbon with the highest isoelectric point. Adsorption was greatest on the carbon with the lowest isoelectric point, but with the smallest specific surface area. The relative capacities of the carbons for the three metals followed the sequence reported by Gadde and Laitinen (25). The $\text{p}K_1$ for Cd, Zn and Pb (as defined by Equation 5) are 10.3, 9.17 and 7.86, respectively (47).

Table 3. SUMMARY OF EXPERIMENTAL ADSORPTION ISOTHERM PARAMETERS FOR NUCHAR WV-L POWDERED ACTIVATED CARBON*

<u>Adsorbate</u>	<u>pH</u>	<u>Langmuir</u>		<u>Freundlich</u>		<u>Ligand/Cd Ratio</u>
		<u>X_m</u>	<u>K</u>	<u>k</u>	<u>1/n</u>	
Cadmium	5.7	6	5	1.6	0.34	0
Cadmium	7.1	--	--	3.7	0.54	0
Cadmium	8.1	247	37	8.4	0.78	0
EDTA	7.1	14	5	3.3	0.41	--
Cd-EDTA	7.1	--	--	3.2	0.50	0.1
Cd-EDTA	7.1	14	7	3.7	0.33	0.5
Cd-EDTA	7.1	5	4	1.8	0.24	1.0
1,10-phen.	7.1	1131	12	57.1	0.83	--
Cd-phen.	7.1	544	12	29.8	0.85	1.0
Cd-Phen.	8.1	684	16	18.7	1.03	1.0

*Range of initial concentrations: 50 to 500 mg/l activated carbon; 5 to 50 μM cadmium; 1 to 50 μM EDTA; and 30 to 90 μM phenanthroline.

Table 4. COMPARISON OF METALS AND CARBONS

Activated Carbon	Surface Area cm ² /g	*IEP	X _m at pH 6.5			X _m at pH 8.0		
			Cd	Zn	Pb	Cd	Zn	Pb
Darco HDC	650	3.8	3.2	5.5	9.2	178	340	870
Nuchar WV-L	1000	4.3	3.2	5.5	9.2	160	310	821
Aqua-Nuchar	1000	6.2	2.0	2.7	5.6	125	220	620
Nuchar S-A	1500	8.3	<0.3	<0.3	<0.3	<10	<10	<10

*Isoelectric pH of carbons by the procedure of Parks and DeBruyn (46).

DISCUSSION AND CONCLUSIONS

Estimation of Langmuir Parameters

Throughout this research, the Langmuir parameters X_m and K were calculated using a nonlinear regression method with computer iteration (45). The procedure most commonly applied, however, involves a linear regression on one of the various transformations of the Langmuir equation. In particular, the double-reciprocal form (Equation 18) is widely used. There are some pitfalls associated with regressions on these linear equations (33). In addition, the limiting assumptions of the simple Langmuir model are not always valid for a given solute-solid system. This frequently is obvious, for example, with data generated when using heterogeneous adsorbents or when there are significant lateral interactions between adsorbate molecules at the solid surface (48, 49).

Both aspects of using the Langmuir equation to calculate X_m and K , its linearization and its applicability, were examined using either the phenanthroline or the Cd-phenanthroline adsorption data shown in Figures 6 and 7. These systems were chosen since both the organic chelating agent and its metal complex were extensively adsorbed, minimizing the relative error of the calculated adsorption densities. Both exhibited typical Langmuirian behavior insofar as the adsorption densities reached a plateau of limiting values; the Cd-phenanthroline data, however, were untypical in that the isotherm formed an "S" curve (see reference 48).

As presented by Snedecor and Cochran (50), the simple linear regression equation has the mathematical form

$$R = \alpha + \beta + E \quad \dots(24)$$

The assumptions involved are that: 1. for each independent variable, I, there is a normally distributed population of dependent or response variables, R, from which the sample value of R is drawn; 2. the population of R for each I has a mean or average value, μ , that lies on the straight line $\mu = \alpha + \beta (I - \bar{I})$ such that $(I - \bar{I})$ is equal to i ; 3. the standard deviation (σ_R) of all R populations is equal; and 4. the independent variable is known with infinite precision. In reality, the independent variable is a measured quantity having a finite precision and, thus, a finite standard deviation. Usually, however, the independent variable can be measured precisely enough so that the standard deviation is negligibly small.

A plot of adsorption density against equilibrium adsorbate concentration which conforms to the Langmuir model closely approximates all of the criteria for application of the linear regression equation except, of course, for criterion 2 above, since the relationship between C and X is not linear. Transformation linearizes the relationship but also tends to alter it so that one or more of requirements of the linear regression model are no longer satisfied. This can be illustrated by Table 5 wherein are listed several values of C and X calculated from the Langmuir equation using X_m and K set equal to 6.0 and 2.0, respectively. The tabulated X values, therefore, represent "exact" Langmuir adsorption quantities. By assigning a small but constant standard deviation to the C values of ± 0.05 and a somewhat larger but constant standard deviation to the X values of ± 0.5 , the tabulated values can be considered "experimental" quantities. The various transformed variables listed in Table 5 were then calculated for three values of X and C. Close examination of the transformed values reveals that the standard deviations are not constant from observation to observation. For example, for X equal to

