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Effect of Complexation on the Adsorption of Cadmium by Activated Carbon

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Abstract

The adsorption of Cd^{2+} in the absence and presence of two chelating agents was examined as a function of pH. Fits of the data to the Freundlich and Langmuir equations were compared as were results with Zn and Pb using four different activated carbons. In general, adsorption increased with increasing pH and was not extensive, particularly for Cd. At low cadmium to carbon ratios, EDTA appeared to enhance adsorption. With more realistic loadings, when competition for surface sites is greatest, the presence of EDTA is shown to be detrimental to the process. 1,10-Phenanthroline, the second chelating agent studied, was more effective for promoting the removal of Cd. The uncomplexed Cd and Cd-EDTA systems were best described by the simple Langmuir adsorption isotherm. The adsorption of 1,10-phenanthroline and its Cd complex were modeled using a modified form of the Langmuir equation.

INTRODUCTION

Activated carbon is an extremely efficient adsorbent for the removal of low levels of organics from water. It is a readily available, inexpensive material with a very large specific surface area. Unfortunately, it has little net surface charge and is thus ineffective for adsorbing free, hydrated metal ions. It seems possible, however, that significant adsorption of metals by activated carbon might be obtained by complexing the metal with an organic molecule prior to contacting the carbon. The complexing

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agent of choice must be highly adsorbable by activated carbon and able to complex strongly with the metal. It would be expected 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 would allow the 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. For example, a significant percentage of cadmium present in sewage and river waters is complexed by organic species (*1*). This complexed cadmium is more or less resistant to removal by chemical precipitation. As a result, cadmium solubility calculated from simple solubility product considerations will 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 is necessary to achieve the low metals concentrations often required. Adsorption represents such an alternative process.

There are a number of such studies described in the literature. In general, it has been found that the removal of free hydrated metal cations by carbon is slight, but reports on the effects of complexing the metals are frequently contradictory. Moreover, there are problems in interpreting adsorption results. Both the Freundlich and Langmuir equations are used, although almost never in the same report. It is also usual that the applicability of the equation to the system being examined is not evaluated. These facets of adsorption for metals removal with activated carbon were examined in this research using cadmium ion. Some studies with zinc and lead, and with several different activated carbons, were also run, although most of the experiments were performed with Cd(II) and one particular carbon. These metals were selected in part since they have environmental significance, but mainly because they have been used in other studies and thus permit comparison and because they differ widely in their ability to hydrolyze.

Adsorption Models

The Langmuir and Freundlich isotherms are the equations most frequently used to represent data on adsorption from solution. The Freundlich equation has the form

$$X = KC^{1/n} \tag{1}$$

where C is the concentration of adsorbate at equilibrium and K and $1/n$ are constants. The commonly used log-log linear transformation of this equation is popular because such equations are easy to use and are relatively insensitive, lending themselves to imprecise data. However, the Freundlich equation does not express X as a linear function of C at low concentrations, a common experimental observation, and it does not provide for a maximum value of X. As a result, the Freundlich equation predicts infinite surface coverage at infinite concentration, a condition which does not occur. Therefore, its application is limited to ranges of intermediate surface coverages.

The Langmuir model predicts that, under equilibrium conditions and constant temperature, simple adsorption should obey a function of the form

$$X = \frac{X_m bP}{1 + bP} \tag{2}$$

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 and multiplying the numerator and denominator by K gives an equation identical in form to the Michaelis-Menton equation of enzyme kinetics

$$X = \frac{X_m P}{K + P} \tag{3}$$

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 is effective at low gas pressure; a high value of X_m indicates a large adsorbent surface area.

The Langmuir equation is strictly applicable only to the adsorption of gas molecules by simple crystalline materials with homogeneous surfaces such as mica and platinum. These simple adsorbents have only one elementary type of adsorption site with a single adsorption energy potential; most adsorbent surfaces are substantially less homogeneous. 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. 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. 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.

