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Evaluation of Stability Constants in the Association between Activated Sludge and Cu(II), Zn(II), and Cr(III) Ions

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Abstract

Adsorption kinetics and adsorption isotherms of Cu(II), Zn(II), and Cr(III) on activated sludge were evaluated in the 0–50 ppm concentration range. The experiments were performed at 0 and 0.1 *M* NaCl ionic strength at pH 5 and 20°C. From the adsorption data the apparent constants for metal–sludge association were evaluated by a standard model. A modification of the treatment allows the determination of true stability constants comparable to those for the association of heavy metals with polypeptides. Adsorption sites are present on greasy particles dispersed at the surface of biomasses.

INTRODUCTION

In previous papers (*1, 2*) the possibility of using modified sludge as an adsorbing medium for acidic solutions of metals was examined. It has been shown that greasy materials at the surface of sludge grains play a major role in determining the adsorptive capacity of sludges. In fact, samples treated with polar solvents exhibit much lower activity. In this paper a characterization of the extractable greasy materials is given. Furthermore, two different kinds of samples are investigated, one being the raw dried sludge, the other having been thermally activated so to gain a larger dispersion of greasy materials.

Kinetics and isotherms of adsorption of copper, chromium, and zinc have

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been followed at pH 5 at 20°C in the 0 to 50 ppm concentration range at 0 and 0.1 *M* NaCl ionic strength (I.S.).

METHODS AND MATERIALS

The two kinds of adsorbent are hereafter called AS and MAS. AS was obtained, following the procedure described in Ref. *1*, using the activated sludge grown in a rotating biological surface (RBS) from raw wastewater from an abattoir in Turin as substrate.

A sample of 10 g of AS was extracted in a Soxhlet extractor with *n*-heptane and chloroform. The solution was membrane filtered (0.45 μm) and freed of solvents at 50°C under vacuum. The extractable materials were characterized by chromatographic separation (*3*) and through their IR spectra (*4*). Seventy percent of the extracted material is polar in nature, and the IR spectra shown in Fig. 1 demonstrate the presence of —OH, —NH_x, and —COOH groups able to bind the metals (5). MAS was obtained by thermal treatment of AS for 24 h at 110°C. The composition of AS and MAS, Table 1, was the same but AS showed a specific surface area (determined by the BET method) of 2 m^2/g; that of MAS was only 0.5 m^2/g. This suggests that thermal treatment causes a redistribution of greasy materials on the whole surface of the grains in agreement with the enhancement of activity (vide infra).

All glass was preconditioned overnight with HNO_3 (1/1) and subsequently washed with double distilled and deionized water. The solutions of metals were prepared from a 1 mg/mL stock solution and all reagents used were ACS pure grade. Adsorption of metals was performed at 20°C and pH 5 ± 0.1 by using 1 g of AS or MAS and a 1000-mL solution of Cu(II), Zn(II), or Cr(III) at 5, 10, 20, 30, or 50 ppm; the solutions were stirred with a magnetic laboratory stirrer.

The adsorption kinetics and isotherms were evaluated at different metal concentrations by using AS or MAS at ionic strengths of 0 and 0.1 *M* NaCl. In the latter case the appropriate quantity, 5.58 g/L, of NaCl was added to the metal solution before the adsorbent. The pH was monitored every 15 min throughout the experiment and corrected if necessary by adding very small amounts of 0.1 *M* NaOH or HCl which do not affect the metal concentration significantly.

The pH 5 was selected because experiments with metals and NaCl only demonstrated for the range of concentrations considered that precipitation phenomena are not involved. On the other hand, at lower pH values the competition of H^+ with the metals is evident. Twenty milliliter samples of solution were taken in the course of the reaction or at equilibrium and