Table 5. TRANSFORMED LANGMUIR ADSORPTION VALUES

$\sigma_c = \pm 0.05$	C	$\sigma_x = \pm 0.5$	X	1/C			1/X			C/X			X/C		
				min.	avg.	max.	min.	avg.	max.	min.	avg.	max.	min.	avg.	max.
	0.50		1.20	1.82	2.00	2.22	0.59	0.83	1.43	0.26	0.42	0.79	1.27	2.40	3.78
	2.00		3.00												
	4.00		4.00												
	6.00		4.50												
	8.00		4.80	0.12	0.13	0.13	0.19	0.21	0.23	1.50	1.67	1.87	0.53	0.60	0.67
	12.00		5.14												
	14.00		5.25	0.07	0.07	0.07	0.17	0.19	0.21	2.43	2.67	2.96	0.34	0.38	0.41

Notes:

$$1/C_{\min} = 1/(C + \sigma_c)$$

$$1/C_{\text{avg}} = 1/C$$

$$1/C_{\max} = 1/(C - \sigma_c)$$

$$1/X_{\min} = 1/(X + \sigma_x)$$

$$1/X_{\text{avg}} = 1/X$$

$$1/X_{\max} = 1/(X - \sigma_x)$$

$$(C/X)_{\min} = (C - \sigma_c)/(X + \sigma_x)$$

$$(C/X)_{\text{avg}} = C/X$$

$$(C/X)_{\max} = (C + \sigma_c)/(X - \sigma_x)$$

$$(X/C)_{\min} = (X - \sigma_x)/(C + \sigma_c)$$

$$(X/C)_{\text{avg}} = X/C$$

$$(X/C)_{\max} = (X + \sigma_x)/(C - \sigma_c)$$

1.20 ± 0.5 the range of $1/X$ is from 0.59 to 1.43, but for X equal to 4.80 the range of $1/X$ is only 0.19 to 0.23. The linear regression equation is not strictly applicable to the analysis of such transformed data. Consequently, linear regression analysis of "experimental" data using the six linear Langmuir forms (Equations 18 through 23) will result in a unique solution of X_m and K for each form. These solutions will only be estimates of the least-squares best fit values of X_m and K obtained from a nonlinear least squares analysis. Except for rounding errors, all seven forms will calculate the same values of X_m and K from "exact" Langmuir adsorption values, however. For a given set of experimental data no a priori judgement as to which of the six linear forms will give the best estimates of X_m and K seems possible since it depends upon the interaction of the following factors: 1. the magnitude of all of the X and C values used in the analysis; 2. the distribution of the experimental X values about the "true" isothermal line; and 3. the distribution of data points along the concentration axis.

Figure 8 shows plots of X against C or their transforms for the Table 5 values and the associated isotherm. The triangle, square and blackened circle represent the values of X for which the transformed variables are listed in the table. For Figure 8A, the non-transformed isotherm, the error bars of the dependent variable are equal for all values of X , and the error of the independent variable C is negligibly small. Thus, except for the linear relationship, all the requirements of the linear regression model are satisfied. Figure 8B shows the C/X against C plot for the three values of C/X given in the table. Note that the error bars for C/X are not constant between observations nor are they uniform about their average values. Thus, two requirements of the linear regression equation are violated. Figure 8C