In spite of these limitations, the simple Langmuir equation is often used to describe adsorption from solution by heterogeneous solids. Replacement of the equilibrium gas pressure with the equilibrium adsorbate concentration gives

$$X = \frac{X_m C}{K + C} \tag{4}$$

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. The following review 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. For the adsorption of alkyl benzenesulfonate detergents by activated carbon, Morris and Weber (*2*) reported X_m values between 160 and 400 μmol/g. K values ranged from 0.5 to 4 μ*M*. 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 μmol/g and a K equal to 9.3 μ*M* at equilibrium phenol concentrations between 5 and 210 μ*M*. For equilibrium phenol concentrations ranging from 1000 to 140,000 μ*M*, they calculated X_m equal to 4500 μmol/g and K equal to 5000 μ*M*. 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 of 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 (*3*) reported on the adsorption of zinc(II) by river silt. They noted that the adsorption process is pH dependent, adsorption increasing as the pH was raised. 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, we calculate X_m equal to 109 μmol/g and K equal to 42 μ*M*.

Posselt, Anderson, and Weber (*4*) demonstrated the high adsorptive capacity of colloidal hydrous manganese dioxide 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 1100 to 3600 μmol/g and K values ranging from 47 to 170 μ*M* were reported.

In a later study, Posselt and Weber (*5*) investigated the removal of trace cadmium by adsorption onto hydrous oxides of manganese, iron, and aluminum. The IEP of iron and aluminum hydroxides is much higher, ranging from 5 to 8.5, and therefore MnO_2 is a much more effective adsorbent for cations. They reported X_m values ranging from 1490 μmol/g at pH 5 to 2300 μmol/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 μ*M*. Gadde and Laitinen (*13*) studied the adsorption of several metals on hydrous manganese oxide and hydrous ferric oxides. In general, adsorption followed the order $Pb^{2+} > Zn^{2+} > Cd^{2+}$ and was pH dependent.

Smith et al. (*6*) 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.

Huang and Wu (*7*) reported the removal of chromate anions from solution by calcinated coke. Their work showed that low pH favors the adsorption of chromate anions by this adsorbent. For their adsorption data collected at pH 2, we calculate X_m equal to 42.8 μmol/g and K equal to 345 μ*M* for the 10 to 20 mesh calcinated coke. Using the 100 to 200 mesh adsorbent, X_m and K are 99 μmol/g and 158 μ*M*, respectively. 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.

TABLE 1
Representative Langmuir Adsorption Parameters

K (μM)	X_m (μmol/g)	pH	Adsorbate		Adsorbent		Ref.
			Solute	Equilibrium concentration (μM)	Solid	Concentration (mg/L)	
0.5–4.0	160–400		ABS detergents	0.5–50	Activated carbon	50	*2*
9.3	1090		Phenol	5–210	Activated carbon	50	*2*
5000	4500		Phenol	1000–140,000	Activated carbon	50	*2*
42	109	7.3	Zn^{2+}	2.9–159	River silt	171	*3*
47–170	1100–3600		Ca^{2+}, Mg^{2+}, Ag^{+}	35–170	MnO_2	8	*4*
0.10	1490	5	Cd^{2+}	10	MnO_2	0.91–12.7	*5*
0.05	2300	8.3	Cd^{2+}	0.8	MnO_2	0.0091–0.0637	*5*
345	42.8	2	CrO_4^{2-}	100–6000	10–20 mesh calcinated coke	5000	*7*
158	99	2	CrO_4^{2-}	100–6000	100–200 mesh calcinated coke	5000	*7*

O'Connor et al. (*8*) and Thiem et al. (*9*) demonstrated that the adsorption of Cd(II) and Hg(II) can be enhanced by chelating agents. 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 μM (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%; 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 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.

METHODS AND MATERIALS

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 Americas, Inc., of Wilmington, Delaware. The Darco carbon was a lignite-based 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 8×30-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.

Stock solutions of 0.01 M were prepared from the reagent-grade hydrated nitrate salts of cadmium, zinc, and lead. 0.001 M 1,10-phenanthroline solutions were prepared from the reagent solid (G. Frederick Smith Chemical Co.). Disodium ethylenediaminetetraacetate

(EDTA) solutions were prepared by drying the dihydrate at 80°C for 4 days and cooling in a desiccator, after which 37.21 g/L was dissolved. Three replicates of EDTA solution standardized against standard calcium solution had an average concentration of 0.0994 *M*. 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. Experiments were run at 24 (± 3)°C.

