

KINETICS OF THE ADSORPTION OF LEAD ON RIVER-MUD

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KEY WORDS

Adsorption Anodic stripping voltammetry (ASV) Kinetics Lead River-mud

SUMMARY

The effects of several factors on the rate and the capacity of lead adsorption by river-mud were studied. These factors included the concentration of mud, the concentration of lead, the organic matter content of mud, pH, time of adsorption, temperature and agitation. The reaction order of the adsorption process with respect to lead and the type of adsorption were determined. Also, indications of the rate-limiting step were discussed and an empirical equation describing the adsorption of lead on river-mud was developed.

INTRODUCTION

The kinetics of adsorption of trace elements on soils or river sediments have not yet been well understood. Although few studies have been made in recent years about this there is still no concordance of opinion and only very little has been reported on the adsorption of lead.

The adsorption of trace metals by soils or fractions of soil has been reported to follow the Langmuir adsorption isotherm, examples are adsorption of copper²⁵, of cadmium^{11,14,19}, and of zinc^{21,22,24}. The adsorption of cadmium on river muds and suspended particles has been reported to follow the Freundlich adsorption isotherm⁸.

The mechanism of adsorption of trace elements on soils or on fractions of soils has been the subject of few publications in the past few years. Bunzl^{2,3} suggested that adsorption of lead, cadmium, zinc or calcium ions onto humic acid and peat occurs through an ion exchange process between the ion adsorbed and hydrogen ions from the organic matter. The rate-limiting step for adsorption of lead was proved to be film-diffusion³. Ong and Swanson¹⁷ considered fixing copper by the organic matter as an attraction between the positively charged ion and the

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negatively charged surface. Thus, adsorption increased with the ionic potential of the cation. Farrah and Pickering^{5,6,7} proposed a mechanism for the adsorption of copper and zinc on clays based on the presence of positive charges at the crystal edges (from broken edges) and negative charges on the crystal faces (from lattice defects).

EXPERIMENTAL

1. The pretreatment of the river-mud

The lead content of the samples used in this work is high (Table 1) compared to the lead concentrations used (20.7 to 207.2 $\mu\text{g/l}$). Therefore, treating the mud samples for desorption of their lead content was necessary before they were used. This was done by treating the samples with 0.1 M perchloric acid (this acid was chosen because of its suitability for ASV) many times until no lead was found in the extract (the method of detection used was ASV). The mud was then washed thoroughly with distilled water and stored under distilled water. Portions of these treated samples were taken for the adsorption experiments.

2. The adsorption experiments

Two hundred and fifty mls polyethylene bottles, which had been frequently used for about two years and thus had a greatly reduced adsorption capacity²⁰, were rinsed thoroughly with $\approx 0.1 M$ perchloric acid to remove contamination and then were washed thoroughly with distilled water. Two hundred ml of distilled water were poured into each bottle. Then, a known weight of the treated river-mud was added to each bottle. The required concentration of metal ions in solution was achieved by addition of the proper amount of a concentrated solution of the metal ion using Oxford pipettes. The bottles were shaken occasionally during the adsorption process. The adsorption process was found to become very slow after about fifteen hours and thus the adsorption was usually left for at least 15 hours for studying the effects of the different factors on the adsorption process. Because of the variation in the properties of the different samples of the river-mud (Table 1) portions of the same sample were used in studying the effect of one factor on the adsorption process.

For the analytical measurements, the above suspension was taken into two halves, one without mud and the other containing the mud. Both halves were then acidified with perchloric acid to pH 2.2, thermostated at 30°C and analyzed by anodic stripping voltammetry (ASV); details of the experimental of ASV are found elsewhere¹⁸.

With the exception of the experiments carried out for studying the effect of temperature on adsorption, all the adsorption processes were conducted at 20°C. Wet mud was always used for the above experiments but the dry weight was always used in representing the results.

Table 1. Some chemical characteristics of the river-mud samples used in this work

Sample	Organic matter content %	Lead content ($\mu\text{g/g}$)	pH of a mixture of untreated mud and water (12.5% by weight)
I	53.8	132.3	6.8
II	38.6	207.8	6.9
III	29.7	448.6	7.4

3. Oxidation of the organic matter

The organic matter was destroyed, in samples used for the effect of organic matter content, by treatment with H_2O_2 . The remaining inorganic part was examined with IR to insure complete oxidation of the organic matter.

