

RESEARCH REPORT SUBMITTED TO THE COPPER-NICKEL
REGIONAL TASK FORCE

of the

Environmental Quality Council
State Planning Agency
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"REMOVAL OF TRACE METALS FROM AQUEOUS SYSTEMS BY
ABSORPTION ON PEAT BOG MATERIAL"

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"Removal of Trace Metals from Aqueous Systems by
Adsorption on Peat Bog Material"

by

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Introduction

Peat lands constitute a vast natural resource which has received little scientific or commercial attention. Most of the scientific work has taken place in the U.S.S.R. and Canada. The four countries with the greatest area of peat are in order: U.S.S.R., U.S.A., Finland and Canada. Within the United States the largest peat areas are found in Alaska, Minnesota, Michigan and Wisconsin (8). Since Minnesota possesses a relatively large amount of peat, information concerning the inherent properties of peat should be accumulated.

Historically, peat has been used as a natural fertilizer and soil conditioner. Peat can also be used as an energy source by direct burning, gasification and wet combustion in briquettes or in combination with other fuels. Due to the current energy situation, utilization of peat as a fossil fuel energy source will increase. Peat has numerous chemical uses. It serves as a source for waxes, carbohydrates and coke. In addition, peat lands are used for forestry, agriculture and recreation, (8), which involves variable quantities.

Recent research indicates that peat can be used to treat wastewater (5) and to treat landfill leachate (2). Both of these studies indicate that it is feasible to remove pollutants, such as trace metals from water using peat. In one study treatment involved chemical pretreatment before contact with the wastewater (5). However, the other study showed that chemical pretreatment was not advantageous (2).

Peat's effectiveness in removing metals from solution may be due to its adsorption capacity (2) and ion exchange capacity (5). The main organic fraction of peat consists of humic and fulvic acids and humin. The humic acids have phenolic, carboxylate and carbonyl functional groups. Humic

acids have been shown to complex copper in solution; however, peat from which the humic acids have been removed had a greater adsorptive capacity than peat which contained the humic acids. This increase was attributed to increased surface area resulting from the removal of humic acids. This indicates that the accumulation of copper in peat cannot be due solely to the formation of Cu-humates (9). Cu-humates and Cu-fulvates have been shown to be very stable at $\text{pH} > 6$ (1). With metals in general, based on the concept that the surface of the organic matter is negatively charged and the ions in solution to be adsorbed are positively charged, as the ionic potential increases the adsorption capacity of the peat increases (9).

In a study of the interaction of copper with peat it was found that the formation of chelate compounds of copper and humic acid occurs in peat in nature. Also, the migration of copper in peat is very slow (7). This indicates that once the copper chelate forms it is bound tightly. A study of the Okefenokee Swamp has shown that metal distributions in peat forming areas can be related to metal levels and distributions in coal due to early stage processes of coal formation (3). This also indicates once the metal is bound in the peat, it remains there as the peat develops into coal. The Tantramar Swamp in New Brunswick, Canada consists of peat containing from 3 to 10 percent copper, which is not present in a specific mineral phase. It is suggested that the copper is sequestered by the organics in the peat forming chelates in which the copper is bound to nitrogen and oxygen. This theory is consistent with all experimental evidence (6).

Based on previous work, in other laboratories, research was initiated in an attempt to determine the ultimate capacity of a peat sample for the

adsorption of metals. Research described in this report constitutes the initial phase of a project involving an investigation into the removal of metals from wastewater by adsorption on peat. Preliminary results are presented here.

Experimental

Adsorption studies were run on a composite peat sample consisting of a mixture of five peat samples. The five peat samples were taken from the following sampling sites in northern Minnesota: a black spruce bog (AMAX), a control bog (AMAX), a cedar bog, a cattail bog, and a sedge bog. The samples were blended together with a mechanical stirrer at constant speed with distilled water until a homogeneous slurry was obtained. The peat slurry was stored in a refrigerator. The slurry was stirred with a piece of glass tubing before withdrawing slurry samples for batch experiments. The slurry samples were filtered through Whatman #4 filter circles on a Buchner funnel. The peat retained on the filter and in the funnel was weighed on a Mettler balance. 1.000 ± 0.001 gm. samples on a wet-basis were used in all tests.

All glassware and plastic sample bottles were acid washed with 25% nitric acid and rinsed with doubly-distilled water before each experiment to remove any metals present. Metal solutions were prepared using metal nitrate compounds and doubly-distilled water. The metals used were copper, nickel, lead, cadmium, cobalt and zinc. Metal concentrations for the stock solutions were 500 ppm or 1000 ppm. Dilutions for the batch experiments produced sample solutions ranging from 5 ppm to 250 or 300 ppm.

