Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Versino, Carlo , Sarzanini, Corrado , Gigante, Rosaria and Kodram, Franco(1979) 'Removal of Cupric Ions by Means of Activated Sludge: Kinetics, Isotherms, and Yields', Separation Science and Technology, 14: 10, 909 — 921

To link to this Article: DOI: 10.1080/01496397908058101

URL: http://dx.doi.org/10.1080/01496397908058101

SEPARATION SCIENCE AND TECHNOLOGY, 14(10), pp. 909–921, 1979

Removal of Cupric Ions by Means of Activated Sludge: Kinetics, Isotherms, and Yields

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Abstract

Adsorption of Cu(II) on activated sludge from the treatment of municipal sewage is studied. The resulting adsorption isotherm is of the Langmuir type.

FOREWORD

In earlier papers (*1–5*) a number of investigations were reported on waste water and municipal sewage of the city of Turin. The study was developed starting from chemical and physicochemical characterization of the primary sludge.

This paper reports the results obtained in a study of the adsorption of cupric ion (Cu^{2+}) from solution at different concentrations by dried activated sludge. The effect of prior solvent extraction of the dried sludge was also investigated. Kinetics, isotherms, and total percentage of Cu^{2+} removal were measured; the adsorption isotherm was of the Langmuir type.

EXPERIMENTAL

Equipment and Operating Conditions

Laboratory expreiments with a Rotating Biological Surface (RBS) (*6*) provided the needed activated sludge; the raw municipal sewage of the city of Turin was used as a substrate.

The activated sludge was collected from the RBS and thickened to a water content between 92 and 94% (w/w). The samples were then dried at 105°C for 2 hr to prepare them for analysis and for use as adsorbent.

Five cubic meters of municipal sewage yelded 980 g of activated sludge (AS) when dried at 105°C, with a ratio of conversion $BOD_5{}^{20}$/AS (Biochemical Oxygen Demand, for 5 days at 20°C) of 0.585. To obtain homogeneous and representative samples, the dried AS was powdered and sieved to a range of 200 to 42 mesh. The AS so obtained had a surface area of 2 m^2/g as evaluated by the BET method (*7*) with N_2. This unusually low value is explained by the fact that the grains are covered with greasy materials which play some role in the adsorption of ions. The effect of these lipid materials was investigated by preparing modified AS treated by extraction with solvents (petroleum ether and chloroform), labeled henceforth EAS (extracted activated sludge). Table 1 presents the composition of the municipal sewage and the activated sludge.

TABLE 1

Composition of the Municipal Sewage and the Activated Sludge

	Municipal sewage (mg/l)	Activated sludge (mg/g)
Ashes	—	191.800
EEP[a]	265.900	7.760
ECL[b]	20.200	2.350
Cd	0.012	0.019
Cr	0.130	0.385
Cu	0.130	0.393
Fe	1.050	6.825
Mn	0.049	0.080
Ni	0.090	0.110
Pb	0.130	0.327
Zn	1.210	3.015

[a] EEP = extractable petroleum ether.

[b] ECL = extractable chloroform.

The rate of Cu^{2+} adsorption is fairly high in the first stages of the process so that, to determine accurate kinetic data, conventional techniques of liquid–solid phases separation were not applicable because they require a separation time larger than the estimated contact time. Equipment designed for good solid to liquid contact without AS dispersion into the liquid phase is shown in Fig. 1. Every reactor consists of 10 vertical slabs of Plexiglas (3.5 × 9.0 cm) supported by a Plexiglas plate. The slabs are covered with a thin layer of inert petroleum jelly which supports the AS without interfering in the adsorption process. This method permits exact control of the sludge–substrate contact time.

The experiments were performed at 20 ± 0.2°C and pH 4.7 ± 0.1. Figure 2 shows that roughly 90% of the copper is present as Cu^{2+} ion at this pH (*8*, *9*).

The AS or EAS supported on the reactor plates was placed into 1000 ml of copper solution stirred with a magnetic laboratory stirrer.

Two milliliter samples of solution were taken in the course of reaction, and the copper concentrations were determined by atomic absorption. Cooper chloride solutions containing 10, 20, 30, and 40 ppm (as Cu^{2+}) were used.

RESULTS

A first set of kinetic experiments was carried out using varying amounts of AS or EAS (fixed by sieving on the slabs). A layer of 1.587×10^{-3} g/cm^2 allowed equilibrium between solid and solution to be reached within a reasonable time, so that this quantity was chosen for use in all subsequent experiments. The relevant adsorption kinetics are plotted in Figs. 3 and 4.