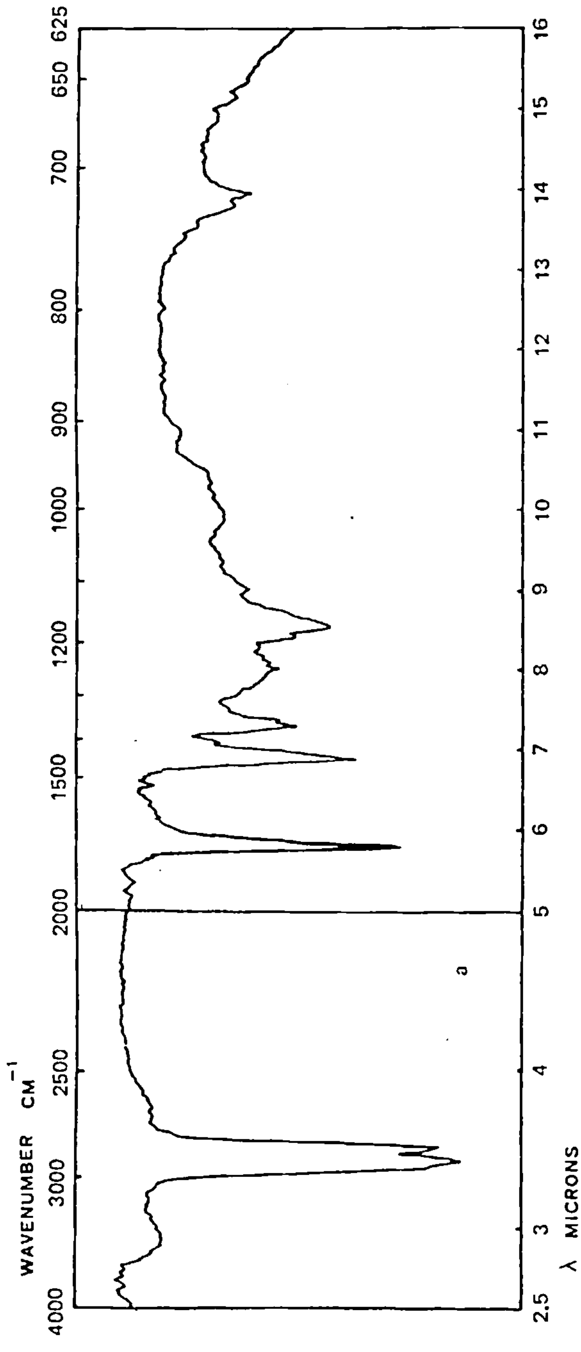

FIG. 1. Infrared spectra of chromatographic fractions of extract: (a) chloroform elute 16.86%, (b) acetone elute 19.69%, and (c) methyl alcohol elute 38.92%.