Batch experiments were run using 250 ml erlenmeyer flasks, each containing

100 ml of metal solution and 1.000 gm peat. The flasks were shaken for four days at $18^{\circ} \pm 0^{\circ} \text{C}$. Blanks containing only peat and water were run each time a set of samples were run. Initial and final pH measurements were made on the peat-metal slurry using an Orion 701 pH/mv meter with an Orion glass electrode. No pH adjustments were made. After shaking, the samples were filtered through Whatman #4 filter circles and then through Nuclepore 0.4 μ polycarbonate membrane filters to remove finely divided peat particles. The filtrate was acidified with four drops of concentrated nitric acid and then analyzed for metal in solution using a Varian 175 flame atomic adsorption spectrophotometer.

Results and Discussion

The results of the experiments are shown in Tables 1-6. These results are expressed in terms of C_0 , the initial metal concentration and C_e , the final metal concentration in solution, that is the equilibrium concentration assuming equilibrium is reached or closely approached after 4 days of continuous shaking. The term, q , is defined as the amount of metal taken up by the peat per gram of peat, that is

$$q = (C_0 - C_e) / \text{wt. of peat}$$

assuming any loss of metal in solution is due solely to the peat. A plot of q vs. C_e gives an adsorption isotherm which illustrates adsorption variations as a function of concentration of metal in solution at a given temperature. Combined adsorption isotherms for Cu, Cd, Zn and Ni are present in Figure 1.

For most of the data, two fundamental equations were considered in an attempt to fit the data to an equation in order to estimate peat capacities for various metals. The Langmuir equation is based on the assumptions that

adsorption occurs in a single monolayer at the peat surface, the energy of adsorption is constant and the metal molecules adsorbed do not migrate along the peat surface. This model was chosen due to its simplicity and the general shape of most of the adsorption isotherms. However, in the case of nickel, a sharp increase in q after an initial plateau indicated the possibility of a second layer forming on top of the first. Due to this, a modified form of the Langmuir equation, which involves multi-layer adsorption, was considered for nickel.

The second equation considered for the data interpretation is the Freundlich equation. However, this equation is mainly empirical and often fits experimental data better than the Langmuir equation. The Freundlich equation generally agrees with the Langmuir for medium concentrations; however at high and low concentration the agreement is poor and the Freundlich becomes inaccurate due to its logarithmic form.

For the Langmuir equation a plot of $1/q$ vs $1/C_e$ should yield a straight line. The intercept, $1/Q^\circ$, is indicative of the q value of a complete monolayer, that is adsorption capacity. The slope, $1/bQ^\circ$, contains the term b which is related to the energy or net enthalpy of adsorption. The Langmuir isotherm equation is:

$$q = \frac{Q^\circ b C_e}{1 + b C_e}$$

while the linearized form is:

$$\frac{1}{q} = \frac{1}{Q^\circ} + \left(\frac{1}{bQ^\circ}\right) \left(\frac{1}{C_e}\right)$$

The term Q° can be taken as the total capacity of the peat for a specific metal. Even though the assumptions for the Langmuir equation may not be

met, the value Q° represents a practical measure of adsorption capacity.

For the Freundlich equation a plot of $\log q$ vs $\log C_e$ should be linear. The intercept, $\log K_F$ at $C_e=1$ ($\log C_e=0$) gives a rough indication of relative sorption capacities of the peat. The slope, $1/n$, also is a rough indicator of relative adsorption intensities of the peat. The general form of the equation is:

$$q = K_F C_e^{1/n}, \quad n > 1$$

while the logarithmic form is

$$\log q = \log K_F + 1/n \log C_e$$

The BET equation is similar to the Langmuir, but involves multi-layer adsorption rather than the special case of mono-layer. A plot of $C_e/(C_s - C_e)q$ vs C_e/C_s should be linear where C_s is a saturation concentration taken from the graph of q vs C_e . The BET equation is

$$q = \frac{BQ^{\circ}C_e}{(C_s - C_e)(1 + [B-1][C_e/C_s])}$$

and the linearized form is

$$\frac{C_e}{(C_s - C_e)q} = \frac{1}{BQ^{\circ}} + \left(\frac{B-1}{BQ^{\circ}}\right) \left(\frac{C_e}{C_s}\right)$$

Plots for both the Langmuir and Freundlich equations as well as the BET for nickel were made and a linear regression analysis done giving slope, intercept and coefficient of correlation (r^2) for the copper, nickel, zinc and cadmium data. Three data points for cadmium were disregarded due to severe discrepancies with other values obtained. The lead samples were not analyzed in the above manner since lead was not detectable for nearly all of the samples. The cobalt data was extremely erratic, including C_e values greater than C_o values, making it impossible to evaluate.

