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Terese RAUCKYTE-ŻAK[1]

ATTEMPTS OF MATHEMATICAL MODELLING TO ACCESS GENERAL TOXICITY OF METAL CONTAINING WASTES

PRÓBY MODELOWANIA MATEMATYCZNEGO NA POTRZEBY OGÓLNEJ OCENY TOKSYCZNOŚCI ODPADÓW ZAWIERAJĄCYCH METALE

Abstract: Attempts to make preliminary assessment of general toxicity of metal containing wastes, including heavy metals in the first place, were made by using a polynomial, static and at the same time predictive mathematical model. The general toxicity was defined for samples of wastes, where metals were determined by using *toxicity characteristic leaching procedure* (TCLP). Gradient factors (a, b, c, …, n) for an equation for general toxicity in the form of $y(x_1, x_2, x_3, \ldots, x_n) = ax_1 + bx_2 + cx_3 + \ldots + nx_n$ were selected with the use of weighted average, considering the contents of the individual metals and their toxicological properties. Seeking the assessment criterion, it was assumed that the contents of metals leached from the tested wastes in toxic concentrations may be hazardous for the components of biosphere when the value of total toxicity fulfils the relation: $y(x_1, x_2, x_3, \ldots, x_n) \geq 1$. The magnitude of general toxicity (y) was calculated by summation of the experimentally determined individual concentrations of elements, taking into account their weighted fraction in the total toxic load. Basing on computing for the assumed model of general toxicity for selected wastes and considering the verification of the model with reference to the toxicity criteria defined in TCLP, it was found that there existed the coincidence of the achieved results.

Keywords: general toxicity assessment, mathematical modelling, metals with toxic concentrations

In literature, you can find two basic attempts to solve the issue of mathematical modelling of natural systems that exist in ecosystems [1]. With the use of the so-called descriptive and prognostic or predictive approach, there are attempts to present mathematically the abstract systems in the way that is the most similar to the actual world. The aim of the descriptive approach is to use the mathematical model to achieve the largest amount of information about the way how the actual system functions, in other words, to obtain the results of modelling with reference to basic experimental data. In case of predictive modelling, the main purpose is to obtain the most likely and representative experimental results describing a given phenomenon to use them as input data for the abstract mathematical modelling. At present, the most popular are predictive models [2]. For instance, the Langmuir and Freundlich sorption models are typical predictive models used eg to describe events of sorption of pollutants in soil and sediments or sludge. They are most highly valued due to the fact that they properly match a theoretical adsorption curve to the experimental data [3]. In literature, you can find much more descriptive approach to the phenomenon of heavy metals sorption in water-soil environment. Sorption on mineral and organic fractions is the most recognised and the most frequently determined. The sorption on mineral fractions are described, among others, by the following models: *Constant Capacitance Model* (CCM), *Diffuse Layer Model* - (DLM), *Triple Layer Model* (TLM), or *Three Plane Model* (TPM). The most frequently used are: CCM, DLM and TLM, which were included into the geochemical speciation code MINTEQ2, also in its complemented and enhanced form: MINTEQ3 [4, 5]. In literature,

[1] Department of Technology and Chemical Engineering, University of Technology and Life Sciences, ul. Seminaryjna 3, 85-326 Bydgoszcz, phone 52 374 90 63, fax 52 374 90 05, email: terra@utp.edu.pl

you can find works concerning mathematical modelling of remediation soils contaminated with heavy metals [6], transport of metals from soil to deciduous trees [7], phytoextraction with eg maize [8], and simulation of the metal mobility in soils contaminated with sewage sludges [9]. Moreover, the literature raises the issues of bioaccumulation of metals in sea benthic deposits [10] or in oceans by comparing complex models with eg a toxicokinetic one [11].

Computational part

Standardised values for metals from the TCLP (*toxicity characteristic leaching procedure*) were used to pre-assess the general toxicity of wastes in a static (ie: not including variations in values in time) predictive and polynomial model in the form:

$$y(x_1, x_2, x_3, \ldots, x_n) = ax_1 + bx_2 + cx_3 + \ldots + nx_n \quad (1)$$

where: y - general toxicity of the tested waste [mg/dm^3]; a, b, c, …, n - weighted conversion factors of limit values of metal concentration in the TCLP criterion (considering toxicological properties); x_1, x_2, x_3, …, x_n - independent variables which present values of determined concentrations for the individual metals in wastes samples acc. to TCLP procedure [12].

In order to calculate general toxicity, the published data where concentrations of heavy and toxic metals were determined according to the TCLP procedure were applied [13, 14].