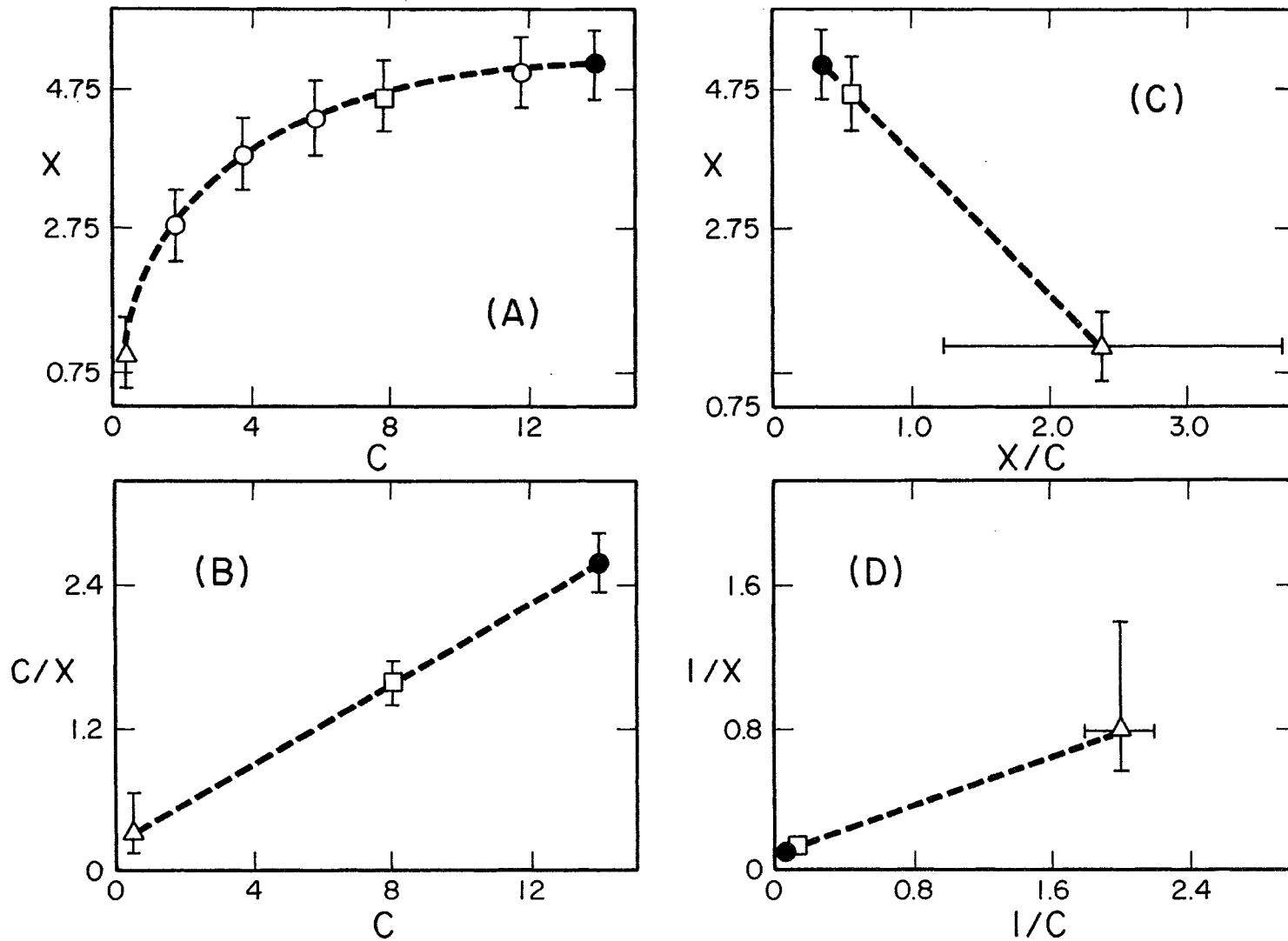


Figure 8. THE EFFECT ON DATA OF THREE LINEARIZED FORMS OF THE LANGMUIR EQUATION. The values are from Table 5.

is similar in that both contain one variable with an experimental quantity in the denominator. Therefore, the uncertainties associated with plots of X vs. X/C and C/X vs. C are analogous. The problems with the double reciprocal form, Figure 8D, are obvious. Not only do low values of X result in high values of 1/X with large errors, but the inverse of small values of C result in significant uncertainty of the plotted independent variable, 1/C. Furthermore, the points corresponding to the largest values of X and C, the ones with the smallest relative error, are compressed near the origin. The result is that small values of X are the most influential in the determining the regression line.

Since the numerical quantities used in the regression analyses vary from form to form, comparison of correlation coefficients is not a valid criterion for determining which regression best fits the data and, therefore, calculates the most accurate estimate of X_m and K. The plots in Figure 9 which employs the 1,10-phenanthroline adsorption data presented in Figure 6, illustrates these points. The open circle is for the value of X of 45 $\mu\text{mol/g}$ for C equal to 2.8 μM . The effect of this data point upon the calculated regression line is shown in the figure for the various transformations. The solid lines are the regression lines with the open point included; the dashed lines are the regressions with the open point deleted from the analysis. For the plot of C/X vs. C (Figure 9B) the deletion of the open point significantly increased the correlation coefficient, r, and resulted in much smaller estimates of X_m and K being calculated. The results with X vs. X/C in Figure 9C were similar, the correlation coefficient increasing upon deletion of the low point. The double reciprocal form, however, showed a higher correlation coefficient with the low point included even though negative values of X_m and K resulted from