The Langmuir plots were not linear, therefore the Langmuir equation is not applicable. Due to this problem a total capacity could not be calculated for the peat for any of the metals. Although the Freundlich plots (Figures 3-6)

were reasonably linear, no ultimate capacities can be calculated. However, relative capacities can be considered for various concentrations. The combined Freundlich plot (Figure 2) indicates that as C_e increases the peat capacity varies. At low concentrations the order of relative capacities is copper > cadmium > zinc > nickel. However, at higher concentrations, the order changes to: cadmium > copper > nickel > zinc. At even higher concentrations the lines cross again, thus changing once more. This changing of order makes it impossible to determine an overall relative capacity for the peat.

The problem of varying ionic strength was not dealt with and may be responsible for some of the variations in data. This problem can be reduced by establishing a high ionic strength solution by the addition of sodium perchlorate ($\sim 0.01M$) which will minimize the effect of varying ionic strength due to varying metal concentrations.

From the present results specific capacities can not be calculated. To obtain ultimate capacity values column adsorption tests should be performed. The use of flow through columns run until break through occurs allows for mass balance calculations from which capacities can be determined. Column tests would require a peat packed column and a steady flow of feed water of known concentration. The effluent is collected until breakthrough occurs, that is the effluent concentration equals influent concentration. An overall concentration is determined for the collected effluent, that is C , as well as the volume of solution passing the column which is V . The weight of the peat in the column is known so a mass balance can be determined. The capacity determined by this equation is

$$\text{capacity} = \frac{V C_0 - V C}{\text{wt. of peat}}$$

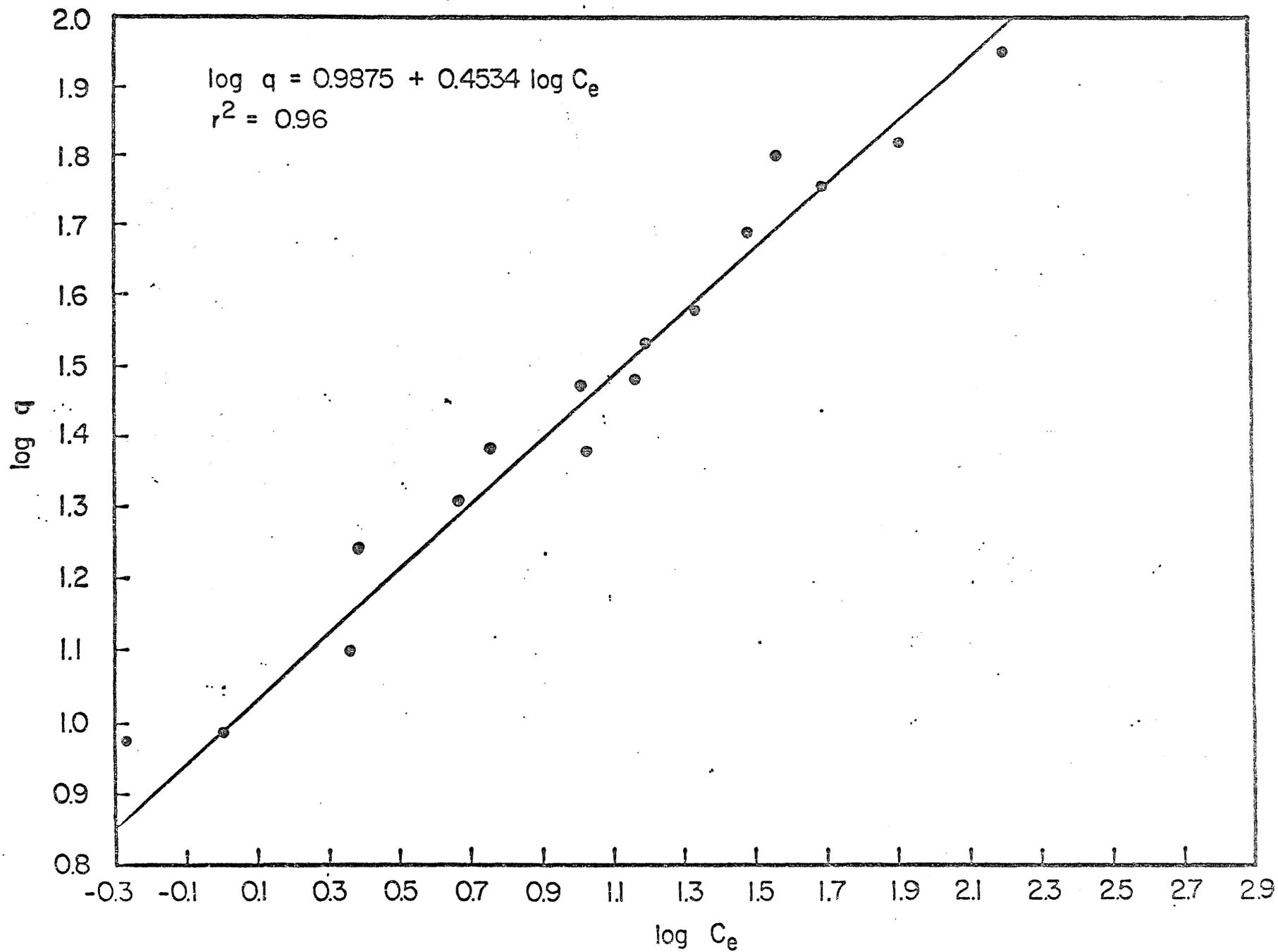
Once total capacities are determined a better understanding of the batch study data might be possible.

