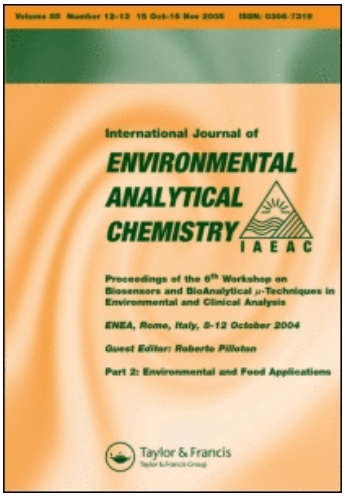

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The Cumulation of Toxic Metals on Alga

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The cumulation of zinc, cadmium, mercury(II), chromium(III)(VI), arsenic(III)(V), methylarsonic acid and dimethylarsinic acid on alga Chlorella kessleri has been radiometrically investigated in the pH range from 4 to 10.5. It has been found that algal cells strongly cumulate hydrogen ions and change by this manner the initial pH-value. The cumulation factor of zinc and cadmium increases with the increase of equilibrium pH whereas the cumulation of other species studied does not depend on pH in a certain pH-region. In neutral medium the cumulation factor decreases in the order: chromium(III), mercury(II), zinc, cadmium, arsenic(V), methylarsonic acid and dimethylarsinic acid. General conclusions concerning the influence of different factors on the cumulation of toxic metals on alga are included.

KEY WORDS: Zinc, cadmium, mercury(II), chromium(III)(VI), arsenic(III)(V), methylarsonic acid, dimethylarsinic acid, alga Chlorella kessleri.

INTRODUCTION

Recently, several papers have been published dealing with the cumulation of toxic metals on alga.[1–10] Unfortunately, the results obtained by different authors cannot be compared (they are often contradictory) which can be probably explained by the following reasons: 1) different alga species and different experimental conditions were used, 2) the change of some factors, influencing the cumulation, was neglected, 3) the analytical procedures used were not sufficient for the determination of the cumulation factor F (the ratio of the concentration of element in question in alga and in the medium); mostly only relative data are published.

The use of radionuclides enables very simple determination of F-value in different experimental conditions with a good precision. Thus, chromium-51 has been used for the study of the cumulation of

chromium(III) and (VI) on four alga species at different metal and algal cells concentrations.[11] The influence of pH, concentration of different reagents and metal salts on the cumulation of zinc, cadmium and mercury(II) on alga Scenedesmus obliquus has been also studied using radionuclides.[12]

The purpose of the present communication is to study and compare the cumulation of zinc, cadmium, mercury(II), chromium(III)(VI), arsenic(III)(V), methylarsonic acid and dimethylarsinic acid on alga Chorella kessleri at different equilibrium pH-values. Our preliminary experiments have shown that the initial pH-value can be substantially changed in the presence of algal cells and for this reason the uptake of hydrogen ions has been also investigated.

EXPERIMENTAL

Reagents and apparatus

All reagents used, unless otherwise stated, were of A.R. quality. Hydrochloric acid and sodium hydroxide, suprapure (Merck) were used for the adjusting of pH.

Solutions of radionuclides (Amersham, England) were prepared by the dilution of stock solutions of zinc-65 chloride (specific activity 10 GBq/g Zn), cadmium-115 m chloride (4 GBq/g Cd), mercury-203 chloride (10 GBq/g Hg), chromium-51 chloride (2,000 GBq/g Cr) and arsenic-74 (carrier free). Labelled methylarsonic acid $CH_3{}^{74}AsO(OH)_2$ and dimethylarsinic acid (cacodylic acid) $(CH_3)_2{}^{74}AsO(OH)$ were prepared using classical synthesis with methyl iodide in microscale level.

Algologically and bacteriologically pure strains of alga Chlorella kessleri were used in the experiments. The mean geometric volume of one cell $V_a = 6.5 \times 10^{-11}\,cm^3$, the mean geometric surface $S_a = 8 \times 10^{-7}\,cm^2$.

Well-type scintillation NaI(Tl) counter was used for the measurement of the radioactivity; Radiometer PHM-52c (Copenhagen, Denmark) for the determination of equilibrium pH-value.