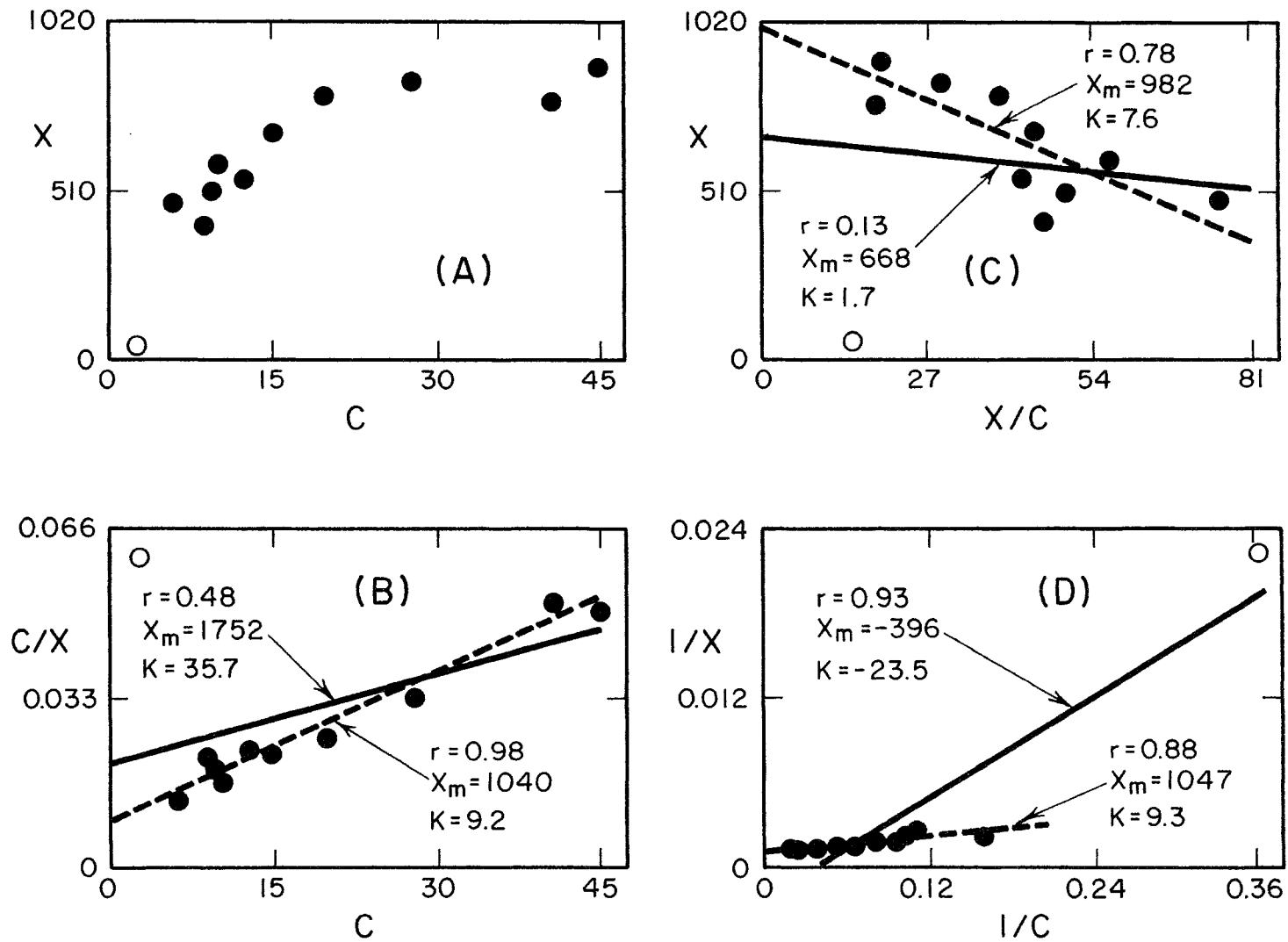


Figure 9. LANGMUIR PARAMETERS FOR 1,10-PHENANTHROLINE DATA CALCULATED BY THREE LINEAR FORMS OF THE EQUATION. Same data as Figure 6. Solid line is regression including all data; dashed line with open circle deleted.

the calculations. Interestingly, when the open point was deleted, plots of C/X vs. C and $1/X$ vs. $1/C$ resulted in almost identical estimates of X_m and K .

Figure 10 shows the Langmuir isotherms generated from the X_m and K values calculated in Figure 9. The isotherm in Figure 10A is for the nonlinear least-squares values of X_m and K calculated using all the data points. Figure 10B shows the fitted isotherms from Figure 9B, and so on. The solid and dashed lines have the same meaning as in the previous figure. Note that when the low point was deleted the linear forms gave a reasonably good fit to the data. The values of X_m ranged from 982 to 1131 $\mu\text{mol/g}$ and K varied between 7.6 and 11.9 μM . for the four "best-fit" isotherms plotted in Figure 10.

Table 6 includes estimates of the Langmuir parameters calculated from all six linear regression models, as well as the nonlinear model, for the phenanthroline and Cd-phenanthroline (pH 7.1 and pH 8.1 at 50 mg/l carbon) adsorption data. The calculated X_m and K values are listed for the regression analyses using all data points (ALL) and in some cases for the regression analyses in which the low point was deleted (DELETE).

Figures 9 and 10 and Table 6 illustrate the instability of the linear regression forms of the Langmuir equation to the inclusion or exclusion of data, and demonstrate the poor ability of the linear forms to accurately predict the true least-squares values of X_m and K . As shown by the resultant isotherms plotted in Figures 10B and 10C, some linear transforms of the Langmuir equation give an uneven weight to individual data points. When the same data (with the low point included) were analyzed using the double reciprocal plot, which gives the most weight to the lowest values of X and C , negative X_m and K were calculated. Consequently, under these circumstances, it is difficult to predict which linear form will best handle a given set of experimental data. Dowd and