RESULTS AND DISCUSSION

1. The effect of the organic matter content

Adsorption isotherms of lead were established on mud and on the same mud after oxidation of the organic matter content. The adsorption isotherm on the organic matter was calculated from these adsorption isotherms with the knowledge of the chemical composition of the mud sample (Sample 1, Table 1). From the results (Fig. 1) we can conclude that the organic matter has higher adsorption capacity than the inorganic part of the river mud, or at least that any clay-humus compound adsorbs relatively more than the clay fraction alone. This agrees with

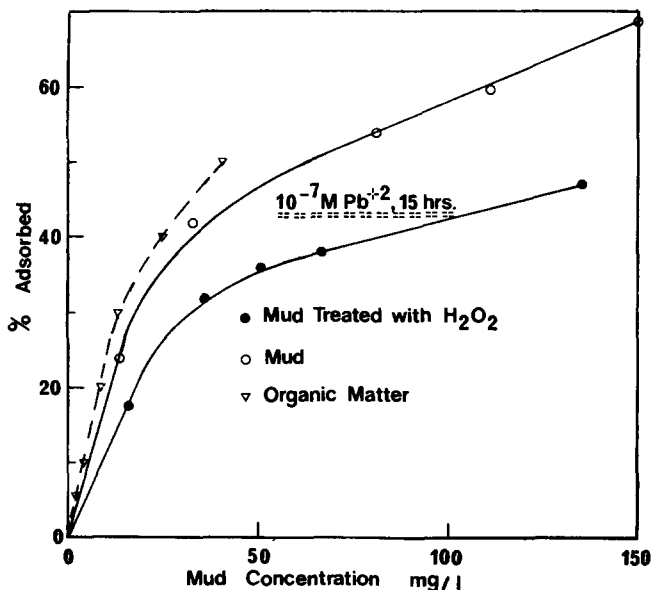


Fig. 1. The effect of the organic matter content on the adsorption of lead on river-mud (Sample I). Lead concentration = $20.72 \mu\text{g/l}$. Time of adsorption = 15 hours.

the results reported in the literature on the effect of organic matter on increasing adsorption of copper^{1, 15, 18, 23}, cadmium^{8, 13, 14} and zinc^{16, 21} on soil.

2. The effect of pH

The effect of pH on the adsorption uptake of lead onto mud is shown in Fig. 2. The maximum shown at around pH 6.5 is probably due to a change in the type of adsorption from a physical to a chemical type of adsorption¹⁰.

3. The effect of mud concentration

To study this effect, various weights of mud ranging between 0.15 to 3.7 g/l were allowed to adsorb lead from solution of $1 \times 10^{-6} M$ (207.2 $\mu\text{g/l}$) initial concentrations for 20 hours. These results (Table 2) indicate that increasing the mud concentration increases the uptake of lead. Plotting C_s against C_1 (Fig. 3) shows

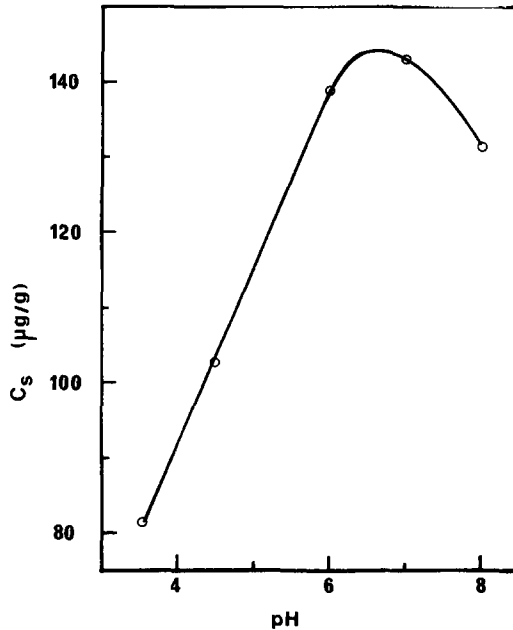


Fig. 2. The effect of pH on the adsorption of lead on river-mud (Sample II).
Mud concentration = 1.1–1.16 g/l.
Lead concentration = 207.2 $\mu\text{g/l}$.
Time of adsorption = 20 hours.