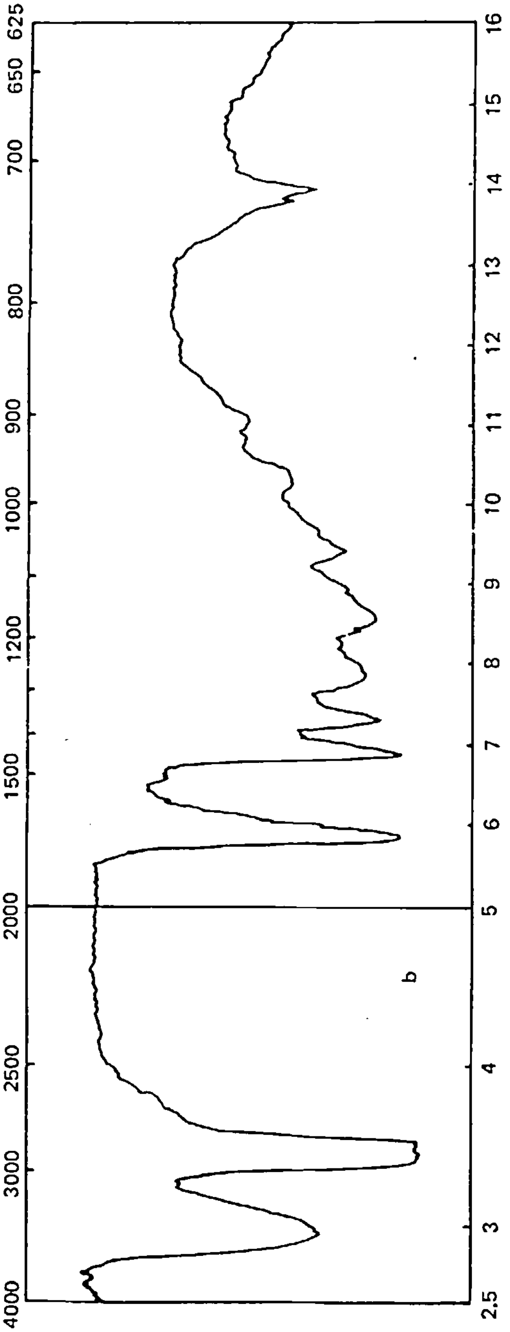

FIG. 1 *(continued)*

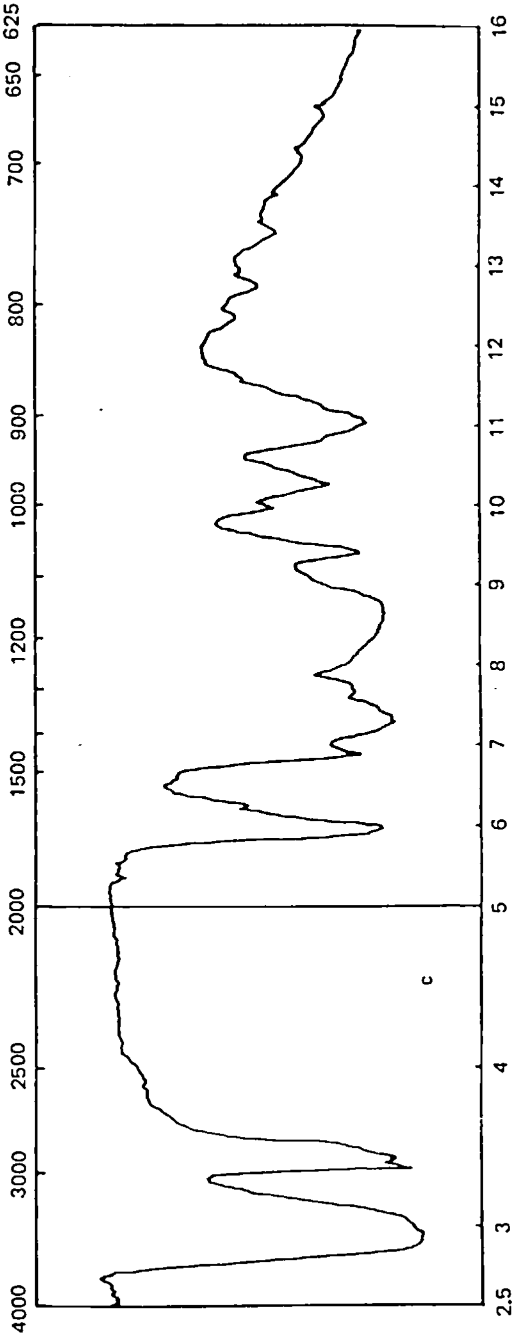

FIG. 1 *(continued)*

TABLE 1

Composition of Dried Activated Sludge

Ash, mg/g	118.320
EEP,[a] mg/g	155.870
ECL,[b] mg/g	58.830
Cu, mg/g	0.077
Cr, mg/g	0.110
Pb, mg/g	0.044
Zn, mg/g	4.759
Fe, mg/g	6.600
SiO_2, mg/g	36.600
Surface area AS, m^2/g	2.0
Surface area MAS, m^2/g	0.5

[a] Extractable petroleum ether.
[b] Extractable chloroform.

filtered. Ten milliliters were used to condition the 0.45 μm filter and the other were used for the determination of free metal concentrations by atomic adsorption spectrophotometry (Perkin-Elmer 5000).

RESULTS AND DISCUSSION

Kinetics of adsorption of Cu(II) onto AS and MAS are reported in Fig. 2. The initial concentration is 50 ppm in all cases, and data are shown both for zero I.S. and 0.1 *M* NaCl. The behavior is similar for all initial concentrations adopted and for all metals: maximum adsorption activity within the first hour and attainment of equilibrium after 300 min (checked after 24 h contact). All this agrees well with what has been found for living biomasses (*6*) and for clays and soils (*7, 8*).

The initial rate of adsorption is smaller on MAS than on AS, irrespective of the final yield.

The occurrence on MAS of activated processes is probably connected to the fact that adsorption is stronger. This is shown on the one hand by the stability constants of metal–sludge association (vide infra) and on the other hand by calorimetric measurements of the heat of wetting (28.25 and 47.54 J/g for AS and MAS, respectively) of the pure solvent.