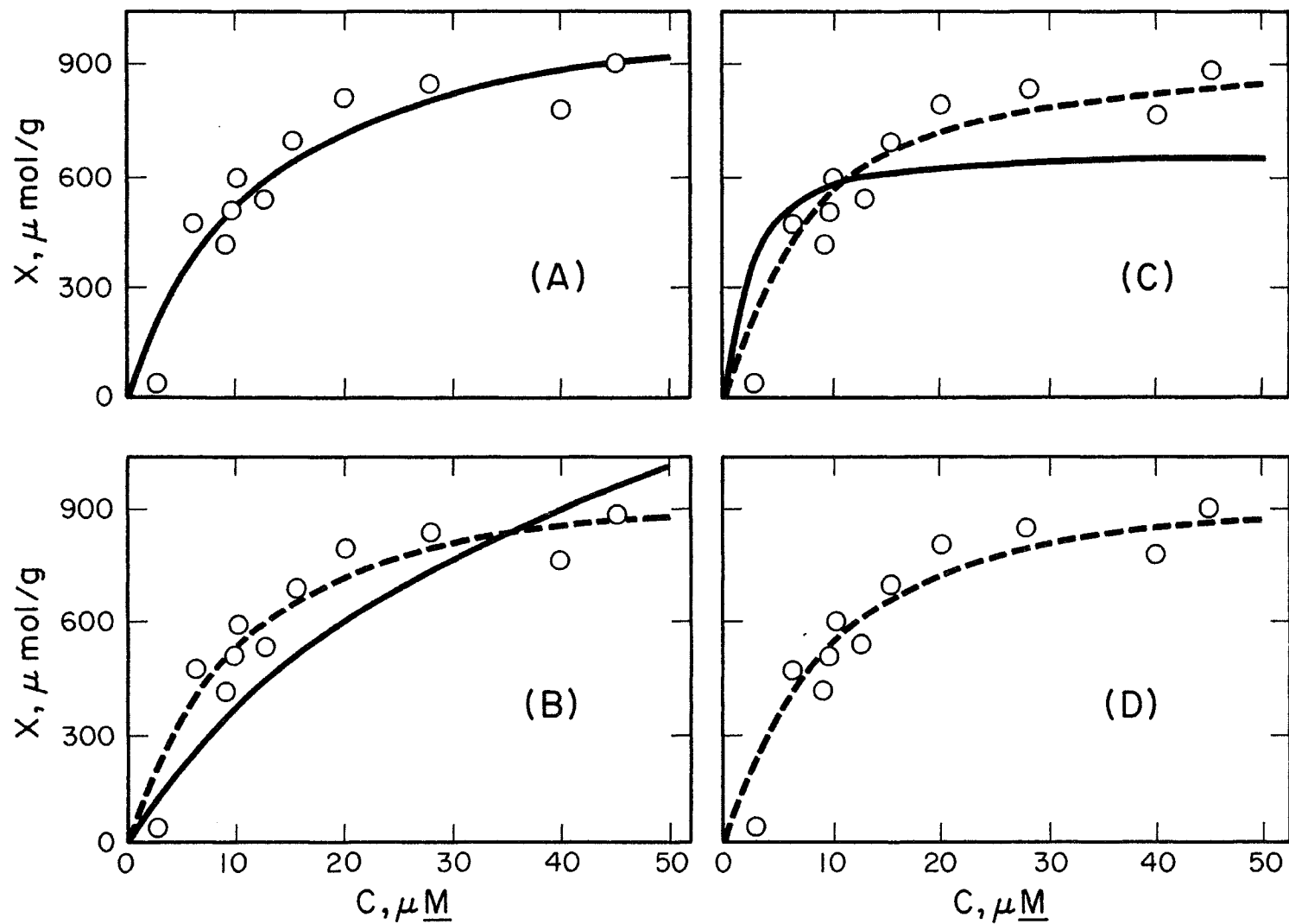


Figure 10. LANGMUIR ISOTHERMS FOR 1,10-PHENANTHROLINE DATA CALCULATED FROM VARIOUS ESTIMATED VALUES OF X_m and K . Same notation as Figure 9.

Table 6. SUMMARY OF CALCULATED LANGMUIR PARAMETERS USING VARIOUS REGRESSION FORMS OF THE LANGMUIR EQUATION*

Adsorbate (**)	X vs. C		C/X vs. C		1/X vs. 1/C		X vs. X/C		C vs. C/X		1/C vs. 1/X		X/C vs. X	
	X_m	K	X_m	K	X_m	K	X_m	K	X_m	K	X_m	K	X_m	K
1,10-Phen (ALL)	1131	11.6	1752	35.7	-394	-23.5	669	1.69	425	-5.1	-282	-19.6	4881	105.6
1,10-Phen (DELETE)			1040	9.2	1047	9.3	982	7.6	1002	8.0	1330	15.4	1198	12.6
Phen-Cd pH 7.1 (ALL)	544	11.6	639	19.1	-1134	-57	374	6.3	481	11.3	-1036	-52	1672	63.8
Phen-Cd pH 7.1 (DELETE)			577	15.0	-3401	-155	427	7.8	482	10.2	-1335	-65.4	1137	38.9
⁵⁵ Phen-Cd pH 8.1 (ALL)	684	16.2	1790	835	-162	-16.2	245	-0.2	144	-5.4	-134	-14.3	-39.80	-1880

* Refer to Equations 16 and 18 through 23.

** See text; refers to possible deletion of a data point.

NOTE: The units of X_m and K are $\mu\text{mol/g}$ and μM , respectively.

Riggs (33), presented evidence suggesting that on the average, the double reciprocal plot is the one most subject to error. Whenever possible, however, it is apparent that a nonlinear regression of the data should be used.

Careful examination of the calculated isotherms in Figure 7 reveals that the simple Langmuir model fits the experimental points rather poorly over most of the range of the plotted data. It predicts too large an X at low and high values of C and too small an X at intermediate values of C.

For adsorption onto a heterogeneous solid, the energy released during adsorption, Q, is usually a nonlinear decreasing function of the surface coverage, θ (20). This suggests that there is a distribution of adsorption energy sites on the adsorbent such that at a very low adsorbate concentration only the most energetic sites are able to adsorb. At higher concentrations the driving force is greater and the less energetic sites become available for adsorption. The fact that Q is not a linear function of θ indicates that the number of adsorption sites, $f(Q)$, is probably not distributed equally over all values of Q. The distribution of energy sites on a heterogeneous adsorbent is thus one of the possible factors in determining the overall shape of the associated isotherm. There are alternate explanations for the S-curve including lateral interaction of the adsorbate at the adsorbent surface. It is quite conceivable that the flat, almost two-dimensional shape of the phenanthroline molecule allows their orientation and close packing upon adsorption.