EDTA and 1,10-phenanthroline concentrations were determined by complexometric titration with 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) "Ionanalyzer." The Gran's plotting procedure which facilitates potentiometric endpoint determination using only four or five values from the titration curve was employed. All concentrations were calculated to the nearest 0.1 μmol/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 milliliter 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 (*10*) 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" (*11*), was used to obtain the best "unbiased" estimates of the Langmuir parameters.

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 CO_2. 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 were 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

Effect of pH, EDTA, and Adsorbent Dose

A few experiments were run to compare the rate of cadmium adsorption by 8 to 10 mesh granular Nuchar WV-L and the same carbon ground to 50 to 200 mesh. 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 the 50 to 200 mesh powdered carbon. A contact time of 24 h was found to provide adequate reaction time for the attainment of equilibrium in all samples.

Figure 1(A) 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 μM. Open symbols represent acetate-buffered samples and blackened symbols are for phosphate-buffered samples. The data show, as expected, that 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 1(B) gives the percent cadmium removal from a solution that was initially 9.8 μM 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 suppressed the removal of cadmium.

Comparison of Isotherms and Models

Isotherms for the adsorption of cadmium ion by Nuchar WV-L are presented in Figs. 2 through 7. Carbon doses in these experiments were

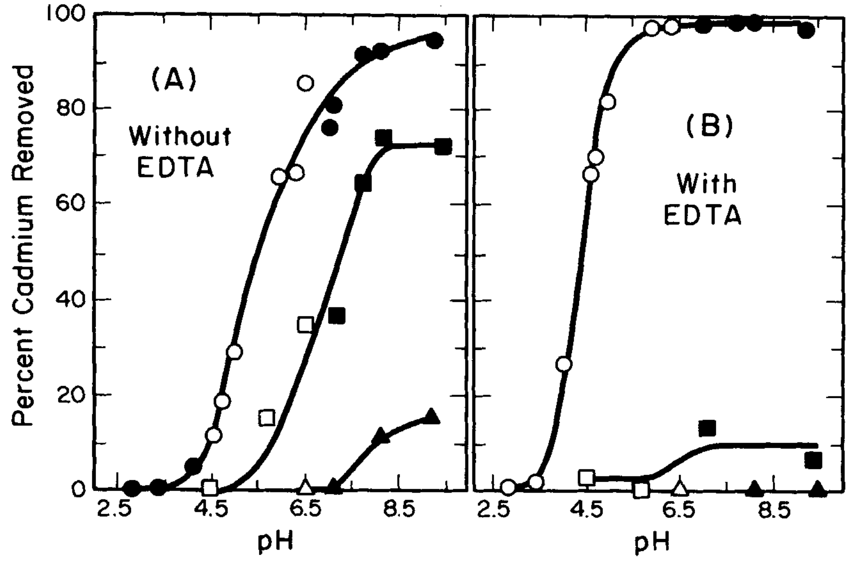

FIG. 1. Removal of cadmium at different carbon doses as a function of pH in the absence and presence of EDTA. Circles represent 5000, squares represent 500, and triangles represent 50 mg/L carbon. Initial Cd^{2+} and EDTA concentrations were each 9.8 μ*M*. Open symbols are acetate and blackened symbols are phosphate buffered systems.

TABLE 2

Summary of Experimental Adsorption Isotherm Parameters for Nuchar WV-L Powdered Activated Carbon[a]

		Langmuir		Freundlich		
Adsorbate	pH	X_m	K	k	$1/n$	Ligand/Cd ratio
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-Phenanthroline	7.1	1131	12	57.1	0.83	—
Cd-phenanthroline	7.1	544	12	29.8	0.85	1.0
Cd-phenanthroline	8.1	684	16	18.7	1.03	1.0

[a] Range of initial concentrations: 50 to 500 mg/L activated carbon, 5 to 50 μ*M* cadmium, 1 to 50 μ*M* EDTA, and 30 to 90 μ*M* phenanthroline. X_m in μmol/g and K in μ*M*.

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. Freundlich parameters k and $1/n$ were calculated from a linear least-squares analysis of the data transformed by taking the logarithm of Eq. (1). These adsorption parameters were then used to calculate the Langmuir and Freundlich adsorption isotherms represented in the figures by the solid and broken lines, respectively. The calculated parameters are summarized in Table 2.