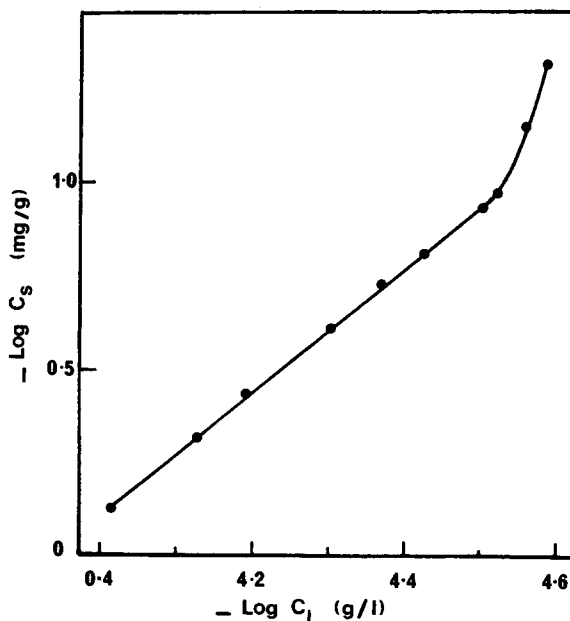


Fig. 3. The effect of mud concentration (Sample III) on the adsorption of lead. Adsorption time is 20 hours.

that the decrease in C_s is due, in fact, to the decrease in the concentration of lead in solution and is independent on mud concentration up to 1.7 g/l mud.

4. The type of adsorption of lead on mud

Adsorption of lead on the acid-treated mud (protonated form) was found to increase the conductivity and the hydrogen ion concentration of the mud suspension (Table 3).

The above results suggest that adsorption of lead on mud is an ion exchange process. This is indicated by the decrease in the pH of the suspension with increasing time of adsorption. Substituting lead ions in solution by hydrogen ions from the mud (every divalent lead ion adsorbed is expected to release two monovalent hydrogen ions, for maintaining electroneutrality) results in increasing the conductivity as a result of the increase of mobility (316.55 and 60.5 for hydrogen and lead ions at 18°C⁴, respectively) and, therefore, the conductivity results in the above table confirm the ionic exchange process.

Table 2. The effect of mud concentration on adsorption of lead from 207.2 µg/l (1×10^{-6} M) initial concentration

Concentration of mud mg/l	Concentration of lead on mud C_s (µg/g)	Concentration of lead left in solution C_i (µg/l)	Concentration of mud mg/l	C_s µg/g	C_i µg/l
148.1	747.1	96.6	1085.9	156.6	37.3
281.0	435.8	84.7	1501.6	117.1	31.3
391.0	365.0	64.0	1665.0	106.6	30.0
638.5	246.9	49.5	2510.0	71.7	27.3
876.4	187.5	42.9	3710.0	48.9	25.9

Table 3. The effect of the adsorption of lead from 2.07 mg/l (1×10^{-5} M) solution on the conductivity and the pH of mud suspension (1 : 6 mud to distilled water, by weight)

Time of adsorption (min)	Conductivity (µmhos)	pH	Time of adsorption (hours)	Conductivity (µmhos)	pH
0	23	4.20	2	68	4.10
10	44	4.15	5	85	4.05
30	58	4.12	9	95	4.02
			24	100	4.00

5. The reaction order of the adsorption process

A set of experiments measuring adsorption from various concentrations of lead were carried out for various times in order to study the dependence of rate of adsorption on the concentration of lead in solution and hence to find the reaction order of the adsorption process. Table 4 summarizes these results.

For each initial concentration of lead used, a graph of C_s against \sqrt{t} was plotted; the graphs were straight lines. From the slopes of these lines (*i.e.* $dC_s/d\sqrt{t}$), the rate of adsorption (dC_s/dt) was calculated from the formula:

$$\left(\frac{dC_s}{dt}\right)_t = \frac{1}{2\sqrt{t}} \left(\frac{dC_s}{d\sqrt{t}}\right)_t \quad (1)$$

Plotting the rate of adsorption of lead $\left(\frac{dC_s}{dt}\right)$ against the concentration of lead in

Table 4. Adsorption of lead on mud (Sample III)

Time of adsorption (hrs.)	Initial concentration of lead ($\mu\text{g/l}$)							
	20.72		62.16		124.32		207.19	
	C_s^* ($\mu\text{g/g}$)	C_1^+ ($\mu\text{g/l}$)	C_s ($\mu\text{g/g}$)	C_1 ($\mu\text{g/l}$)	C_s ($\mu\text{g/g}$)	C_1 ($\mu\text{g/l}$)	C_s ($\mu\text{g/g}$)	C_1 ($\mu\text{g/l}$)
1	5.7	15.9	17.3	46.9	39.5	92.5	61.7	152.9
3	10.2	11.7	30.5	35.5	71.6	68.1	112.2	111.3
7	14.1	8.5	44.0	24.1	94.0	43.0	146.3	77.7
15	19.6	4.2	60.3	13.3	110.8	21.9	188.0	34.2

The concentration of mud ranges between 0.80 and 0.90 g/l.