In Figs. 3a, 3b, and 3c equilibrium data for the partition of ions between the solution and the sludge are reported as adsorption isotherms. In similar work (*6, 9*), isotherms have been found with almost linear behavior; in the present case the shape of the isotherms is typically Langmuirian. The reason

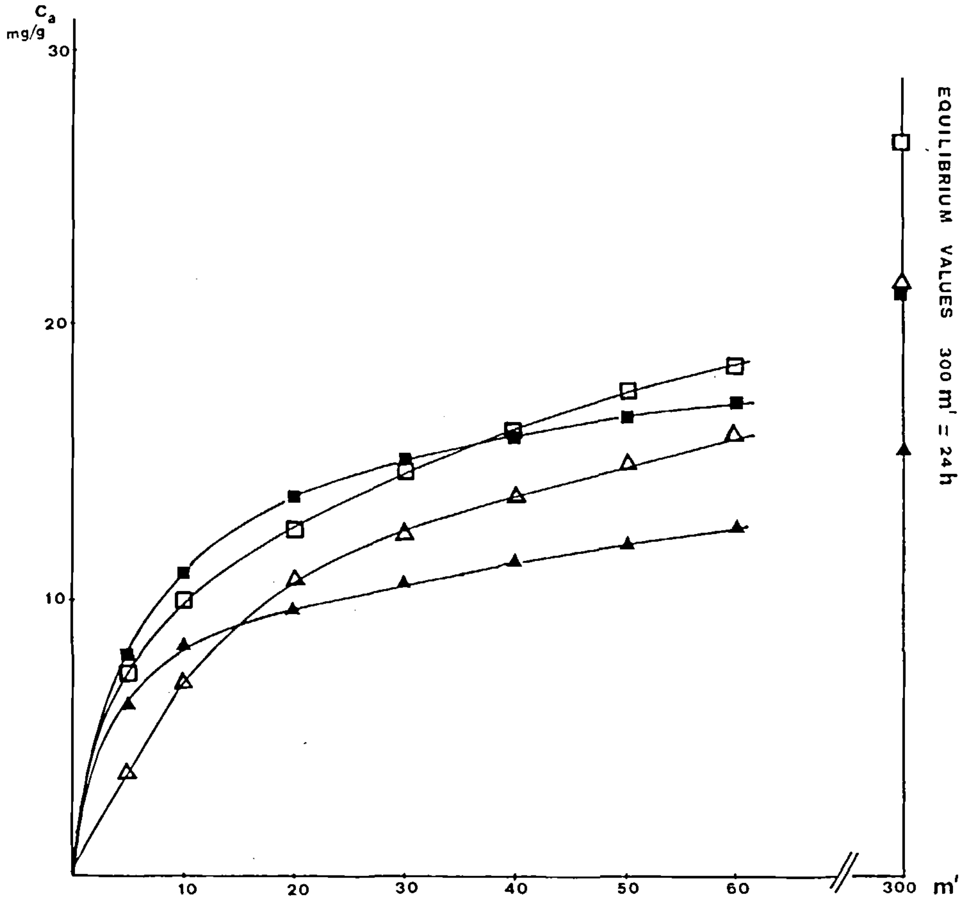

FIG. 2. Kinetics of adsorption of Cu(II) on AS (■, ▲, I.S. 0 and 0.1 *M* NaCl) and on MAS (□, △, I.S. 0 and 0.1 *M* NaCl).

is that the range of concentrations explored in those papers is narrower and encompasses only the linear portions of the Langmuir plots of the present work.

By means of the linearized form of the Langmuir isotherm (the meaning of the symbols is given below):

$$C_e/C_a = (C'/C_M) + (C_e/C_M)$$

we have evaluated the Langmuir constant C' and the maximum concentrations of the adsorbed ions C_M. The coefficients of linear regression indicate in