Figure 2 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 shown clearly. 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 fit the pH 7.1 data successfully to the Langmuir equation. This can be understood

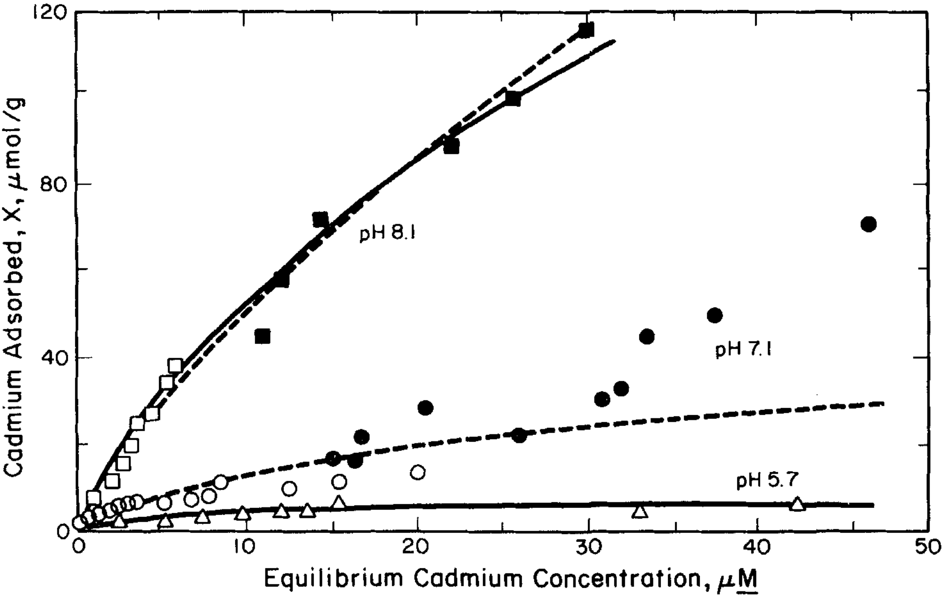

FIG. 2. Adsorption of cadmium on Nuchar WV-L at pH 5.7, 7.1, and 8.1. Solid lines are calculated Langmuir isotherms; broken lines are calculated Freundlich isotherms. Carbon dose: 500 mg/L (open symbols) and less than 500 mg/L (blackened symbols).

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 parameters are 247 μmol/g and 37 μ*M* for X_m and *K*, respectively; these 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 submonolayer surface coverage is precisely the range where the Freundlich equation gives a good fit, as shown in the figure.

The seemingly contradictory observation indicated by Fig. 1, 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 Fig. 3. The free Cd^{2+} ion adsorption

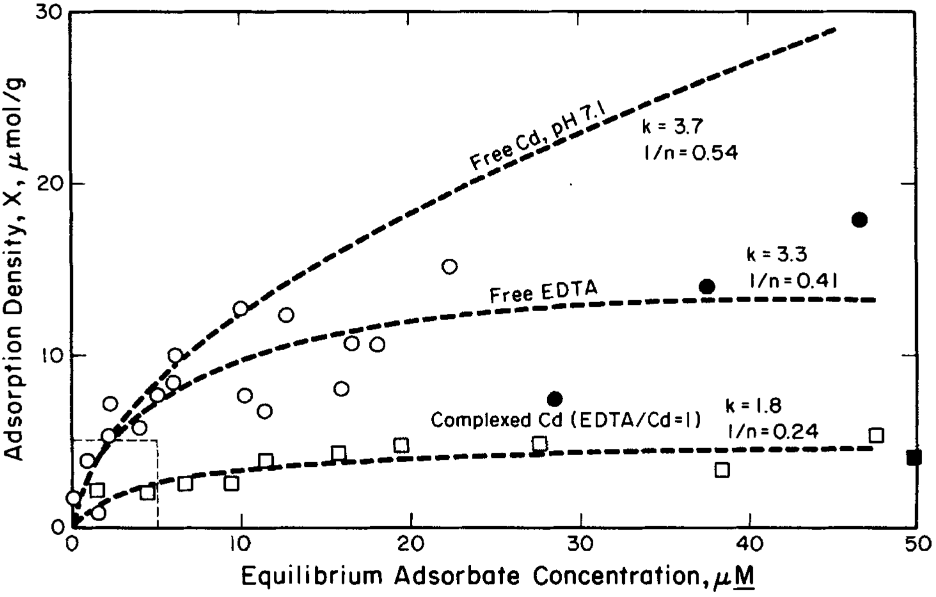

FIG. 3. Adsorption of free EDTA and complexed cadmium by Nuchar WV-L at pH 7.1. Circles are EDTA, squares are complexed cadmium. Carbon dose: 500 mg/L (open symbols) and less than 500 mg/L (blackened symbols).