* C_s = the concentration of lead adsorbed on mud.

+ C_1 = the concentration of lead remaining in solution.

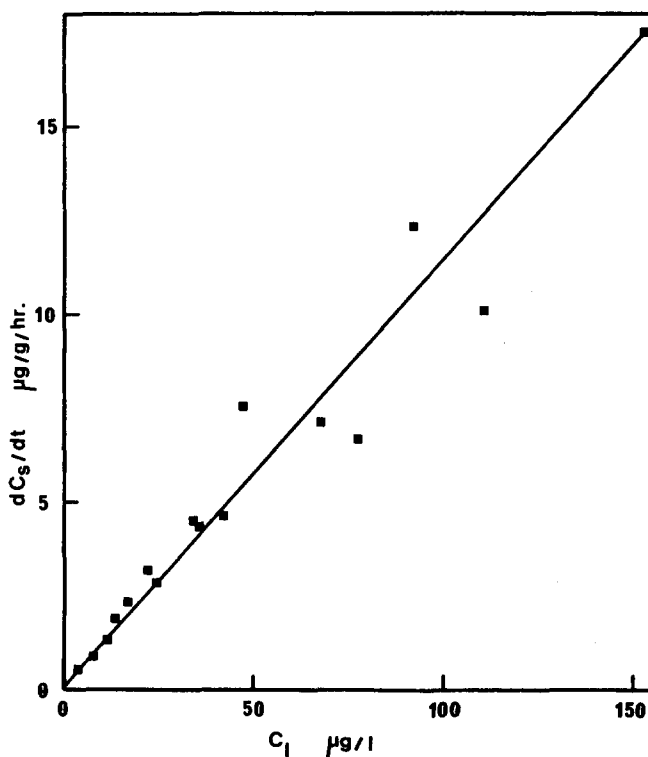


Fig. 4. The dependence of the rate of lead adsorption on river-mud on the concentration of lead remaining in solution.

solution (C_1) gives a straight line (Fig. 4) which shows that the rate of adsorption of lead is proportional to the concentration of lead remaining unadsorbed at a certain time, irrespective of the initial concentration of lead in solution. Therefore it can be concluded that the adsorption process of lead on river mud is a first order reaction with respect to lead.

6. *An empirical equation describing the adsorption of lead on river-mud*

An empirical Equation, similar to that developed by Kuo and Lotse¹² for the adsorption of phosphates on lake sediments, can be developed for the adsorption of lead on river-mud. For doing this, the results shown in Table 4 are taken as an example of the adsorption of lead on river-mud.

Fig. 5 shows that the results of Table 4 agree with the Freundlich equation with

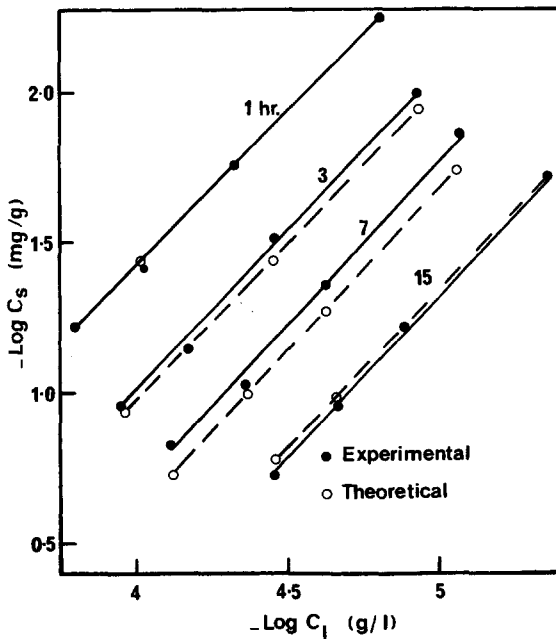


Fig. 5. The application of the Freundlich Equation for the adsorption of lead on river-mud after several times of adsorption.

a straight line obtained for each time of adsorption from various concentrations of lead in solution. This indicates that these results agree with the Equation:

$$\log C_s = \log K + \frac{1}{n} \log C_1 \quad (2)$$

where

C_s = the concentration of lead adsorbed on mud
 C_1 = the concentration of lead remaining in solution
 K and n = constants under certain conditions.