Adamson (20) has shown that substitution of the distribution function, $f(Q) = ke^{-\alpha Q}$, into the adsorption equation (Equation 13), letting $\theta(Q,P,T)$ be the Langmuir model, and integration between zero and infinity yields the Freundlich equation. Therefore, the failure of the Freundlich equation to

adequately fit adsorption data above minimal surface coverage can be viewed from the standpoint that an unrealistic $f(Q)$ function was assumed. Integration of Equation 13 using a normal distribution, $f(Q) = Ce^{-bQ^2}$, and $\theta(Q,P,T)$ as the Langmuir model results in

$$X = \frac{\frac{X}{m} b' C^n}{1 + b' C^n} \quad \dots(25)$$

and therefore

$$X = \frac{\frac{X}{m} C^n}{K' + C^n} \quad \dots(26)$$

In order to preserve the original definition of the constant K and to keep its units the same as C gives

$$X = \frac{\frac{X}{m} C^n}{K^n + C^n} \quad \dots(27)$$

Some of the data suggest such a normal distribution (51), and therefore, it seems reasonable to attempt a fit to Equation 27. The Cd-phenanthroline adsorption data given in Figure 7 were used at several values of n .

An excellent fit was obtained using n equal to 2 as shown in Figure 11. The solid line is the isotherm calculated from the parameters. Compare with Figure 7 ($n=1$). The Langmuir parameters for both curves in Figures 7 and 11 are also compared in Table 7. The values of X_m generated for the data by the modified equation are lower and more realistic. The K 's are also acceptable in that they reflect the values of C on the curves at $\frac{1}{2}X_m$. The difficulty

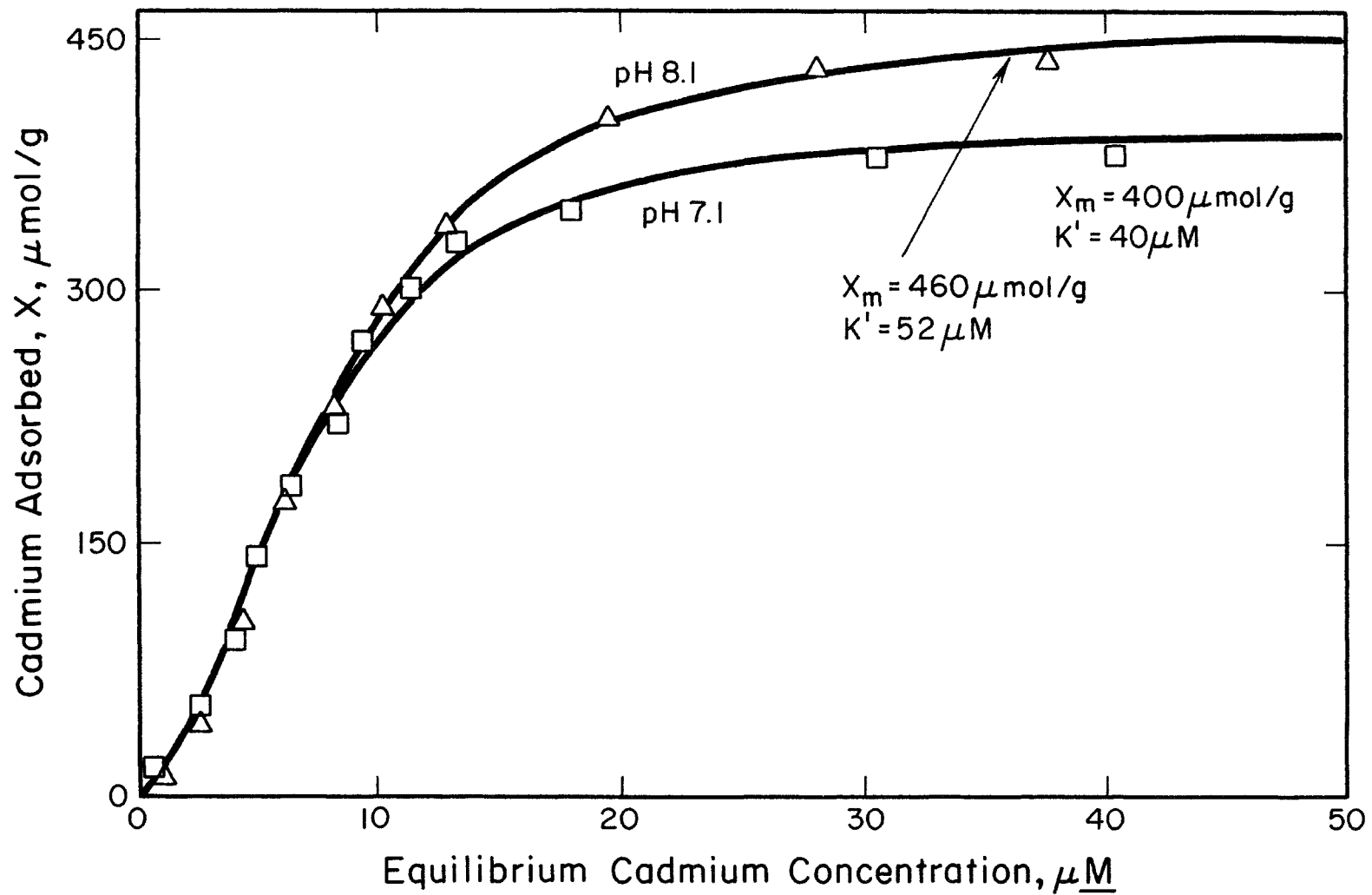


Figure 11. FIT OF THE MODIFIED LANGMUIR EQUATION TO THE 1,10-PHENANTHROLINE-CADMIUM ADSORPTION DATA. The value of n is 2.0. 50 mg/l Nuchar WV-L activated carbon. Compare with Figure 7.