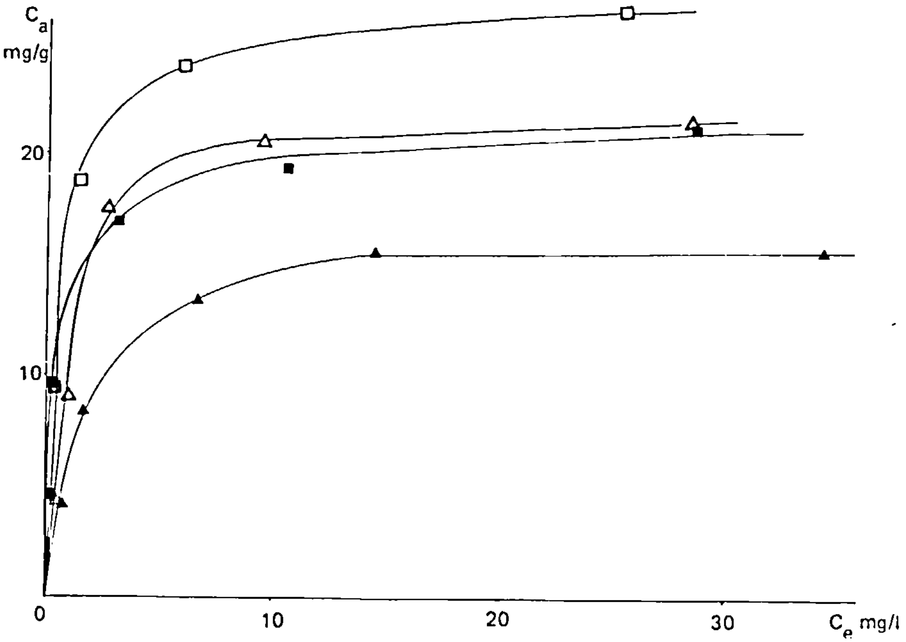

FIG. 3a. Isotherms of copper on As (■, ▲, I.S. 0 and 0.1 *M* NaCl) and on MAS (□, △, I.S. 0 and 0.1 *M* NaCl) adsorption.

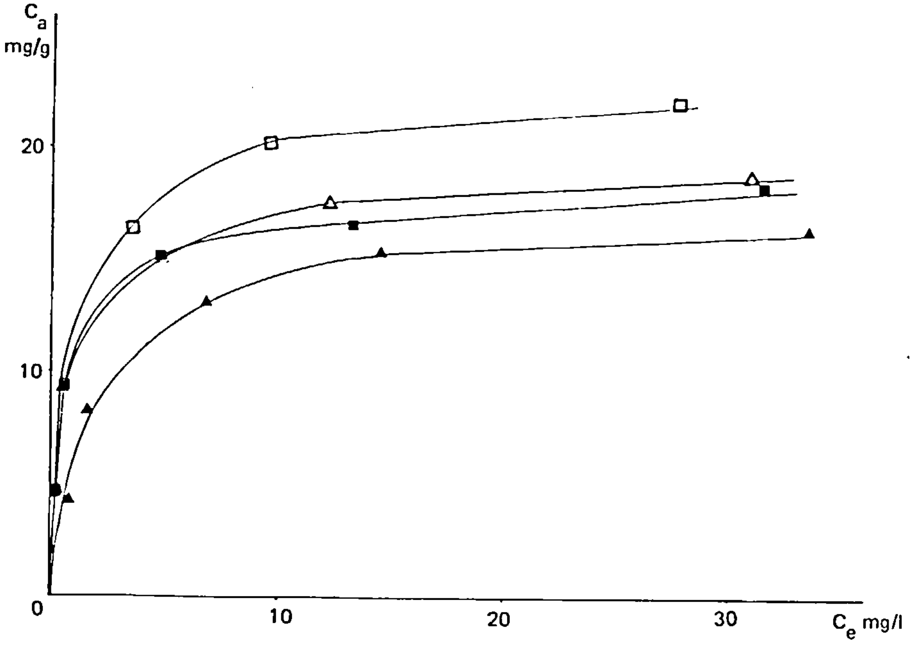

FIG. 3b. Isotherms of zinc on AS and on MAS adsorption. Symbols as in Fig. 3a.