Procedures

The uptake of hydrogen ions by alga has been studied as follows: an appropriate volume of alga suspensium (containing a known amount of alga cells) was centrifuged and the supernatant was discarded. Then 10 ml of hydrochloric acid of different concentration were added and the suspensium was shaken for three hours. After a certain period the equilibrium pH-value was measured and compared with pH-value of the

simultaneously shaken hydrochloric acid of the same concentration in the absence of algal cells.

The investigation of the cumulation of metals has been carried out as follows: an appropriate volume of 0.01 M hydrochloric acid or sodium hydroxide was added to alga suspensium to which the radioisotope of the element in question was added. The volume was made up to 10–20 ml with distilled water and the suspensium was shaken for 3 hours. After an appropriate interval, 3,0 ml of the suspensium were pipetted into a centrifugation tube and centrifuged for 5 min. The equilibrium pH-value, the radioactivity of algae (A_a) and that of the medium (A_m) were measured and the cumulation factor F was calculated according to the Eq.

$$F = \frac{A_a}{A_m N_a V_a} \tag{1}$$

where N_a is the number of alga cells in cm^3, V_a is the mean geometric volume of one cell in cm^3.

Total concentration of zinc, cadmium and mercury(II) was about 10^{-6} M, that of chromium(III), arsenic(V) and methylarsonic acid 10^{-7} M and that of dimethylarsinic acid 10^{-5} M.

All experiments were carried out at $22 \pm 1°C$.

RESULTS AND DISCUSSION

The uptake of hydrogen ions on alga Chlorella kessleri is illustrated on Fig. 1. This uptake is a relatively slow process; a constant pH-value was established only after 2–3 hours of shaking. As it follows from Fig. 1, alga cells have a strong tendency to take up hydrogen ions from solutions and change by this manner the initial pH-value. The uptake is directly proportional to the number of alga cells. Similar results were obtained with alga Scenedesmus obliquus.[12]

The influence of pH on the cumulation of elements studied can be seen from Fig. 2. The cumulation of zinc and cadmium increases with the increase of equilibrium pH-value (the slope of the curve $\log F$ vs. pH equals to 0.8–0.9 for both elements). The equilibrium F-value is reached very quickly; a little higher F-values after three hours of exposition lay on the same curve as those after one hour (the equilibrium pH was shifted during the shaking). The cumulation of mercury(II) is practically constant at $pH > 5.5$, that of chromium(III) at $pH > 7$. The kinetics of the uptake of mercury(II) is slower than that of zinc and cadmium; after five hours of exposition the F-values were higher than that after three hours. Such

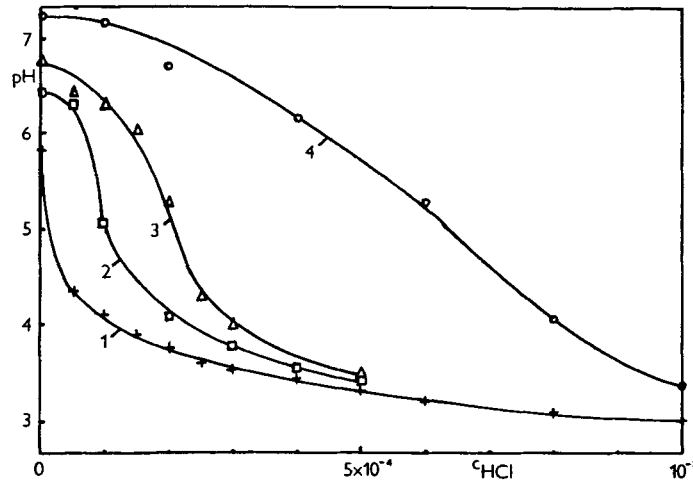

FIGURE 1 The equilibrium pH in the absence (curve 1) and in the presence of alga Chlorella kessleri (curve $2-2\times10^6$ cells.mL^{-1}, curve $3-4\times10^6$ cells.mL^{-1} and curve 4 -16×10^6 cells.mL^{-1}).