Table 7. COMPARISON OF PARAMETERS FOR SIMPLE AND MODIFIED LANGMUIR ISOTHERMS

<u>pH</u>		<u>n=1</u>	<u>n=2</u>
8.1	X_m	648	460
	K	16	7.2
7.1	X_m	544	400
	K	12	6.3

with Equation 27 is finding the exact magnitude of n. In the present case, n=2 was probably fortuitous.

Effect of Adsorbent

Figure 1 compares the rate of cadmium adsorption by an 8-10 mesh granular carbon and by the same carbon ground to 50-200 mesh. The powdered carbon reached equilibrium much faster than the granular form (approximately 6 hours as opposed to 95 hours). The equilibrium capacities of the two were nearly identical, however. Morris and Weber (21), in discussing the effects of adsorbent particle size, concluded that intraparticle diffusion is often the rate limiting step in adsorption by activated carbon. Consequently, small particles will adsorb faster than larger ones because the mean diffusion path decreases with decreasing adsorbent size. Also, for adsorbents which have a large internal surface area relative to external surface area, such as activated carbon, there is a negligible increase in total adsorptive capacity as a result of grinding. Both of these phenomena are illustrated by the data presented in the figure.

Figures 2A and 3 show that the equilibrium adsorption of free Cd^{2+} ion by Nuchar WV-L activated carbon is strongly affected by the pH of the solution, as is the adsorption of zinc and lead. Metal adsorption is enhanced by increasing the pH. Even at fairly high pH, however, adsorption of free Cd^{2+} ions by activated carbon was slight compared to the reported adsorption of Cd^{2+} by materials such as manganese dioxide. The Langmuir parameters X_m and K for the adsorption of free Cd^{2+} ion by Nuchar WV-L activated carbon at pH 8.1 were $247 \mu\text{mol/g}$ and $37 \mu\text{M}$, respectively; the corresponding values reported by Posselt and Weber (29) for Cd^{2+} adsorption by colloidal MnO_2 at pH 5 were $1370 \mu\text{mol/g}$ and $0.04 \mu\text{M}$. At pH 8.3 Posselt and Weber reported an X_m value of $2200 \mu\text{mol/g}$ (see Table 1). These values indicate that in the pH range 8.1 to 8.3 colloidal MnO_2 has nearly a ten times higher adsorptive capacity for free Cd^{2+} ions than does the activated carbon. As demonstrated by Posselt, Anderson and Weber (28) the adsorption of cations follows an electrostatic mechanism. Consequently, the difference in Cd^{2+} adsorption by these two materials can be largely accounted for by the surface charge characteristics of the adsorbents. It seems reasonable, therefore, that if an activated carbon could be produced with a large negative surface charge it would be a highly effective adsorbent for cationic metals.

The effect of surface charge was also examined by comparing activated carbons with different isoelectric pH values (see Table 4). Carbons with the lowest isoelectric points (IEP) will be relatively more negative at any given pH. Accordingly, it was found that X_m for a specific metal increased with decreasing IEP. Nuclear WV-L had a relatively low IEP and thus was a good choice for comparison with other adsorbents. Hence, the conclusion is that activated carbon is an ineffective adsorbent for uncomplexed metals in solution.

From the data presented in Table 4 it is also concluded that the sequence of adsorption of metals on activated carbon is the same as with other charged adsorbents. Generally, the more acid the metal (the greater its tendency to hydrolyze) the greater will be its adsorption.

Effect of Chelating Agent

Figure 2B shows that EDTA increases the adsorption of cadmium when a relatively high carbon dose is employed (5000 mg/l) and reduces cadmium adsorption at lower carbon doses (500 mg/l or less). Figure 4 compares the adsorption isotherms for free Cd^{2+} , free EDTA and the Cd-EDTA complex. Over the equilibrium adsorbate concentration range between 5 and 50 μM , EDTA was less extensively adsorbed than free Cd^{2+} at pH 7.1. Presumably, this is because of the high aqueous solubility of EDTA. The Cd-EDTA complex was adsorbed to an even lesser extent, being only about as adsorbed as free Cd^{2+} ion at pH 5.7 (Figure 3). This is consistent with the data presented in Figure 2 indicating that EDTA suppressed cadmium adsorption at 500 and 50 mg/l carbon. Figure 5 illustrates that the suppressive effect of EDTA upon cadmium adsorption is proportional to the EDTA to Cd^{2+} molar ratio over the equilibrium adsorbate concentration range from 5 to 50 μM . Figure 12 shows the portion of Figure 4 enclosed by the dotted lines after expanding the scale five times. The blackened symbols are data from Figure 2, and the isotherm lines represent a visual fit to the data. The crossing of the two isotherms at low equilibrium adsorbate concentration as depicted in Figure 12 accounts for the observation that under certain conditions EDTA can enhance the adsorption of cadmium by activated carbon. Also, this interpretation is consistent with the data of O'Connor et al. (40) who reported the increased adsorption of the Cd-EDTA complex over that of free Cd^{2+} ion at equilibrium concentrations less than

or equal to $0.45 \mu\text{M}$. If the isothermal relationships given in the figure are essentially correct, the usefulness of EDTA to enhance cadmium adsorption to activated carbon is quite limited at best.

1,10-phenanthroline was highly adsorbed by all four activated carbons as could have been predicted from its low aqueous solubility. The calculated X_m value for the 1,10-phenanthroline data presented in Figure 7 is $1131 \mu\text{mol/g}$ and is of the same order of magnitude as the X_m values reported by Morris and Weber (21) for the adsorption of ABS detergents by activated carbon. At equilibrium adsorbate concentrations between 30 and $40 \mu\text{M}$, 1,10-phenanthroline was over 50 times more adsorbable on Nuchar WV-L than EDTA and about 30 times more adsorbable than free Cd^{2+} ion at pH 7.1, based on a comparison of the isotherms presented in Figures 3 and 6.