A dynamic reactor study also should prove to be useful. Parameters such as pH, free metal ion concentration and temperature would be monitored continuously with time to follow the approach to equilibrium which would provide useful information for predicting the fate of trace metals in bog water systems.

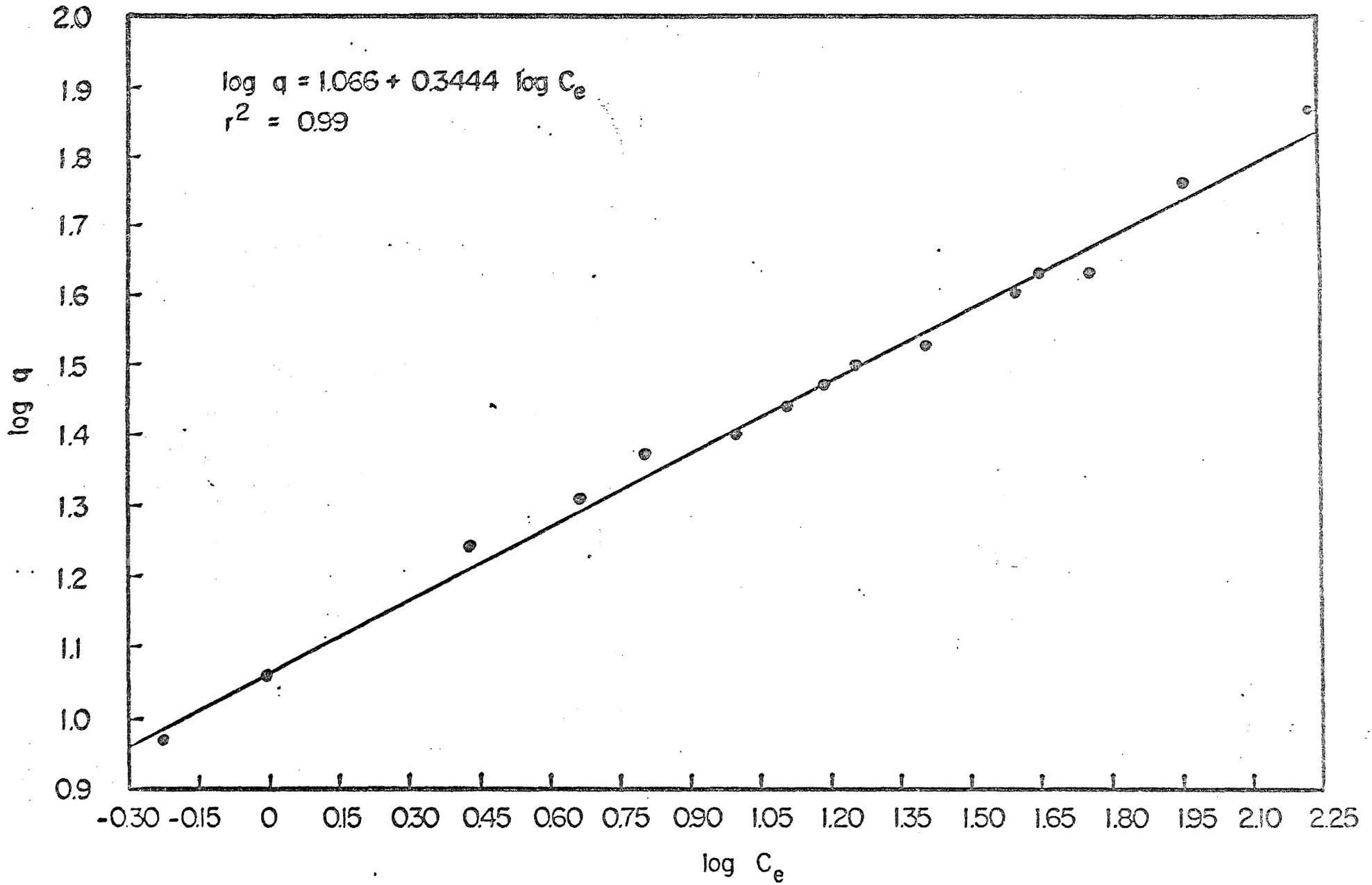
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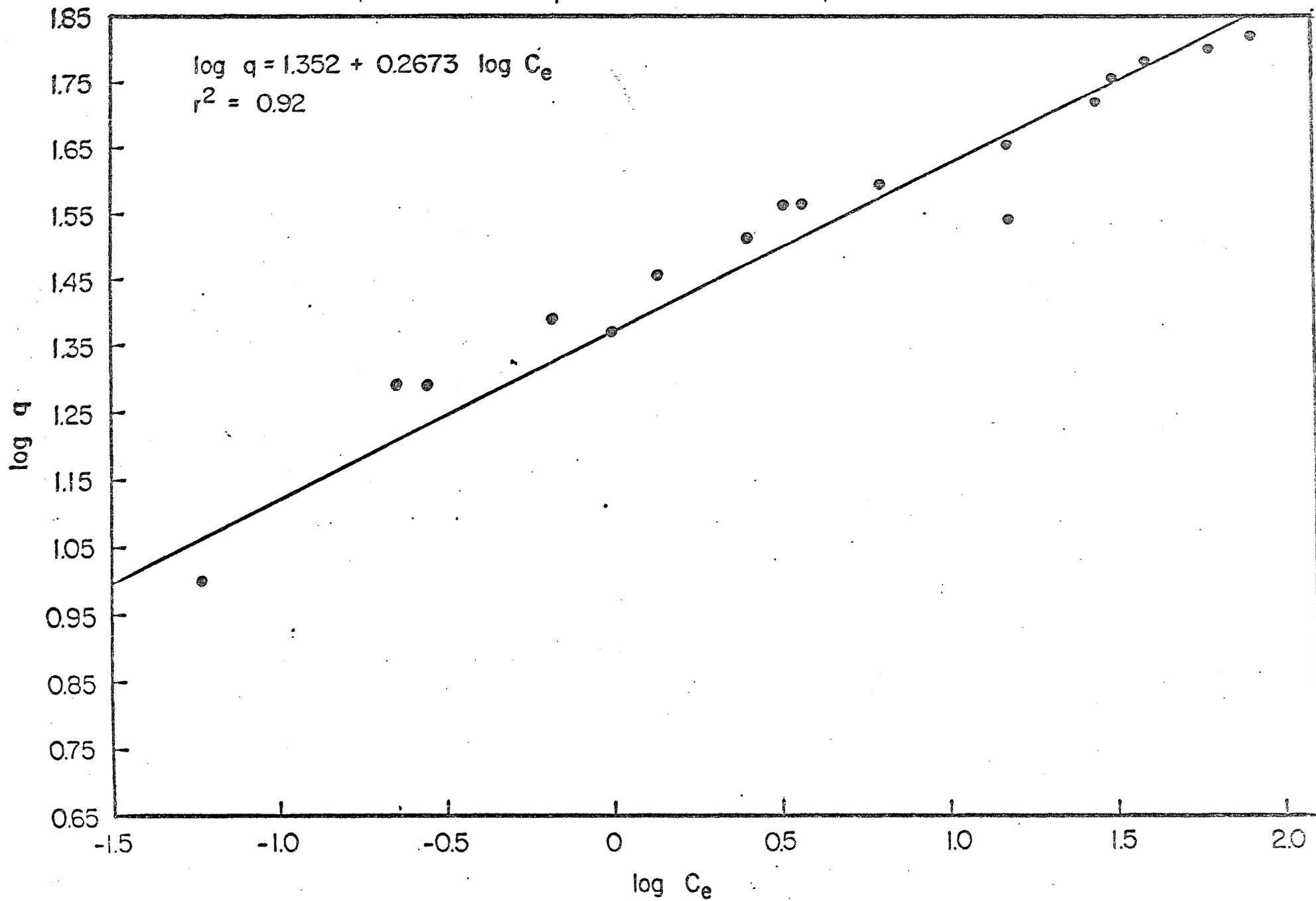
Freundlich Plot for Nickel