isotherm at pH 7.1 from Fig. 2 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 Fig. 3 is expanded four times relative to Fig. 2. 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 Fig. 3 corroborate the data of Fig. 1 (and Table 2), showing, at carbon doses of 50 or 500 mg/L, that free Cd^{2+} ion is more adsorbable than the Cd–EDTA complex over the equilibrium adsorbate concentration range between 5 and 50 μ*M*.

To study further the suppressive effect of EDTA upon the adsorption of cadmium by activated carbon, the ratio of EDTA to cadmium in the test solution was varied. The results are shown in Fig. 4. The free Cd^{2+} and the complexed cadmium (EDTA to metal ratio of 1.0) isotherms presented in Fig. 3 are included for comparison. The circles and squares represent an EDTA to Cd ratio of 0.1 and 0.5, respectively. Figure 4 indicates that

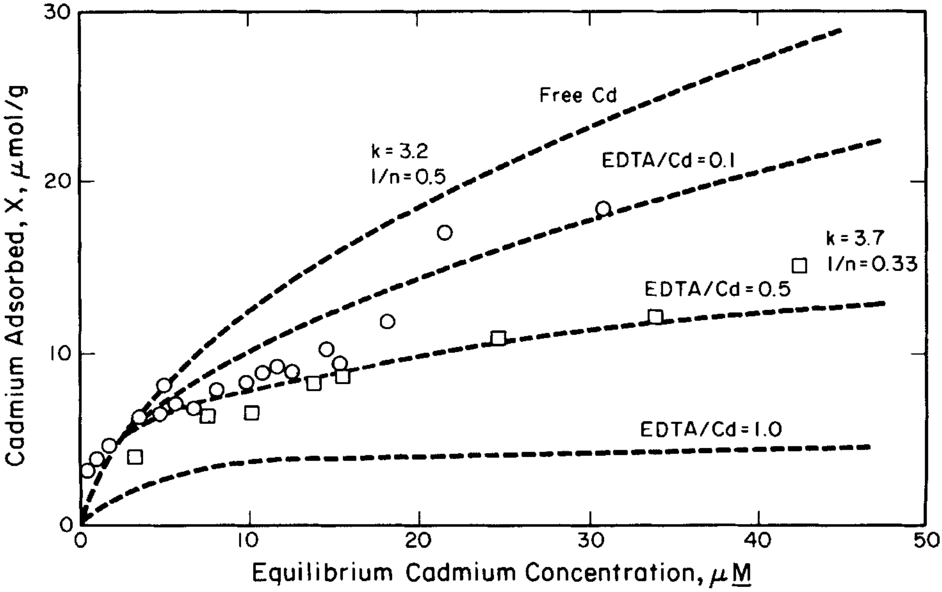

FIG. 4. Effect of the molar ratio of EDTA to cadmium upon adsorption by Nuchar WV-L at pH 7.1. Circles are EDTA/Cd = 0.1, squares are EDTA/Cd = 0.5. Carbon doses are 500 mg/L.

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 5 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 (*2*) for the adsorption of benzenesulfonate detergents onto activated carbon. The solid line is the calculated Langmuir isotherm with X_m equal to 1131 μmol/g and K equal to 12 μ*M*. The 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