From the results presented in Fig. 5, $\frac{1}{n}$ is constant for all the times of adsorption (equal 1.06) but K is constant for one time of adsorption but varies with varying the time, with values of 2.82, 3.22, 3.59 and 3.98 for the lines corresponding to 1, 3, 7 and 15 hours adsorption time, respectively.

Plotting a logarithmic relation between the above values of K against the corresponding times of adsorption gives a straight line with a slope of 0.95 and an intercept of 2.82. Thus the relationship between the parameter K of Equation (2) and time of adsorption (t) can be represented by the Equation:

$$\log K = 2.82 + 0.95 \log t. \quad (3)$$

Substituting for log K and $\frac{1}{n}$ from above into Equation (2) gives:

$$\log C_s = 2.82 + 0.95 \log t + 1.06 \log C_1 \quad (4)$$

This above Equation can be represented in a more general form as:

$$C_s = K't^{0.95}C_1^{1.06} \quad (5)$$

where K' is a constant which is equal to 661 for the results presented here. This Equation has been proved in very good agreement with the experimental results of Table 4 (see Fig. 5). However, this Equation is expected to be applicable only for concentrations of mud less than 1.7 g/l (see Fig. 3).

The above Equation can be further developed to take account of the initial concentration of lead in solution (C_0), which is independent of time, instead of C_1 .

Fig. 6 indicates a linear logarithmic relationship between C_1 and C_0 with parallel straight lines representing different times of adsorption. These lines have a slope of 0.95 and intercepts of -0.33, -0.54, -0.72 and -0.92 for the lines representing adsorption after 1, 3, 7 and 15 hours respectively. Plotting these values for the intercepts of the different lines against the logarithmic values of the

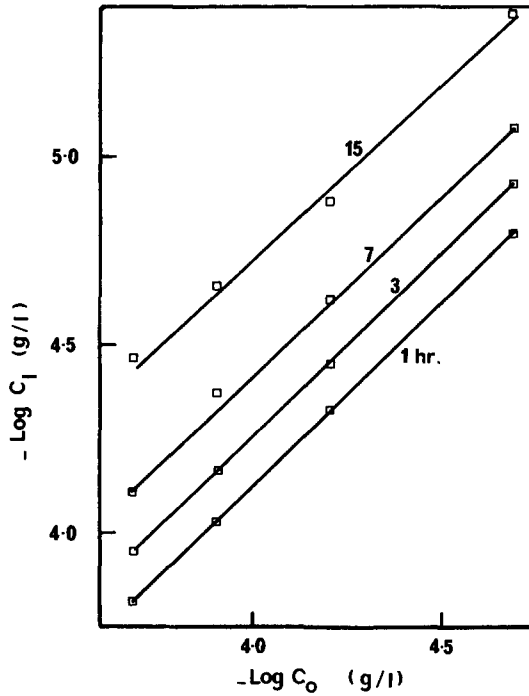


Fig. 6. Relations between the initial concentrations of lead (C_0) and the concentrations remaining (C_1) after several times of adsorption on river-mud.

time of adsorption, corresponding to these lines, gives a straight line having a slope of -0.47 and an intercept of -0.33 .

From above, it can be concluded that the present results can be represented by the Equation:

$$\log C_1 = -0.33 - 0.47 \log t + 0.95 \log C_0 \quad (6)$$

Substituting for C_1 from the above equation into Equation (4) gives:

$$\log C_s = 2.47 + 0.45 \log t + \log C_0 \quad (7)$$

This Equation can be represented in another form as:

$$C_s = 295t^{0.45}C_0 \quad (8)$$

This Equation has been again proved to be in a very good agreement with the experimental results of Table 4 (see Fig. 7). However, this Equation is expected to

be applicable only when the concentration of mud is constant or, at least, is only varied within a small range. A general equation for the adsorption of lead on mud may have the form:

$$C_s = Kt^n C_o^m \quad (9)$$

where K , n and m are constants for a certain concentration of mud.