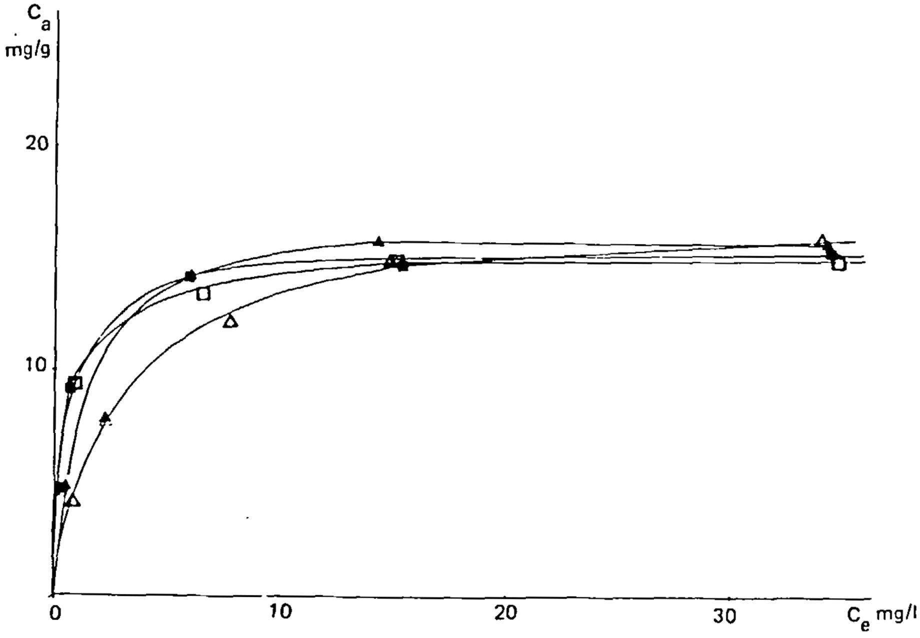

FIG. 3c. Isotherms of chromium on As and on MAS adsorption. Symbols as in Fig. 3a.

all cases a very good fit of the Langmuir isotherm to the experimental data. In Tables 2, 3, and 4 are reported the relevant equilibrium concentrations in solution (C_e: expressed in mg/L) and adsorbed amounts of metal per gram of biomass (C_a), together with the computed values of C', C_{Mf}, and LR for all cases.

For Cu(II) and Zn(II) the amount adsorbed depends on the nature of the exposed surface (AS or MAS) as well as on the ionic strength.

Final uptakes C_{Mf} are always higher on MAS than on AS at the same value of I.S. On the other hand, increasing I.S. tends to decrease C_{Mf}.

As to Cr(III), there is no substantial change in C_{Mf} induced by the kind of surface or the ionic strength.

STABILITY CONSTANTS

In heterogeneous systems like those considered here, it is usually difficult to put on a quantitative basis the description of formation of surface complexes. One difficulty often encountered is, for instance, ignorance of the real concentration of the substrate. Because of this, a paper similar in subject to the present one (*6*) makes use of an apparent constant $K = C_{Mf}/C'$ expressed in L/g of sludge.

In the present case the computation of stability constants of the metal–sludge complexes is made possible by the availability of both the Langmuir constants C_{Mf} and C' and use of a mathematical rearrangement.

The formation of a surface complex MS between a site S and a metal ion M is

$$\mathrm{M} + y\mathrm{S} = \mathrm{MS}_y$$

We consider only 1:1 stoichiometry because otherwise Langmuir behavior of the isotherm would not be obtained. The adsorption equilibrium constant is

$$K = \frac{a_{\mathrm{MS}}}{a_{\mathrm{M}} a_{\mathrm{S}}}$$

Assuming that the adsorbent phase is ideal

$$a_{\mathrm{MS}} = \text{activity of MS complex} = C_a/C_{Mf}$$

$$a_{\mathrm{S}} = \text{activity of adsorbent} = (C_{Mf} - C_a)/C_{Mf}$$

TABLE 2

Distribution of Cu(II) between AS or MAS and Liquid Phase at Equilibrium (I.S. 0 and 0.1)[a]

Adsorbent	I.S.	Added Cu(II) conc (ppm), C_i	Final Cu(II) conc (ppm), C_e	Removed Cu(II) conc (mg/g), C_a	LR	C_M	C'
AS	0	5	0.17	4.83			
		10	0.23	9.77			
		20	3.12	16.88			
		30	10.70	19.30			
		50	28.73	21.27	0.999	21.59	0.69
	0.1	5	0.78	4.22			
		10	1.66	8.34			
		20	6.55	13.45			
		30	14.45	15.55			
		50	34.55	15.45	0.999	16.30	1.56
MAS	0	5	0.13	4.87			
		10	0.26	9.74			
		20	1.35	18.75			
		30	6.00	24.00			
		50	23.56	26.44	0.999	27.06	0.60
	0.1	5	0.54	4.46			
		10	1.00	9.00			
		20	2.56	17.44			
		30	9.48	20.52			
		50	28.50	21.50	0.999	22.65	1.40

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

$$a_M = \text{activity of free metal ions} = \gamma C_e \times 10^{-3}\ \text{MW}^{-1}\ (\text{mol/L})$$

where MW is the atomic weight of the metal and γ is the activity coefficient.