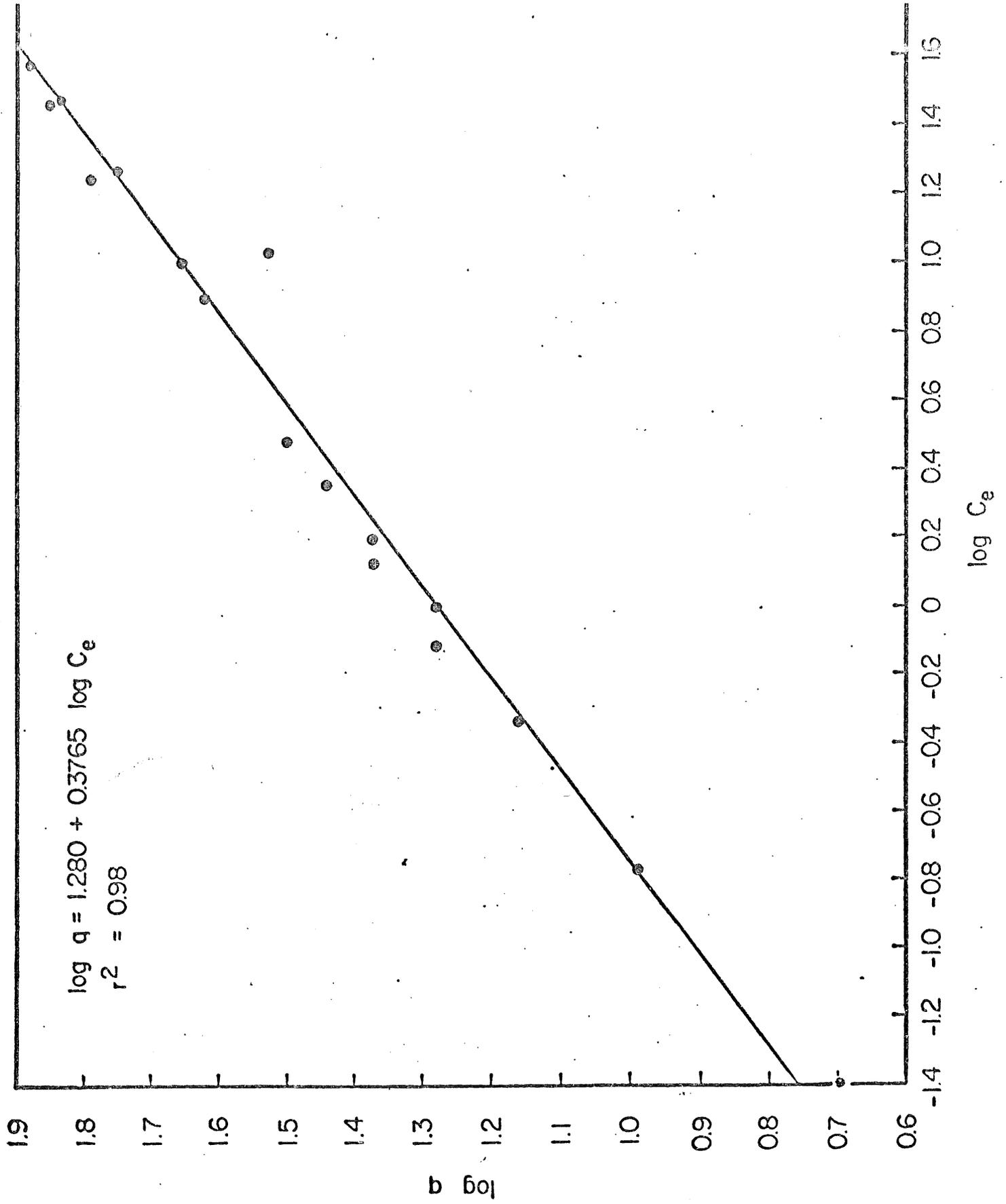
Freundlich Plot for Zinc



Freundlich Plot for Copper



Freundlich Plot for Cadmium



Freundlich Plots for Cu, Cd, Zn, and Ni

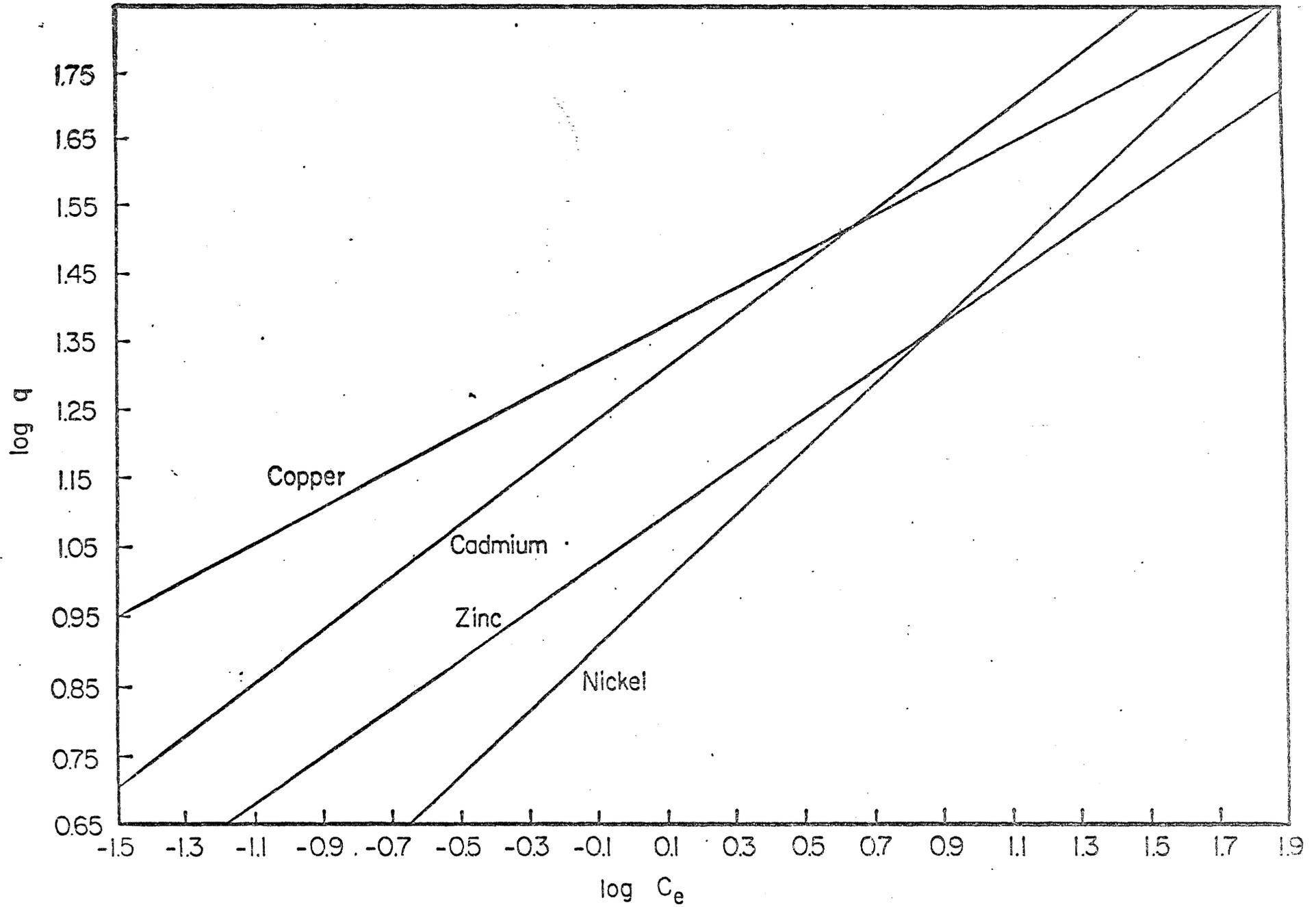


TABLE 1
Cu Adsorption Data

Sample #	Co (ppm)	Ce (ppm)	q (ppm/gm)	log q	log Ce
1	0	0.01	0	-	-
2	5	0.03	4.97	0.696	-1.52
3	10	0.06	9.93	0.997	-1.22
4	20	0.23	19.7	1.29	-0.638
5	40	3.31	36.7	1.56	+0.520
6	60	15	45.0	1.65	1.18
7	80	28	52.0	1.72	1.45
8	100	40	60.0	1.78	1.60
9	125	62	63.0	1.80	1.79
10	150	84	66.0	1.82	1.92
1	0	0	0	-	-
2	20	0.28	19.7	1.29	-0.553
3	25	0.66	24.3	1.39	-0.180
4	30	1.38	28.6	1.46	+0.140
5	35	2.59	32.4	1.51	0.413
6	40	3.74	36.3	1.56	0.573
7	45	6.40	38.6	1.59	0.806
8	50	15.5	34.5	1.54	1.19
9	300	210	90.0	1.95	2.32

TABLE 2

Cd Adsorption Data

Sample #	Co (ppm)	Ce (ppm)	q (ppm/gm)	log q	log Ce
1	0	0	0	-	-
2	25	1.58	23.4	1.37	0.199
3	50	8	42.0	1.62	0.903
4	75	19	56.0	1.75	1.28
5	100	31	69.0	1.84	1.49
1	0	0	0	-	-
2	5	0.04	4.96	0.696	-1.40
3	10	0.17	9.83	0.993	-0.770
4	15	0.46	14.5	1.16	-0.337
5	20	0.77	19.2	1.28	-0.112
6	25	1.37	23.6	1.37	+0.137
7	30	2.25	27.7	1.44	0.352
8	35	3.02	31.9	1.50	0.480
9	40	20	20.0	1.30	1.30
10	45	11	34.0	1.53	1.04
11	50	43	7.0	0.845	1.63
12	60	34	26.0	1.41	1.53
13	80	18	62.0	1.79	1.26
14	100	30	70.0	1.85	1.48
15	115	40	75.0	1.88	1.60