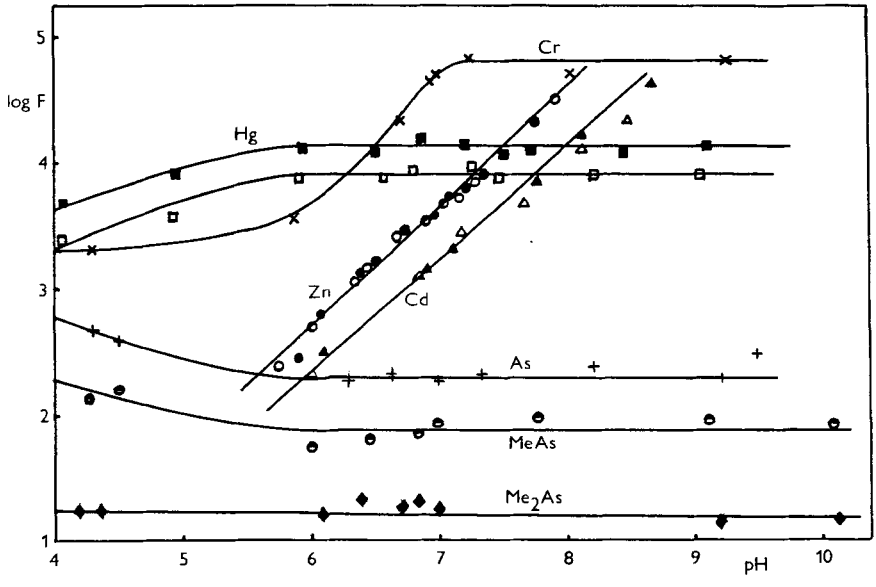

FIGURE 2 The cumulation factor F of zinc, cadmium, mercury(II), chromium(III), arsenic acid (As), methylarsonic acid (MeAs) and dimethylarsinic acid (Me_2As) after three hours of shaking (free points – one hour shaking) at different equilibrium pH ($(2–6)\times10^6$ cells.mL^{-1}).

different behaviour is probably connected with the fact that cadmium and zinc are present in conditions studied predominantly as cations Cd^{2+} and Zn^{2+}, whereas mercury(II) as neutral complex $Hg(OH)_2$ or $HgCl_2$; chromium(III) is present predominantly as a cation $Cr(OH)^{2+}$ at pH 4.5–6 and $Cr(OH)_2^+$ at pH > 7. Similar results were obtained on alga Scenedesmus obliquus.[12]

The cumulation of arsenic acid (at pH ~ 4 predominates $H_2AsO_4^-$, at pH ~ 7 $HAsO_4^{2-}$), methylarsonic acid (at pH ~ 5 $CH_3AsO_2(OH)^-$, at pH > 8 $CH_3AsO_3^{2-}$) and dimethylarsinic acid (at pH ~ 4 $(CH_3)_2AsO(OH)$ at pH > 7 $(CH_3)_2AsO_2^-$) practically does not depend on equilibrium pH; a small increase of F-values was observed for the first two species in acid medium. Arsenic(III) is partially oxidised (especially in low concentrations) in the presence of algal cells to arsenic acid; log F equals in neutral medium to about 2. The kinetics of the cumulation of all arsenic species studied is rapid; the same values of F were obtained after one and three hours of shaking.

The presence of different reagents influenced the cumulation of zinc, cadmium and mercury(II) in a similar manner as it was found for alga Scenedesmus obliquus:[12] only reagents, forming in conditions studied negatively charged metal complexes, decrease the cumulation factor. The influence of different reagents on the cumulation of chromium(III) is given in Table I. The cumulation of arsenic(V) is not influenced by the presence of 0.05 M NaCl, $NaNO_2$ and $NaNO_3$; in the presence of 0.001 M and 0.01 M Na_2HPO_4 the F-value decreased 8 and 12 times, respectively.