A second part of the research was devoted to the evaluation of equilibrium adsorption isotherm data at 20 ± 0.2°C. After approximately 24 hr of stirring, the Cu^{2+} concentration in the solution remained constant, and this value was assumed to be the equilibrium Cu^{2+} concentration (C_e).

In Table 2 the concentrations of adsorbate originally present in solution (C_i), the equilibrium concentrations (C_e), and the decreases in adsorbate concentration at equilibrium (C_a) are summarized for 1 liter solutions containing 10, 15, 20, 25, 30, 35, 40, 45, 50, 100, and 150 ppm of Cu^{2+} and treated with 1 g of AS or 1 g of EAS. The same data are plotted in Figs. 5 and 6 where we have used concentration of adsorbate per unit weight of adsorsorbent instead of a concentration per unit surface because the surface areas evaluated are not representative.

All the isotherms exhibit definite Langmuir behavior. We have there-

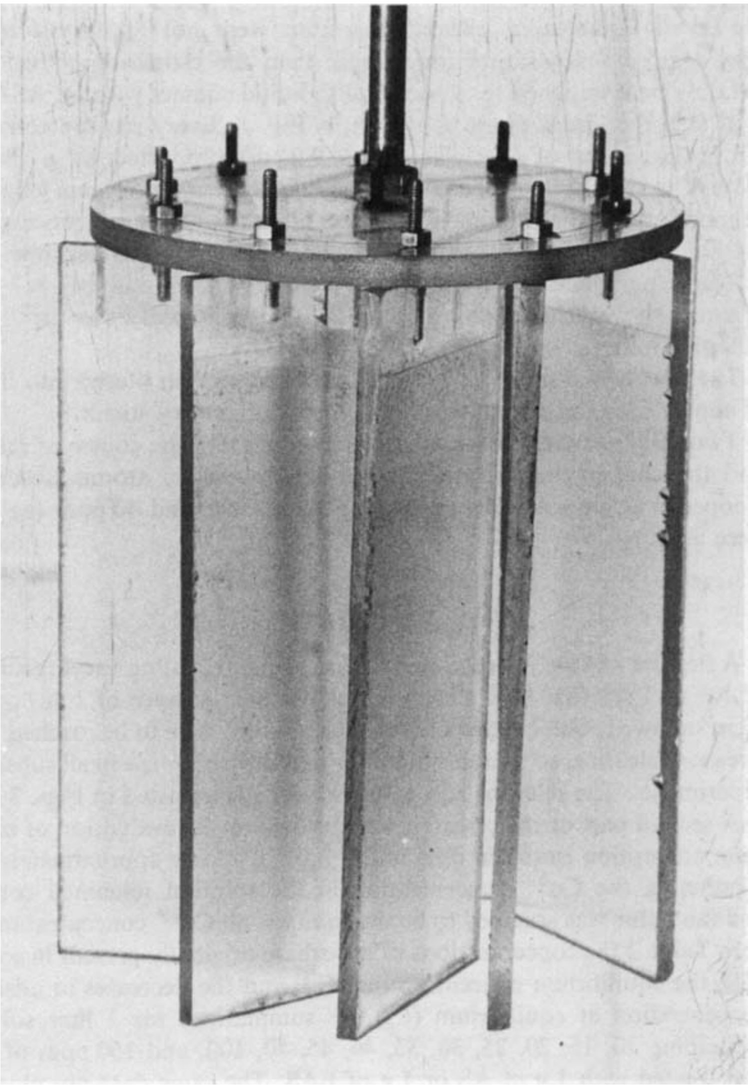

FIGURE 1.

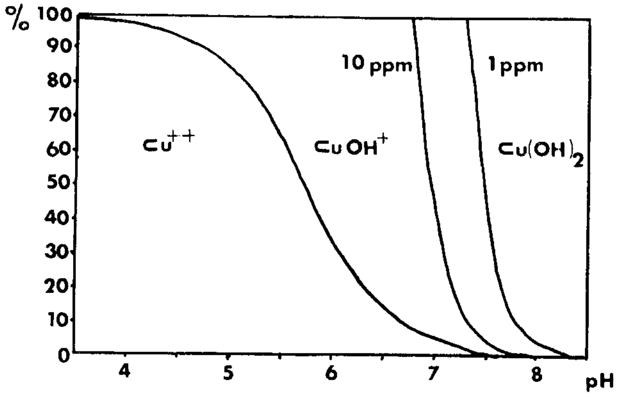

FIG. 2. Percentage of Cu^{2+} at various pH values.