We obtain

$$K = \frac{C_a/C_M}{\gamma C_e(\bar{C}_M - C_a)/C_M} \times 10^3\ \text{MW}$$

or

$$\frac{C_a}{C_M} = \frac{C_e}{\left(\dfrac{1}{K\gamma} \times 10^3\ \text{MW} + C_e\right)}$$

TABLE 3

Distribution of Zn(II) between AS or MAS and Liquid Phase at Equilibrium (I.S. 0 and 0.1)[a]

Adsorbent	I.S.	Added Zn(II) conc (ppm), C_i	Final Zn(II) conc (ppm), C_e	Removed Zn(II) conc (mg/g), C_a	LR	C_M	C'
AS	0	5	0.35	4.65			
		10	0.61	9.39			
		20	4.65	15.35			
		30	13.35	16.65			
		50	31.50	18.50	0.999	18.92	1.06
	0.1	5	0.82	4.18			
		10	1.62	8.38			
		20	6.80	13.20			
		30	14.50	15.50			
		50	33.60	16.40	0.999	17.48	2.10
MAS	0	5	0.34	4.66			
		10	0.61	9.39			
		20	3.41	16.59			
		30	9.60	20.40			
		50	27.80	22.20	0.999	23.14	1.21
	0.1	5	0.34	4.66			
		10	0.61	9.39			
		20	4.80	15.20			
		30	12.20	17.80			
		50	31.10	18.90	0.999	19.47	1.03

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

By comparison with the Langmuir formula

$$C_a/C_M = C_e/(C' + C_e)$$

we get

$$C' = \frac{1}{K\gamma} \times 10^3\,\mathrm{MW}$$

or

$$K = \frac{1}{C'\gamma} \times 10^3\,\mathrm{MW}$$

TABLE 4

Distribution of Cr(III) between AS or MAS and Liquid Phase at Equilibrium (I.S. 0 and 0.1)[a]

Adsorbent	I.S.	Added Cr(III) conc (ppm), C_i	Final Cr(III) conc (ppm), C_e	Removed Cr(III) conc (mg/g), C_a	LR	C_M	C'
AS	0	5	0.23	4.77			
		10	0.69	9.31			
		20	5.89	14.11			
		30	15.28	14.72			
		50	34.41	15.59	0.999	15.79	0.65
	0.1	5	0.55	4.45			
		10	2.06	7.94			
		20	5.88	14.12			
		30	14.22	15.78			
		50	34.19	15.81	0.999	16.61	1.45
MAS	0	5	0.42	4.58			
		10	0.64	9.36			
		20	6.50	13.50			
		30	15.08	14.92			
		50	34.84	15.16	0.999	15.50	0.75
	0.1	5	0.85	4.15			
		10	2.13	7.87			
		20	7.82	12.18			
		30	14.94	15.06			
		50	34.04	15.96	0.999	17.26	2.69

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

Table 5 reports the K values calculated by Nelson's approximation (*9*) and by our method. The activity coefficients γ has been computed by the Debye-Hückel limiting law $\gamma = 10^{-Az^2\sqrt{\mu}}$ (0.222 for Cu and Zn and 0.0324 for Cr).

The K values evaluated by us are correct from the dimensional point of view (unlike Nelson's values) and moreover are in good numerical agreement with similar overall formation constants for complexes involving organic molecules or polypeptides as ligands (*10*).

The stability of the metal–sludge complexes is clearly important in determining the efficiency of biomasses as sequestering agents, in particular under conditions far from those of the laboratory.

Thermal modification of AS leads to higher adsorption constants for Cu(II) and Zn(II) if I.S. is increased from 0 to 0.1. Chromium adsorption

TABLE 5

Stability Constants of Cu(II), Zn(II), and Cr(III) Complexes with Sludge at pH 5

		$K = (1/C'\gamma) \times 10^3$ MW (L/mol)[a]			$K = C_M/C'$ (L/g)[b]		
Adsorbent	I.S.	Cu	Zn	Cr	Cu	Zn	Cr
AS	0	0.92×10^5	0.62×10^5	0.80×10^5	31.29	17.85	24.39
	0.1	1.85×10^5	1.40×10^5	11.21×10^5	10.45	8.32	11.46
MAS	0	1.06×10^5	0.54×10^5	0.69×10^5	45.10	19.12	20.67
	0.1	2.06×10^5	2.88×10^5	6.04×10^5	16.18	18.90	6.42

[a] From our model.
[b] From Nelson's model (*9*).

yields seem unaffected by the nature of the surface, but stability constants are increased by increasing I.S.

The possibility of utilizing exhausted biomasses as metal adsorbents is confirmed, together with the possibility of optimizing the yield for divalent ions by means of thermal treatment.

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