7. The rate-limiting step for the adsorption of lead on mud

1 Steps of adsorption

Adsorption of lead from solutions by mud occurs through three main consecutive steps:

1. The transport of the cation by diffusion through a thin film of the external solution, surrounding an adsorbent particle, to the exterior surface of this

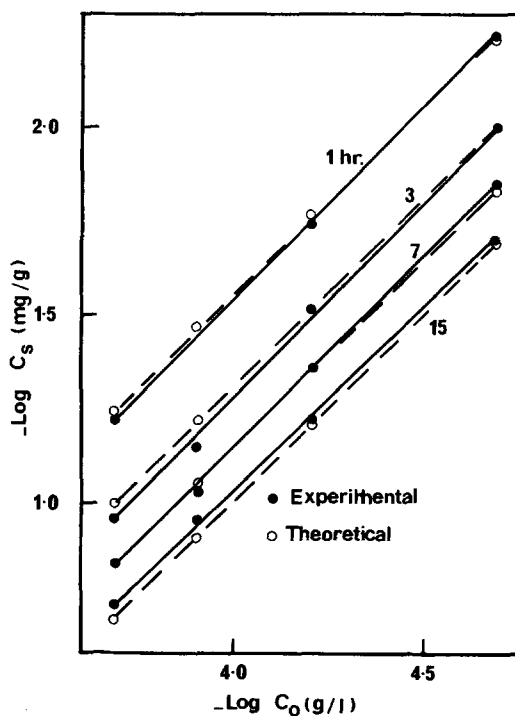


Fig. 7. Comparison between calculations based on Equation (8) and the experimental results of Table 4.

particle. The cations are driven through this film by a concentration gradient. This step is called 'film diffusion'.

2. The second step, with the exception of a small amount of adsorption which occurs on the exterior surface of the adsorbent, is the diffusion of the adsorbate within the pores of the adsorbent. This step is called 'intraparticle diffusion'.

3. The last step is the actual adsorption of lead on the interior surfaces bounding the pore and capillary spaces of the adsorbent. This step is called 'adsorption step'.

II. Determining whether the rate-limiting step is adsorption or diffusion

Certain properties of the adsorbate and the adsorbent can be useful in determining the nature of the rate limiting step. The following factors were studied experimentally to determine whether the overall adsorption process is controlled by strictly adsorption (*i.e.* step 3 above) or by diffusion (*i.e.* steps 1 and 2 above).

1. *The effect of time.* A straight line relationship has been noted between the concentration of lead (C_s) adsorbed on mud and the square root of time of adsorption for the results shown in Table 4 (Section 5). This straight line relationship has also been proved true, by doing other sets of experiments, up to around 100 hour time of adsorption after which it deviates from linearity. This linear relationship suggests that the rate-limiting step for the adsorption process is diffusion^{9, 26}.

2. *The effect of temperature.* Equation (5) has been shown to be applicable to the adsorption of lead under certain conditions. With varying conditions (*e.g.* temperature) the constant in this equation would vary.

Measuring the variations of this constant with temperature can be used as a means of measuring the activation energy for the adsorption process by applying the Arrhenius Equation:

$$K = Ae^{-E/RT}$$

where

K = a constant related to the reaction rate (in the present case it is K' of Equation 5)

A = a constant

E = the activation energy for the adsorption process

R = the gas constant (1.98 cal/mole)

T = the temperature (Kelvin degrees).

A set of experiments was done for the purpose of measuring the activation energy of the adsorption process of lead on mud. These results are shown in Table 5.

Table 5. The effect of temperature on the adsorption of lead on river-mud from 207.2 $\mu\text{g/l}$ ($1 \times 10^{-6} M$) solution after 24 hours

Temperature $^{\circ}\text{C}$	Concentration of mud (mg/l)	Concentration of lead adsorbed (C_s) ($\mu\text{g/g}$)	Concentration of lead in solution (C_l) ($\mu\text{g/l}$)
3	500	297.0	58.7
25	503	309.1	51.7
40	498	320.3	47.7
60	497	331.0	42.7