TABLE 2

Absorption of Cu(II) with AS and EAS

Added Cu(II) conc (ppm),[a] C_i	Final Cu(II) conc (ppm) AS[b] C_e	Final Cu(II) conc (ppm) EAS[b] C_e	Removed Cu(II) conc (mg/g) AS[b] C_a	Removed Cu(II) conc (mg/g) EAS[b] C_a
10	0.43	0.60	9.56	9.40
15	0.84	1.09	14.16	13.91
20	1.39	1.83	18.61	18.17
25	2.25	2.90	22.75	22.10
30	3.61	4.50	26.39	25.50
35	6.20	7.50	28.80	27.50
40	9.54	11.29	30.46	28.71
45	13.20	14.60	31.80	30.40
50	17.11	18.84	32.89	31.16
100	66.90	68.60	33.10	31.40

[a] Duration of run = 24 hr.

[b] All runs made with 1 g of AS or 1 g of EAS. C_i, C_e, C_a: concentrations of adsorbate originally present, at equilibrium in solution, and on activated sludge extracted or not.

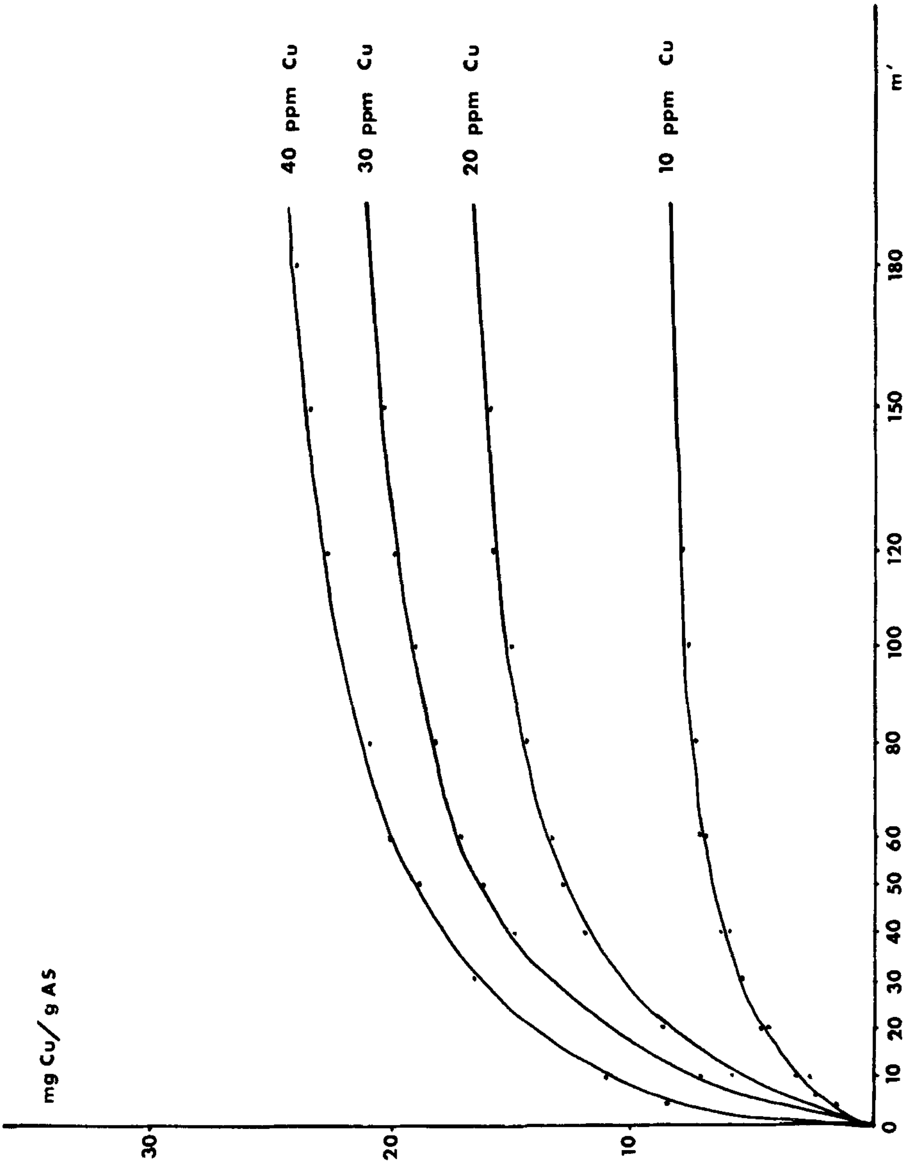

FIG. 3. Kinetics of adsorption.