TABLE 3

Ni Adsorption Data

Sample #	Co (ppm)	Ce (ppm)	q (ppm/gm)	log q	log Ce
1	0	0	-	-	-
2	10	0.53	9.47	0.976	-0.276
3	20	2.45	17.5	1.24	+0.389
4	30	5.8	24.2	1.38	0.763
5	40	10.5	29.5	1.47	1.02
6	50	15.8	34.2	1.53	1.20
7	60	22	38.0	1.58	1.34
8	80	31	49.0	1.69	1.49
9	100	37	63.0	1.80	1.57
10	150	84	66.0	1.82	1.92
11	5	0.4	4.60	0.663	-0.398
12	15	2.3	12.7	1.10	+0.362
13	25	4.7	20.3	1.31	0.672
14	35	10.8	24.2	1.38	1.03
15	45	14.8	30.2	1.48	1.17
16	250	161	89.0	1.95	2.21

$$\begin{aligned}
 \text{Slope} &= 0.4534 & 1/n &= 0.4534 \\
 \text{Intercept} &= 0.9875 & K_f &= 9.716 \text{ ppm/gm} \\
 r^2 &= 0.9592 & q &= 9.72 \text{ Ce}^{(0.453)} \\
 & & & (1.70, 1.758)
 \end{aligned}$$

TABLE 4

Zn Adsorption Data

Sample #	Co (ppm)	Ce (ppm)	q (ppm/gm)	log q	log Ce
1	0	0	-	-	-
2	10	0.6	9.40	0.973	-0.222
3	20	2.66	17.3	1.24	+0.425
4	25	4.65	20.4	1.31	0.667
5	30	6.4	23.6	1.37	0.806
6	35	10.1	24.9	1.40	1.00
7	40	12.5	27.5	1.44	1.10
8	45	15.4	29.6	1.47	1.19
9	50	18.2	31.8	1.50	1.26
10	60	26	34	1.53	1.41
11	80	40	40	1.60	1.60
12	100	57	43	1.63	1.76
13	150	92	58	1.76	1.96
14	250	175	75.0	1.87	2.24

$$\text{Slope} = 0.3444$$

$$1/n = 0.3444$$

$$\text{Intercept} = 1.066$$

$$K_f = 11.64 \text{ ppm/gm}$$

$$r^2 = 0.9904$$

$$q = 11.6 \text{ Ce}^{(0.344)}$$

$$(1.65, 1.634)$$

TABLE 5

Co Adsorption Data

Sample #	Co (ppm)	Ce (ppm)	q (ppm/gm)	1/Ce	1/q
1	-	-	-	-	-
2	10	0.86	9.14	1.16	1.09×10^{-1}
3	20	5.2	14.8	1.92×10^{-1}	6.76×10^{-2}
4	30	19.0	11.0	5.26×10^{-2}	9.09×10^{-2}
5	40	37.0	3.0	2.70×10^{-2}	3.33×10^{-1}
6	50	71	-21.0	1.41×10^{-2}	-4.76×10^{-2}
7	60	86	-26.0	1.16×10^{-2}	-3.85×10^{-2}
8	80	90	-10.0	1.11×10^{-2}	-1.00×10^{-1}
9	100	120	-20.0	8.33×10^{-3}	-5.00×10^{-2}
10	150	194	-44.0	5.15×10^{-3}	-2.27×10^{-2}
1	-	-	-	-	-
2	5	0.1	4.90	1.00×10^{-1}	2.04×10^{-1}
3	15	1.3	13.7	7.69×10^{-1}	7.30×10^{-2}
4	20	3.3	16.7	3.03×10^{-1}	5.99×10^{-2}
5	25	6.3	18.7	1.59×10^{-1}	5.35×10^{-2}
6	35	20.0	15.0	5.00×10^{-2}	6.67×10^{-2}
7	40	26.0	14.0	3.85×10^{-2}	7.14×10^{-2}
8	45	30.0	15.0	3.33×10^{-2}	6.67×10^{-2}
9	55	53.0	2.0	1.89×10^{-2}	5.00×10^{-1}
10	70	94.0	-24.0	1.06×10^{-2}	-4.17×10^{-2}
11	90	94.0	-4.0	1.06×10^{-2}	-2.50×10^{-1}
12	200	260	-60	3.85×10^{-3}	-1.67×10^{-2}

TABLE 6

Pb Adsorption Data

Sample #	Co (ppm)	Ce (ppm)	q (ppm/gm)	1/Ce	1/q
1	-	-	-	-	-
2	10	ND	10	-	1.00×10^{-1}
3	20	ND	20	-	5.00×10^{-2}
4	25	ND	25	-	4.00×10^{-2}
5	30	ND	30	-	3.33×10^{-2}
6	35	ND	35	-	2.86×10^{-2}
7	40	ND	40	-	2.50×10^{-2}
8	45	ND	45	-	2.22×10^{-2}
9	50	ND	50	-	2.00×10^{-2}
10	60	ND	60	-	1.67×10^{-2}
11	80	0.04	80	25	1.25×10^{-2}
12	100	0.09	100	11.1	1.00×10^{-2}
13	150	2.0	148	0.50	6.76×10^{-3}
14	250	38.2	212	2.62×10^{-2}	4.72×10^{-3}