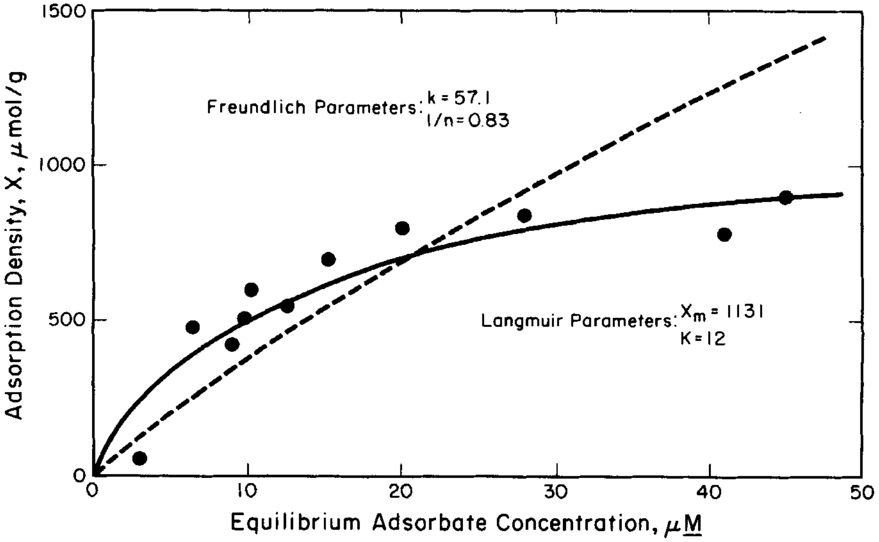

FIG. 5. Adsorption of 1,10-phenanthroline by 50 mg/L Nuchar WV-L. Dashed line is Freundlich isotherm; solid line is Langmuir isotherm.

allowance for a maximum surface coverage and therefore frequently gives a poor fit to curvilinear data.

Figure 6 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. 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 2 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

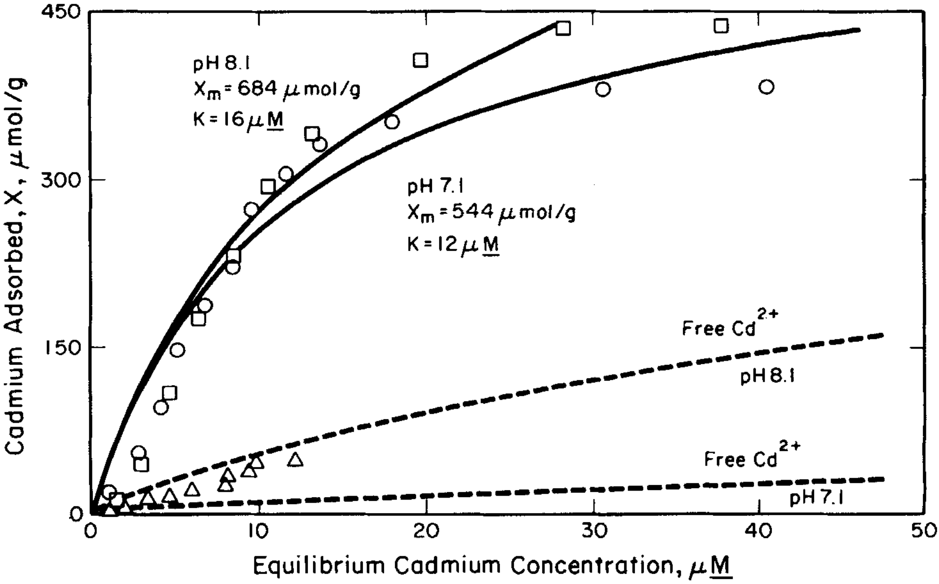

FIG. 6. Adsorption from a 1,10-phenanthroline–cadmium equimolar mixture by Nuchar WV-L. Triangles are pH 7.1 and 500 mg/L carbon. Circles are pH 7.1 and 50 mg/L carbon. Squares are pH 8.1 and 50 mg/L carbon.

procedure described by Parks and DeBruyn (*12*), 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 3.

The adsorptive capacity of each of the carbons for 1,10-phenanthroline at pH 7.1 was also determined. The initial phenanthroline concentrations ranged from 5 to 1000 μmol/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 (data not shown).

X_m values for Cd, Zn, and Pb at pH 6.5 and 8.0 were also determined for the four carbons and are included in Table 3. There was no significant adsorption of the metals of 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 (*13*). The pK_1 for Cd, Zn, and Pb are 10.3, 9.17, and 7.86, respectively (*14*).