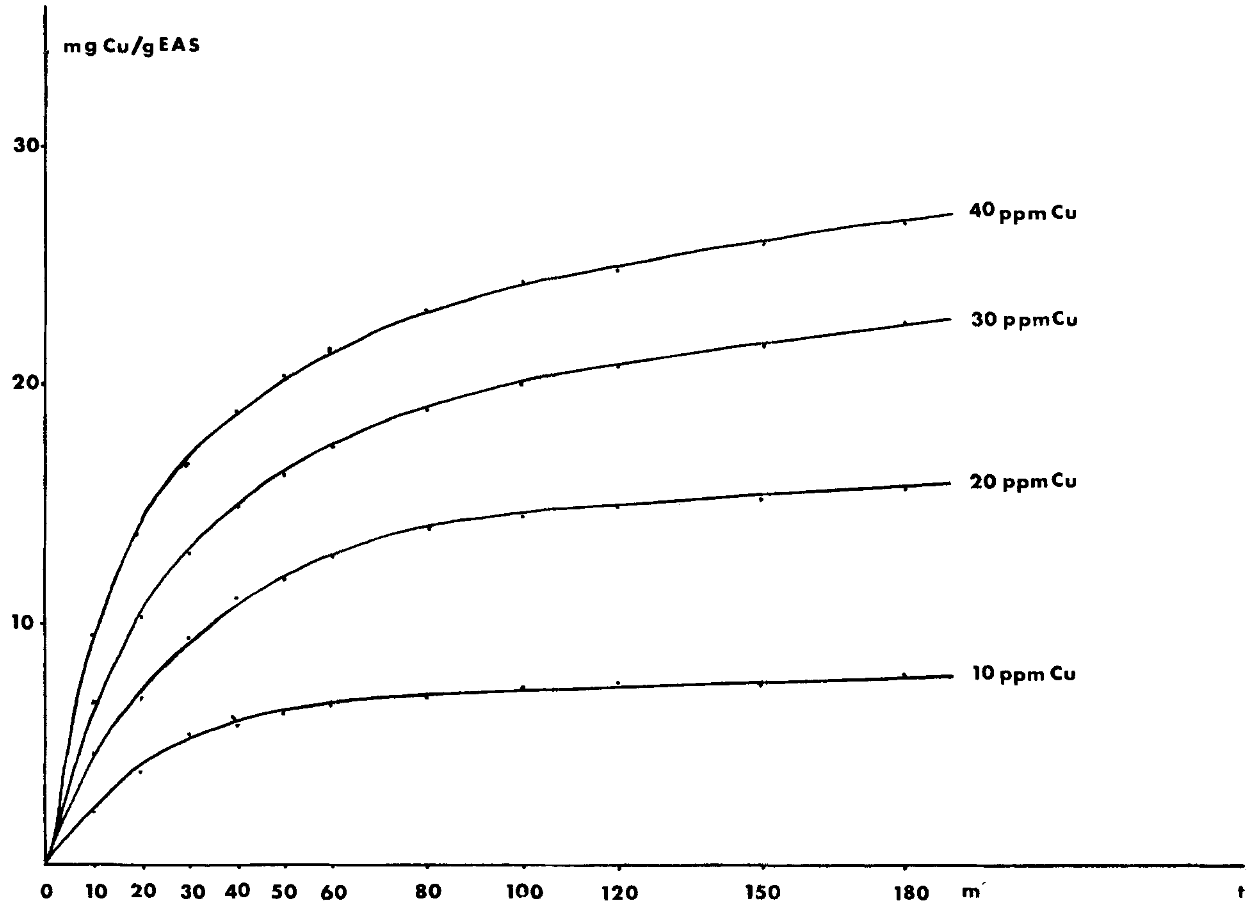

FIG. 4. Kinetics of adsorption.