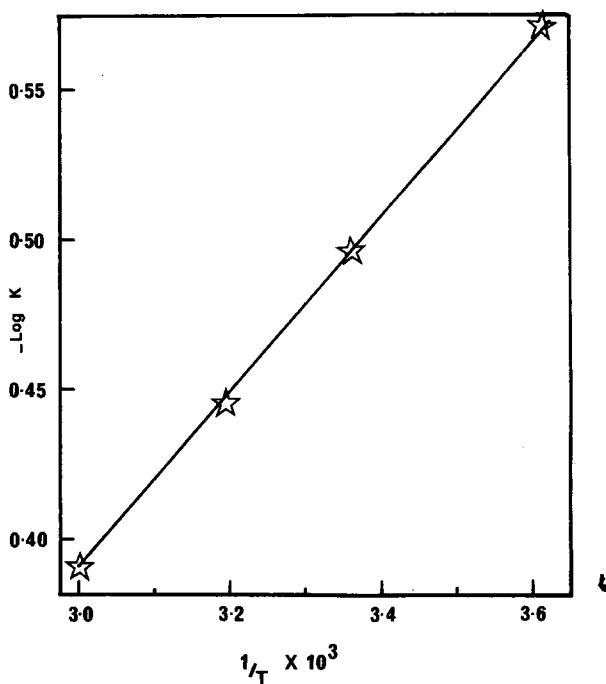


Fig. 8. The application of the Arrhenius Equation for the adsorption of lead on river-mud (Sample III).

Mud concentration = 0.5 g/l.

Lead concentration = 207.2 $\mu\text{g/l}$.

Time of adsorption = 24 hours.

The above results were used to calculate K' (of Equation 5) at different degrees of temperature after changing to $\mu\text{mole/g}$, $\mu\text{mole/l}$ and hours for C_s , C_1 and t , respectively. The results gave a linear relationship between $\log K'$ and $1/T$ (Fig. 8). The activation energy of the adsorption of lead on mud was calculated from the slope of this straight line to be 1.38 Kcal/mole. This low value of the activation energy suggests again that the rate limiting-step is diffusion (it would have been negative or positive but high for physical or chemical adsorption, respectively, if adsorption was the rate-limiting step).

III. Determining whether the rate-limiting step is film diffusion or intraparticle diffusion

Differentiating between film diffusion-controlled processes and intraparticle-controlled ones is not easy. In many cases the process is controlled by both types of diffusion when the rate of transfer by both types of diffusion is similar⁹. In other cases the adsorption process changes from being controlled by one type of diffusion to become controlled by the other by slightly varying the conditions²⁷. However, the following factors were studied in order to throw more light on the rate-limiting step.

1. *The effect of agitation.* In the case of film diffusion-controlled processes, agitation of the suspension is expected to increase the rate of adsorption. On the other hand, agitation is expected to have no effect on the rate of adsorption when adsorption is controlled by intraparticle diffusion.

Table 6 shows a considerable effect of agitation on the rate of adsorption of lead from various concentrations of lead on river-mud. This suggests that the rate-limiting step is a film diffusion. However, a conclusion based on the effect of agitation is not always reliable for determining the rate-limiting step⁹.

2. *A comparison between the experimental values and the theoretical equations describing adsorption processes controlled by diffusion.* The consideration of the

Table 6. The effect of agitation on the adsorption of lead on river-mud

Concentration of lead ($\mu\text{g/l}$)	Concentration of lead ($\mu\text{g/g}$) adsorbed on 0.4 g/l mud in 2.5 hours	
	Without agitation	With agitation
20.72	10.9	34.2
62.16	29.5	101.3
124.32	57.2	185.9
207.19	89.1	302.5

adsorption of lead on river-mud as an ion-exchange process allows the application of the theoretical equations of ion exchange processes controlled by diffusion. The following equations are simplified forms of these given by Helfferich⁹ describing ion exchange processes controlled by film diffusion (Equation 10) or by intraparticle diffusion (Equation 11):

$$\ln \frac{C_1}{C_0} = - \frac{t}{\tau} \quad (10)$$

$$\frac{C_1}{C_0} = e \left(\frac{t}{\tau} \right)^2 \left(1 - \operatorname{erf} \frac{t}{\tau} \right) \quad (11)$$

where

C_1 = the concentration of lead remaining in solution (mole/l)

C_0 = the initial concentration of lead in the aqueous solution (mole/l)

τ = a time constant (sec).

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt.$$

τ in the above equations is given by:

$$\tau = \frac{S}{3D_1 C_p Z} \quad \text{for } \tau \text{ in Equation (10), and}$$

$$\tau = \frac{1}{9K^2 C_p^2 D_s Z^2} \quad \text{for } \tau \text{ in Equation (11),}$$

where

D_1 = the diffusion coefficient in aqueous solutions (cm²/sec)

D_s = the diffusion coefficient within the particles (cm²/sec)

C_p = the concentration of the solid (gm/cm³)

K = the ratio of lead in aqueous solution to that in the particles, at equilibrium.