Figure 7 shows that at pH 7.1 and 8.1 the adsorption of cadmium from a one to one molar mixture with 1,10-phenanthroline was about 4 to 10 times greater than the corresponding adsorption of free Cd^{2+} ions. Also, the adsorption of the Cd-phenanthroline complex seemed less sensitive to pH over most of the equilibrium adsorbate concentration range investigated. This can be explained by assuming that ionic adsorption is controlled by an electrostatic mechanism and molecular adsorption is controlled by a solubility-limited mechanism. The result of complexation is that adsorption becomes less dependent on electrostatic considerations and more dependent upon the solubility of the resultant complex. Because each Cd^{2+} ion can complex with up to three phenanthroline molecules in the presence of excess phenanthroline, ratios of phenanthroline to Cd^{2+} ion greater than one should result in more extensive complexation of the metal. These higher order complexes should have an even lower charge density and, hence, should be more highly adsorbed by activated carbon. This was not investigated during the study, however.

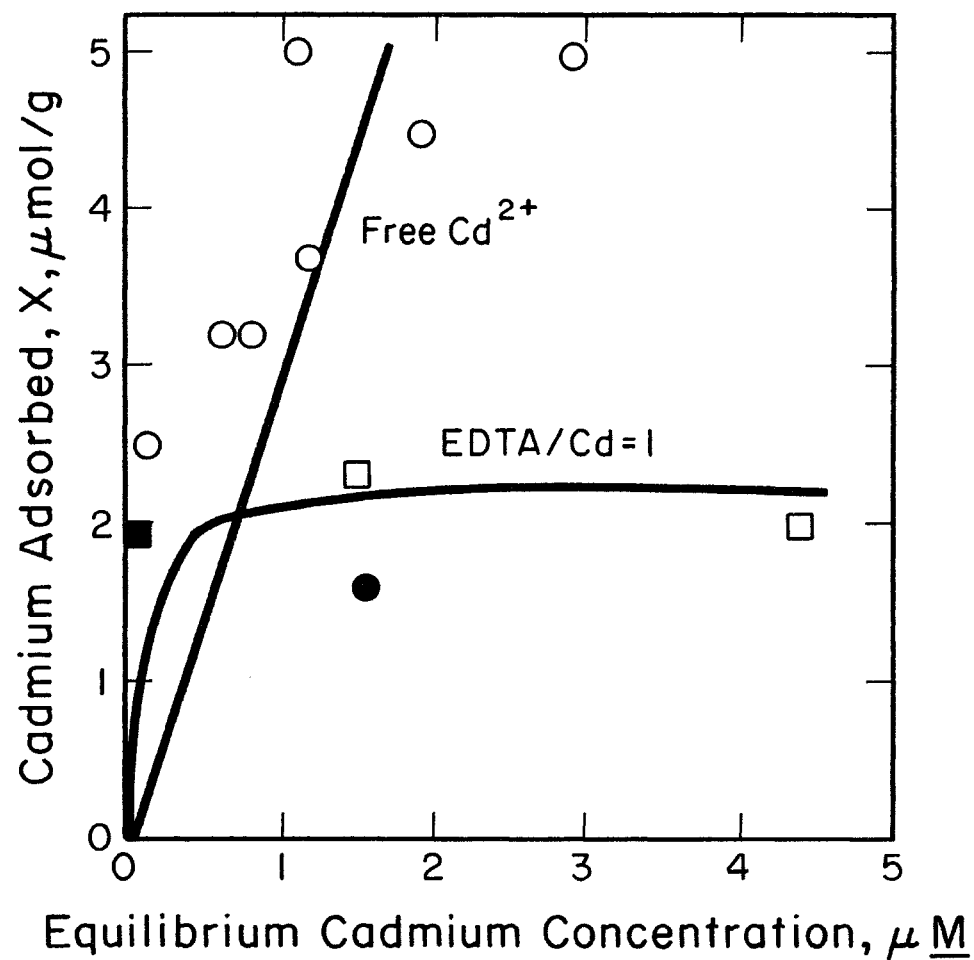


Figure 12. SHAPE OF ISOTHERMS FOR LOW EQUILIBRIUM ADSORBATE CONCENTRATIONS. Open circles are Cd^{2+} adsorption data from Figure 3; blackened square is from Figure 2A (5000 mg/l). Open squares are EDTA-Cd adsorption data from Figure 4; blackened square is from Figure 2B (5000 mg/l). All at pH 7.1 on Nuchar WV-L.

In summary, at very low surface coverage, as when an excess of adsorbent is used, EDTA appears to enhance the sorption of cadmium. Under more realistic conditions, that is, at high surface coverages the effect of this soluble chelating agent is to suppress adsorption of the metal. Therefore, it must be concluded that the use of EDTA is detrimental to metals removal. It can be further concluded that complexation with relatively insoluble chelating agents such 1,10-phenanthroline can significantly promote metals removal by activated carbon.

As is evident from the present study, there are several limitations to the Langmuir model for representing equilibrium adsorption data. It was also shown, however, that the Freundlich equation is even less successful in this regard. The chief utility of the Langmuir isotherm is in the use of its parameters X_m and K for the comparison of adsorbents and adsorbates.

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