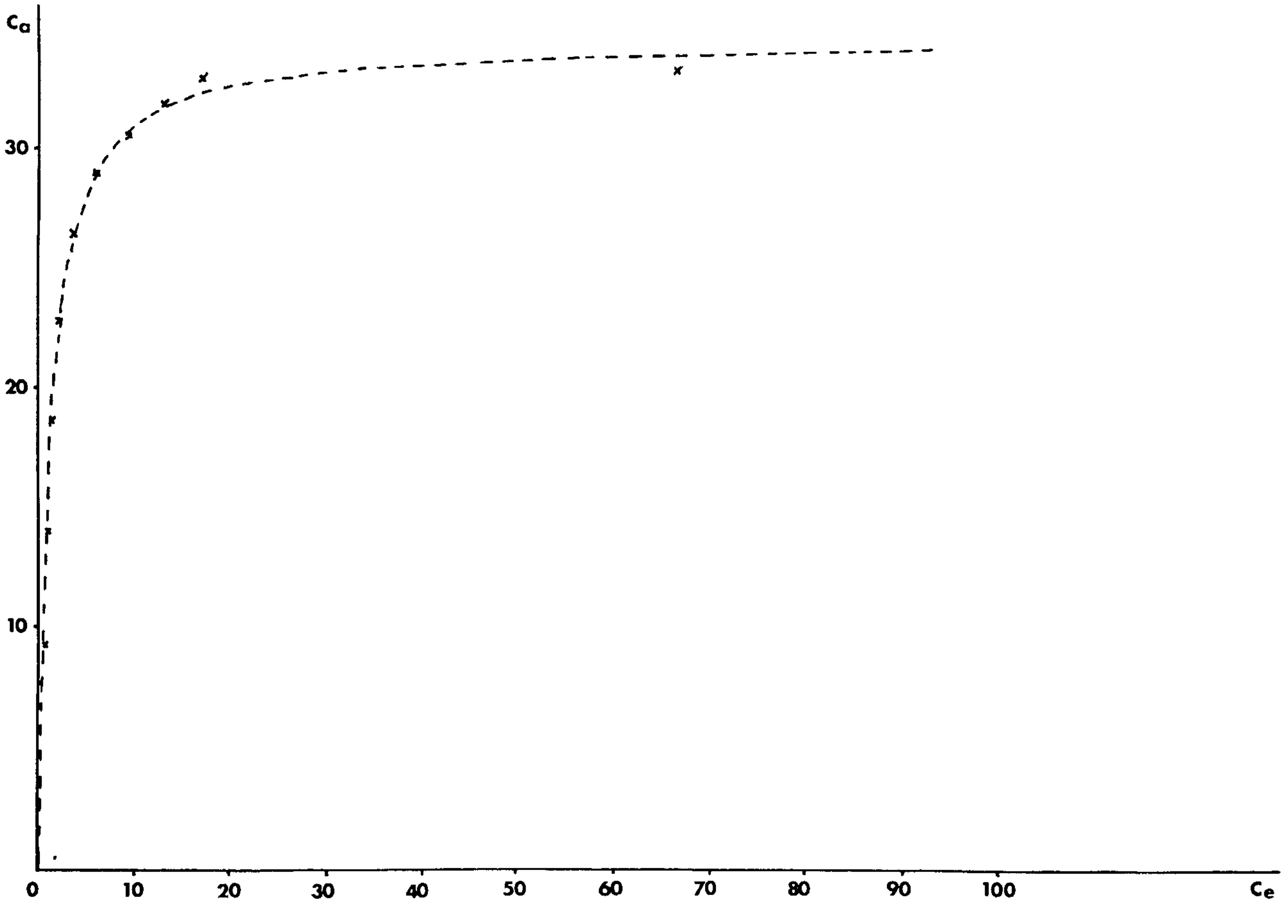

FIG. 5. Isotherm of Cu^{2+} adsorption on AS.