This ratio is constant for a given mud at a fixed pH and is expected to be large (one measured value was 6.6×10^4)

$Z = \frac{1}{r}$, where r is the radius of a particle.

This assumes that no particle is so small to become saturated with lead before the solution is depleted of lead.

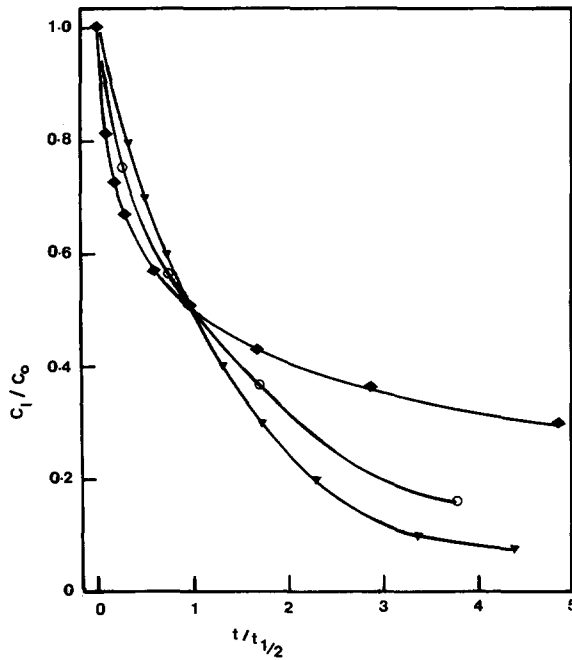


Fig. 9. Comparison between the experimental results for the adsorption of lead on river-mud (Table 4) with theoretical relations describing adsorption when controlled by either film diffusion or intraparticle diffusion.

Legend:

- Intraparticle diffusion-theoretical.
- Experimental results for the adsorption of lead on river-mud.
- ▲ Film diffusion-theoretical.

The simplification of the above equations from the equations given by Helfferich is by the assumption that the concentration of lead on particles, at equilibrium, is very much greater than in solution (the thing which has been proved experimentally in this work).

The above equations are compared in Fig. 9 with the experimental results of Table 4 by plotting C_1/C_0 against $t/t_{1/2}$, where $t_{1/2}$ is the time needed to make $C_1 = \frac{1}{2}C_0$. It is obvious from Fig. 9 that the experimental results do not agree completely with either type of diffusion-controlled processes. Instead, the experimental results lie in between the theoretical graphs of the two types of diffusion-controlled processes, but closer to the curve representing the film diffusion-controlled processes. This suggests that the rate-limiting step, in the case of the adsorption of lead on river-mud, is not controlled completely by either type of

diffusion and that film-diffusion is more effective in controlling this adsorption process.

CONCLUSIONS

The following conclusions can be drawn from the results:

1. Studying adsorption of trace metals on river-mud is a difficult process because of the inconsistency of the properties of the different samples of mud, the high content of some metals in the mud and the adsorption on the container surfaces.

2. The rate of adsorption of lead on mud is high at the beginning but then slows down and equilibrium is approached very slowly after several days for the range of lead concentrations used in this work.

3. The organic content of the mud has higher capacity for adsorption of lead than the inorganic component.

4. The amount of adsorption of lead on river-mud increases with the increase of pH, reaching a maximum at about pH 6.5 and then decreases with the increase of pH.

5. The adsorption uptake of lead on mud is linearly dependent on the square root of the time of adsorption.

6. Adsorption of lead on mud increases with the increase of temperature. The activation energy of this adsorption is 1.38Kcal/mole.

7. The rate of adsorption of lead on mud increases with agitation of the suspension.

8. Adsorption of lead on river-mud is a first order ion-exchange process. There are indications that the rate limiting step is not completely film diffusion or intraparticle diffusion but is closer to the case of film diffusion-controlled processes.

9. Adsorption of lead on river-mud follows the Freundlich Equation when using mud concentrations up to 1.7 g/l. An empirical Equation can be developed to describe lead adsorption on a constant mud concentration, this is:

$$C_s = Kt^n C_o^m$$

where

C_s = the concentration of lead on mud

C_o = the initial concentration of lead in solution

t = time of adsorption

K = a rate constant

n and m = constants.

Received 9 March 1979

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