DISCUSSION AND CONCLUSIONS

Model for Heterogeneous Adsorbents

Careful examination of the calculated isotherms in Fig. 6 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. The limiting assumptions of the simple Langmuir model are not always valid

TABLE 3
Comparison of Metals and Carbons

Activated carbon	Specific surface area (m^2/g)	IEP[a]	X_m at pH 6.5 Cd	X_m at pH 6.5 Zn	X_m at pH 6.5 Pb	X_m at pH 8.0 Cd	X_m at pH 8.0 Zn	X_m at pH 8.0 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

[a] Isoelectric pH of carbons by the procedure of Parks and DeBruyn (*12*). X_m in μmol/g.

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 (*15, 16*).

For adsorption onto a heterogeneous solid, the energy released during adsorption, Q, is usually a nonlinear decreasing function of the surface coverage, θ (*17*). 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 molecules allows their orientation and close packing upon adsorption.

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 the adsorption equation given by

$$\theta(P,T) = \int_0^\infty \theta(Q,P,T) f(Q)\, dQ \tag{5}$$

where $\theta(P,T)$ is the fractional surface coverage, X/X_m, as a function of pressure and temperature; $\theta(Q,P,T)$ is the fractional surface coverage as a function of adsorption energy, pressure, and temperature; and $f(Q)dQ$ is the adsorption energy distribution function. Adamson (*17*) has shown that substitution of the distribution function, $f(Q) = ke^{-\alpha Q}$, into the adsorption equation (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 fit adsorption data above minimal surface coverage adequately can be viewed from the standpoint that an unrealistic $f(Q)$ function was assumed. Integration of the adsorption equation using a normal distribution, $f(Q) = Ce^{-\beta Q^2}$ ($\theta(Q,P,T)$ is the Langmuir model) and using concentration instead of pressure, results in

$$X = \frac{X_m C^n}{K' + C^n} \tag{6}$$

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

$$X = \frac{X_m C^n}{K^n + C^n} \tag{7}$$

Some of the data suggest such a normal distribution, and therefore it seems reasonable to attempt a fit to Eq. (7). The Cd–phenanthroline adsorption data given in Fig. 6 were used at several values of n. An excellent fit was obtained using n equal to 2 as shown in Fig. 7. The solid line is the isotherm calculated from the parameters. Compare with Fig. 6 ($n = 1$). The Langmuir parameters for both curves in Figs. 6 and 7 are also compared in Table 4. 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 with Eq. (7) is finding the exact magnitude of n. In the present case, $n = 2$ was probably fortuitous.

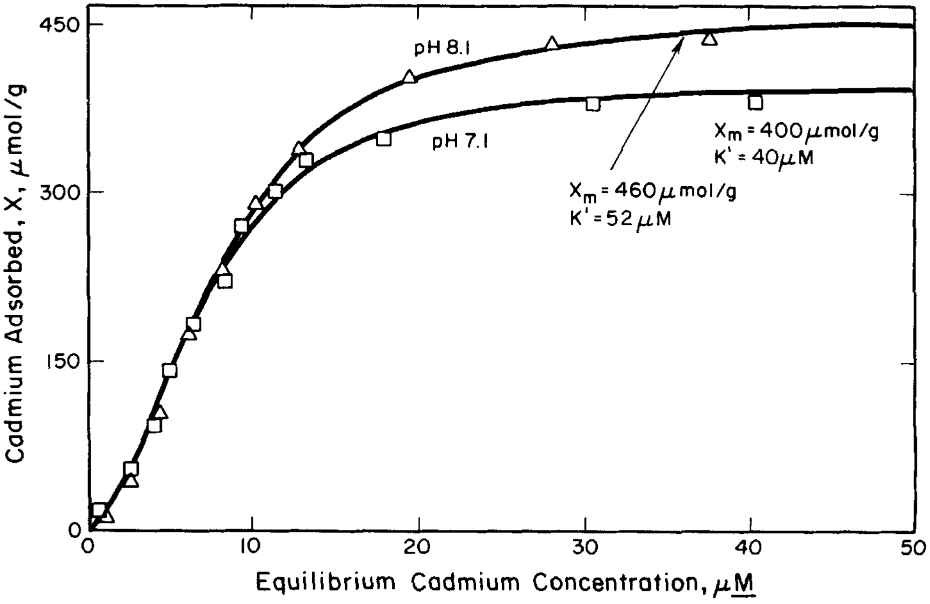

FIG. 7. Fit of the modified Langmuir equation to the 1,10-phenanthroline–cadmium adsorption data. The value of n is 2.0. 50 mg/L Nuchar WV-L activated carbon. Compare with Fig. 6.