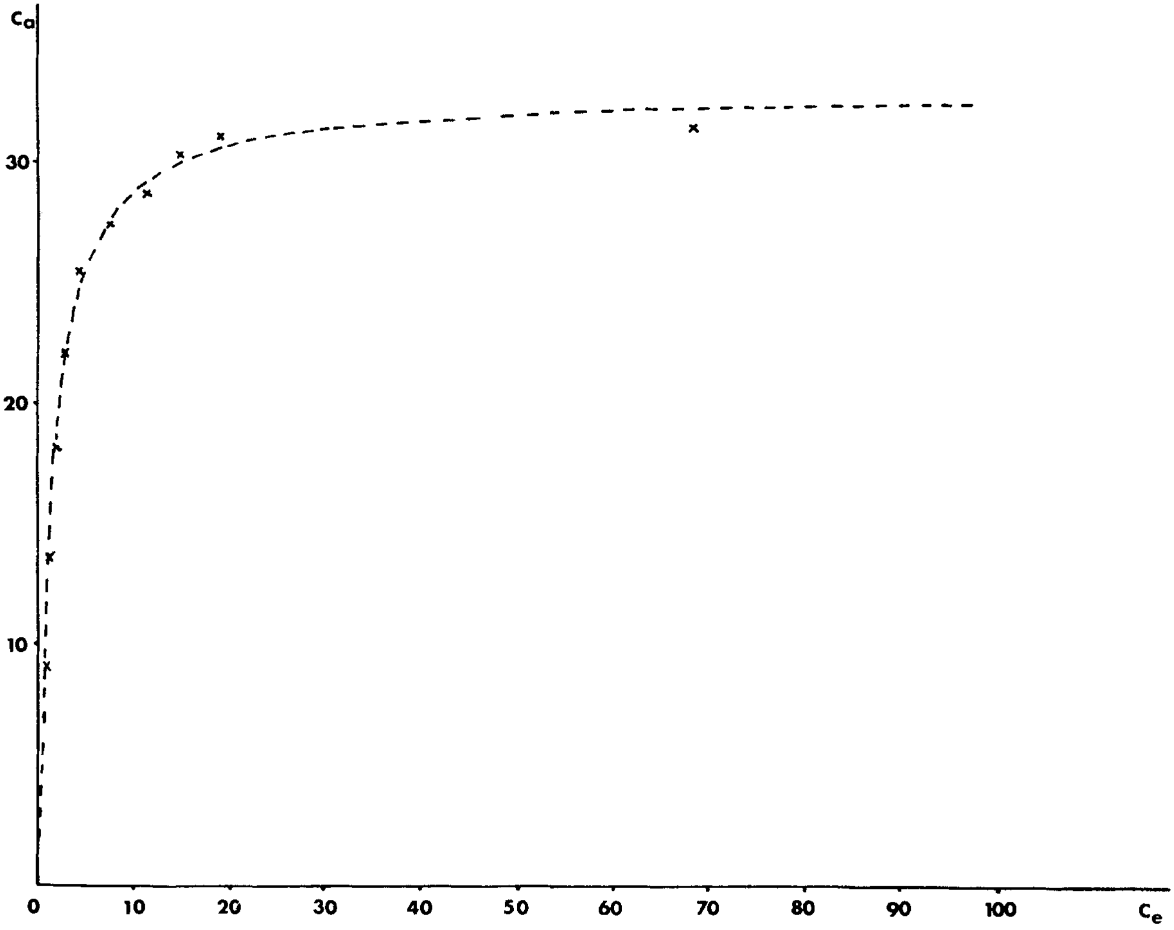

FIG. 6. Isotherm of Cu^{2+} adsorption on EAS.

fore assumed that the isotherms follow Langmuir's adsorption isotherm equation for solutions:

$$C_a = \frac{C_a{}^M C_e}{C' + C_e} \tag{1}$$

where $C_a{}^M$ = maximum surface coverage
C' = the C_e value leading to a surface coverage of 1/2 of $C_a{}^M$

From this we obtain

$$\frac{1}{C_a} = \frac{1}{C_a{}^M} + \frac{C'}{C_e C_a{}^M} \tag{2}$$

Graphical determination of the constants of the Langmuir adsorption isotherm is made by plotting $1/C_a$ vs $1/C_e$, as is done in Fig. 7. It is evident that linear dependence of $1/C_a$ vs $1/C_e$ satisfies Langmuir's isotherm very well. The values of $C_a{}^M$ and C' are determined from the graph. According to Eq. (2), $C'/C_a{}^M$ is the slope of the straight line and the value $1/C_a{}^M$ is read on the ordinate axis for $1/C_e = 0$. From this, $C_a{}^M = 34.29$ mg/g, $C' = 1.1447$ mg/l for AS; and $C_a{}^M = 33.2557$ mg/g, $C' = 1.5322$ mg/l for EAS.

The amount adsorbed can then be calculated from Eq. (1), using these values of the constants for the various concentrations of Cu^{2+}. These were then compared with the values obtained experimentally (dashed line in Figs. 5 and 6). It is seen that the calculated data differ from the experimental values by 3.5% (AS) and 5.5% (EAS) at the most.

The Langmuir isotherm is thus suitable for describing the adsorption of Cu^{2+} on AS and EAS.

The stability of adsorbed copper was tested by treatment of the sludge with HCl solutions at pH 5, 4, 3, and 2 by using the same apparatus and method used for the adsorption studies. The desorption data are shown in Fig. 8 and Table 3. Desorption took place to any extent only at pH 2.

DISCUSSION

The kinetics of Cu^{2+} show fairly rapid adsorption of Cu^{2+} by both AS and EAS. The extent of Cu^{2+} removal after 120 min at equilibrium is summarized in Table 4. The data show good efficiency in a short time, an important factor in industrial applications.

The EAS is a little less active than AS in adsorption. This behavior is explained by the loss of the chemisorption activity of the extractable materials removed from EAS, which is evidently greater than the adsorption activity of the sites exposed by this treatment.