TABLE I

Ratio of the cumulation factor of chromium(III) ($C_{Cr} = 10^{-7}$ mol.L^{-1}) in the absence and in the presence of different reagents (2×10^6 cells.mL^{-1})

Reagent	Concentration mol.L^{-1}	Time of exposition (hours) 0.5	1.5	3.0	4.5
NaCl	0.01	1.1	1.2	1.1	1.4
	0.10	1.5	1.8	1.6	2.0
Na_2SO_4	0.02	1.2	1.3	1.2	1.3
Na_2HPO_4	0.01	0.3	0.2	0.3	0.3
Na_2Tart	0.01	0.2	0.3	0.3	0.2
Na_2Oxal	0.01	0.15	0.15	0.10	0.15
Na_2EDTA	0.01	0.18	0.23	0.18	0.20
	0.01[a]	0.13	0.11	0.18	0.16
$MgSO_4$	0.01	1.0	1.4	1.1	
$HgCl_2$	0.001	1.0	0.8	0.8	

Na_2Tart – sodium tartarate, Na_2Oxal – sodium oxalate, Na_2EDTA – disodium salt of ethylenediaminotetraacetic acid.
[a]Na_2EDTA was boiled with chromium(III) for 1 hour.

Foreign metal salts present in higher concentrations decreased the cumulation of zinc and cadmium (mercury is affected in a lower extent) in the same manner as in the case of alga Scenedesmus obliquus.[12] On the contrary, the F-value of arsenic(V) increases in the presence of metal cations forming insoluble arsenates. This effect increases in the order $Mg^{2+} < Zn^{2+} < Cu^{2+} < Cr^{3+} < Fe^{3+}$ i.e. in the order of decreasing solubility of metal arsenates. It should be noted, that in the conditions studied (total concentration of arsenic(V) is about 10^{-7} M, the equilibrium concentration of anion AsO_4^{3-} is several orders lower in the dependance of equilibrium pH) the insoluble precipitates were not formed.

CONCLUSION

The following general conclusions can be made from the present as well as previous investigation:[11,12]

1) The cumulation of elements studied is predominantly (at least in the first stage) a physico-chemical process on the surface of algal cells.

2) The cumulation factor F is independent in a certain region on the concentration of algal cells. Approximately the same F-values were obtained for living as well as for dead cells.

3) The F-value for individual elements increases with the decrease of the mean geometric volume of one cell V_a ($\log F$ of chromium(III) equals in neutral medium to about 6.1 and 4.6 for alga Microcystic incerta ($V_a = 1.2 \times 10^{-12}$ cm^3) and Chlamydomonas geitleri ($V_a = 1.3 \times 10^{-9}$ cm^3),[11] respectively; higher F-values were obtained on alga Scenedesmus obliquus using algal cells with lower V_a). The product $F \cdot V_a \cdot S_a^{-1}$ (where S_a denotes the mean geometric surface of one cell) is approximately constant value.

4) The cumulation factor in neutral medium decreases in the order: chromium(III), mercury(II), zinc, cadmium, arsenic acid, methylarsonic acid and dimethylarsinic acid, i.e. in the order of decreasing solubility product of metal hydroxides or solubility of acids. F-value of chromium(VI) is at least three orders lower than that of chromium(III).

5) F-value of zinc and cadmium increases with the increase of equilibrium pH (the slope of the curve $\log F$ vs. pH is about 0.8–0.9), whereas the cumulation of other species studied does not depend on pH in a certain pH region. Because of the tendency of algal cells to cumulate hydrogen ions the equilibrium pH has to be always measured.

6) The cumulation of elements studied is independent in a certain range on their concentration. The increase of the concentration of zinc, cadmium, mercury(II) and chromium(III) may lead (because of hydrolysis) to the decrease of equilibrium pH and therefore to the decrease of F-value. This effect is especially pronounced at low algal cells concentrations.

7) The cumulation of zinc, cadmium, mercury(II) and chromium(III) can be substantially decreased only in the presence of reagents forming negatively charged complexes in given conditions. The cumulation of arsenic(V) decreased in the presence of phosphates.

8) *F*-value is not influenced by the presence of foreign metal salts present in low concentrations. The increase of metal concentration leads (because of hydrolysis) to the decrease of equilibrium pH and therefore the cumulation of zinc, cadmium, mercury(II) and chromium(III) decreases (the neutralisation of metal salts solutions may lead to the formation of insoluble hydroxides and the cumulation of metal studied increases because of its coprecipitation). The cumulation of arsenic(V) increases in the presences of metals forming insoluble arsenates.

9) *F*-value may be influenced by the change of temperature and for this reason a constant temperature has to be maintained during the experiment.

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