TABLE 4
Comparison of Parameters for Simple and Modified Langmuir Isotherms

pH	Parameter	$n = 1$	$n = 2$
8.1	X_m	648	460
	K	16	7.2
7.1	X_m	544	400
	K	12	6.3

Effect of Adsorbent

In some preliminary studies the rate of cadmium adsorption by an 8-10 mesh granular carbon was compared to the rate of uptake by the same carbon ground to 50-200 mesh. The powdered carbon reached equilibrium much faster than the granular form (approximately 6 h as opposed to 95 h). The equilibrium capacities of the two were nearly identical, however. Morris and Weber (*2*), 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. Powdered carbon was used in all subsequent studies, and attempts were made to assure that equilibrium adsorption had been attained.

Figures 1(A) and 2 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 cation 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 μmol/g and 37 μM, respectively; the corresponding values reported by Posselt and Weber (*5*) for Cd^{2+} adsorption by colloidal MnO_2 at pH 5 were 1490 μmol/g and 0.10 μM. AT pH 8.3, Posselt and Weber reported an X_m value of 2300 μmol/g (see Table 1). These values indicate that in the pH range 8.1 to 8.3, colloidal MnO_2 has nearly a 10 times higher adsorptive capacity for free Cd^{2+} ions than does the activated carbon. As demonstrated by numerous workers, including Posselt, Anderson, and Weber (*4*), 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 3). 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 3 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 1(B) 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 3 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 (Fig. 2). This is consistent with the data presented in Fig. 1 indicating that EDTA suppressed cadmium adsorption at 500 and 50 mg/L carbon. Figure 4 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 8 shows the portion of Fig. 3 enclosed by the dotted lines after expanding the scale five times. The blackened symbols are data from Fig. 1, 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 Fig. 8 accounts for the observation that under certain conditions EDTA can enhance the adsorption of cadmium by activated carbon. Also, this interpretation is

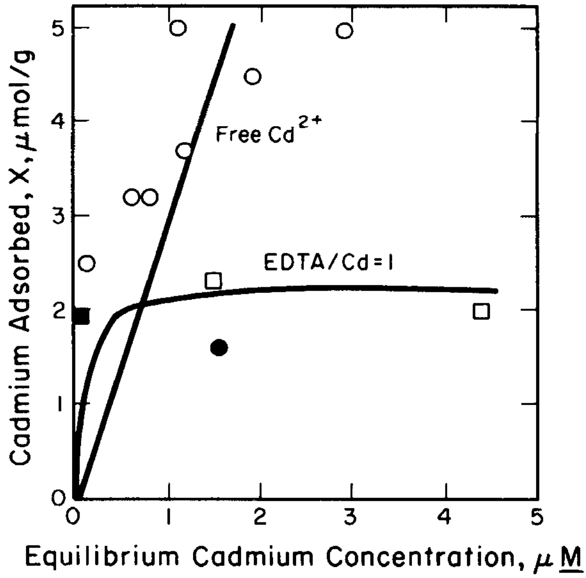

FIG. 8. Interpretation of the shape of isotherms for low equilibrium adsorbate concentrations. Open circles are Cd^{2+} adsorption data from Fig. 3; blackened circle is from Fig. 1(A) (5000 mg/L). Open squares are EDTA–Cd adsorption data from Fig. 4; blackened square is from Fig. 1(B) (5000 mg/L). All at pH 7.1 on Nuchar WV-L.

consistent with the data of O'Connor et al. (unpublished) 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 *μM*. 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 Fig. 6 is 1131 μmol/g and is of the same order of magnitude as the X_m values reported for the adsorption of ABS detergents by activated carbon (*2*). At equilibrium adsorbate concentrations between 30 and 40 *μM*, 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 Figs. 2 and 5.

Figure 6 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. 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 1 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 examined during the study, however.

In summary, at very low surface coverage, as when an excess of adsorbant is used, EDTA appears to enhance the adsorption 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 as 1,10-phenanthroline can significantly promote metals removal by activated carbon.

As is evident from the present study, there are limitations to the Langmuir model for representing equilibrium adsorption data (*18*). 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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