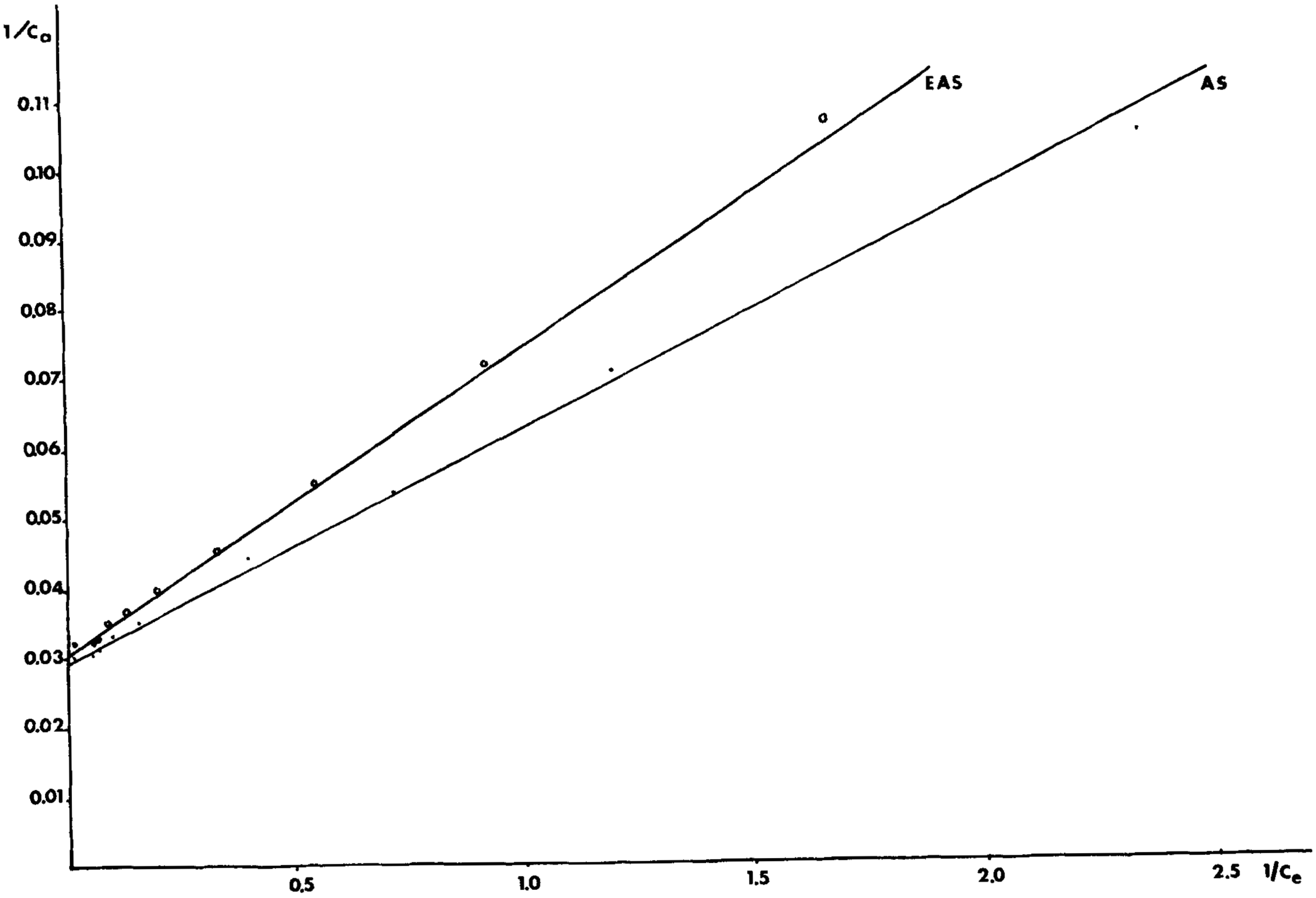

FIG. 7. Graphical determination of the Langmuir adsorption isotherm.

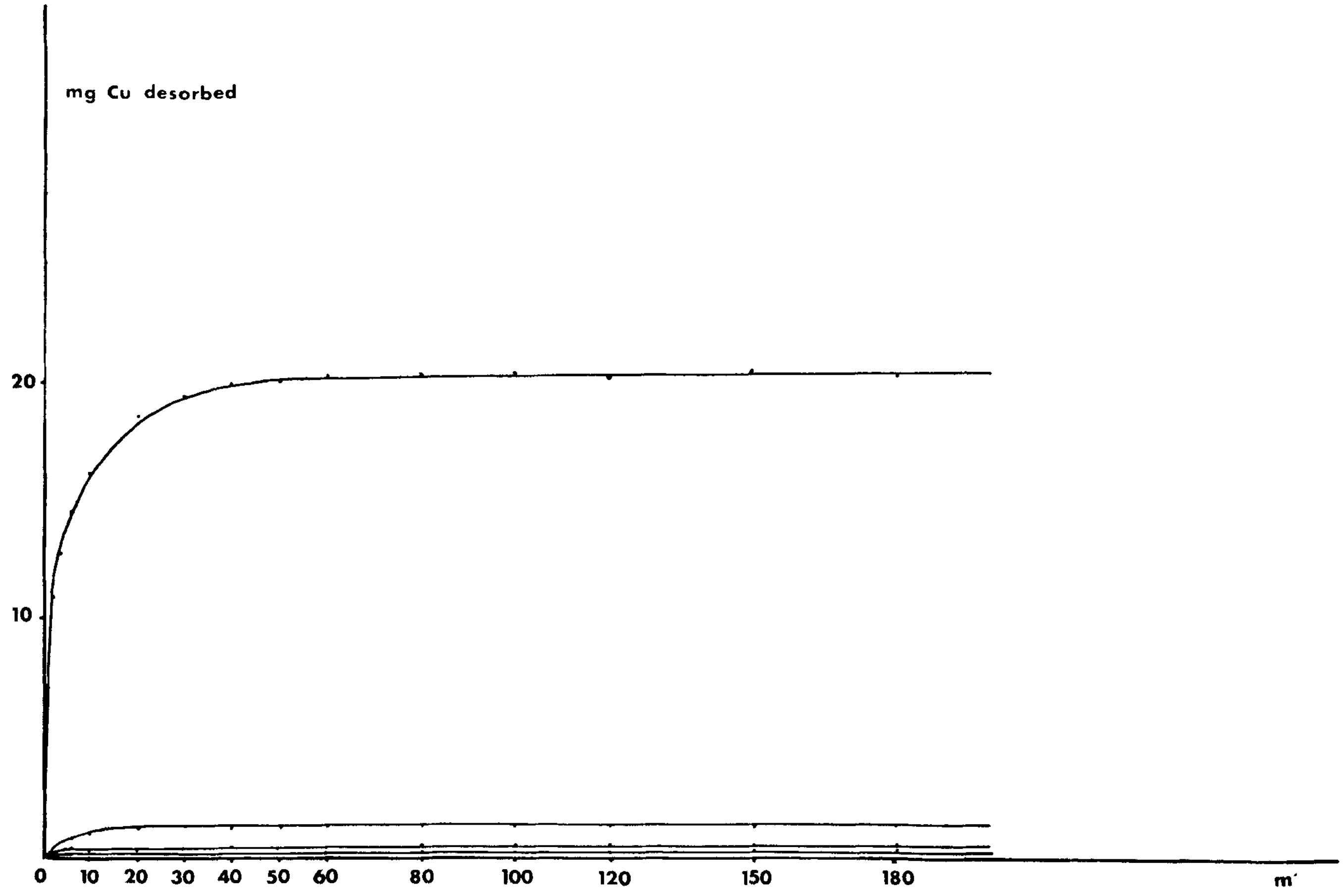

FIG. 8. Kinetics of desorption.

TABLE 3

The Effect of pH on Cu(II) Desorption

pH	Initial Cu(II) adsorbed conc (mg/g)	Cu(II) desorbed conc (ppm)	% Cu(II) desorbed
5	33.15	0.489	1.48
4	31.25	0.593	1.90
3	34.07	1.373	4.03
2	32.80	20.990	63.99

TABLE 4

Comparison of Cu(II) Adsorption on AS and EAS at Different Times

Initial Cu(II) conc (ppm)	Cu(II) % removal at 24 hr		Cu(II) % removal at 120 min	
	AS	EAS	AS	EAS
10	90.30	87.00	79.50	74.70
20	93.70	89.30	78.20	74.70
30	87.97	85.97	66.03	69.63
40	74.88	72.73	56.28	62.13

CONCLUSION

The ability of AS as an adsorbent of metals appears satisfactory. EAS is a slightly less efficient adsorbent. We note, however, that EAS furnishes extractable compounds and can give clean combustion (Q_e = 3,500 kcal/kg) and ash rich in metals. The fit to the Langmuir's isotherm appears satisfactory. Its applicability and the nature of adsorbent–adsorbate bonds will be studied in subsequent research by means of calorimetric determinations.

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Received by editor May 25, 1979