Results and discussion

The test of toxic leaching assumes that wastes are submitted to react with more aggressive leaching agents than with those which can occur in natural soil environment [15, 16]. The limit of toxic leaching procedure for each metal leached from soil or sludge was established at the level of hundred times exceeding the maximum concentration of metal pollutions in potable water. For instance, for cadmium: 0.01 mg/dm^3 in potable water, and 1.0 mg/dm^3 - a limit value of toxic leaching [17]. Eluted or toxic forms of metals, eg, lead, make as a rule approx. 10÷30% of total value of metal data determined in concrete environmental components or in wastes [18, 19]. With this respect, it was not possible to use data of metals total concentrations to undertake modelling attempts. The selection of gradient factors for polynomial equation was based on permissible limit values for metals in TCLP procedure, presented in Table 1.

Table 1

Limit, permissible contents of toxic metals according to the TCLP criterion [12, 20]

Toxic metals	Pb	As	Ba	Cd	Cr	Hg	Se	Ag
Maximum concentration of toxic metals acc. to TCLP [mg/dm^3]	5	5	100	1	5	0.2	1	5

Gradient factors were selected by using weighted mean method, considering a number of metals with toxic concentrations basing on the criteria stated in TCLP procedures for the assessment of general toxicity of the indicated waste. On the ground of the achieved results an attempt was made to indicate which of the tested wastes should be classified as wastes toxic for the environment and which ones can be treated as environmentally safe. The assessment of the toxicity level (y) for the indicated group of wastes was quantified with the assumption of the following criterion:

$y(x_1, x_2, x_3, \ldots, x_n) \geq 1$ - the tested waste is environmentally toxic;

$y(x_1, x_2, x_3, \ldots, x_n) < 1$ - the waste is not toxic.

It was assumed that the contents of forms of the leached metals with toxic concentrations in wastes is hazardous for the components of ecosystems when the value of general toxicity fulfils the following relationship $y(x_1, x_2, x_3, \ldots, x_n) \geq 1$. For instance, in order to make computations, concentrations of toxic metals [mg/dm^3] determined in samples of processing wastes (A1-A3) and hospital wastes (B1 and B2) were used acc. to TCLP procedure, and the experimental data for one's own calculations were taken from reports [13] and [14] (Table 2).

Table 2

The level of metal concentrations [mg/dm^3] in exemplary processing wastes A(1-3) and hospital wastes B(1, 2) determined acc. to the TCLP procedure and used for one's own modelling attempts

Sample \ Metal	As	Ba	Pb	Ag	Cd	Cr
A1[a)]	3.5	-	16	-	1.26	32
A2[a)]	9.1	-	15	-	1.28	31.2
A3[a)]	6.3	-	18.3	-	1.12	30.4
B1[b)]	41.01	38.67	16.75	6.59	-	20.64
B2[b)]	28.2	46.96	7.93	3.86	-	36.82

where: the experimental data were taken from reports: [a)] [13], [b)] [14]; gradient factors were matched basing on literature data, respectively, for: As - 0.31 [13] and 0.0417 [14], Cd - 0.06 [13], Cr - 0.31 [13] and 0.0417 [14], Pb - 0.31 [13] and 0.0417 [14], Ba - 0.8333 [14], Ag - 0.0417 [14]

Basing on the experimental data found in literature, the assumed model of general toxicity was computed and the results were listed for the analyzed types of wastes in Table 3.

Table 3

A list of calculated general toxicity values (y) according to the assumed model

$$y(x_1, x_2, x_3, \ldots, x_n) = ax_1 + bx_2 + cx_3 + \ldots + nx_n$$

Sample	Calculated general toxicity value $y(x_1, x_2, x_3, \ldots, x_n)$	Assessment of waste in accordance with the assumed criterion	Verified values of general toxicity [c)]
A1[a)]	16.04	y > 1, the waste qualified as toxic	52.76
A2[a)]	17.22	y > 1, the waste qualified as toxic	56.58
A3[a)]	17.12	y > 1, the waste qualified as toxic	56.12
B1[b)]	36.00	y > 1, the waste qualified as toxic	123.66
B2[b)]	42.30	y > 1, the waste qualified as toxic	123.77

where: calculations were based on the experimental data published in reports: [a)] [13], [b)] [14]; [c)] made on the TCLP criterion [12, 20]

Calculations of general toxicity and their verification, confirm the toxicity of two types of wastes exemplary selected for the needs of modeling.

Conclusion

The search for simple mathematical models to assess general toxicity of the tested wastes basing on the known contents of metals speciation fractions is an issue of current interest regarding mathematical modelling for the needs of the essential problems concerning environmental protection. The static predictive and polynomial model for the assessment of general toxicity of wastes could be applied for experimental data obtained in tests of sequential extraction, for instance, for the so-called ion-exchanging and carbonate fractions which are comparable with the values achieved using the TCLP procedure.

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PRÓBY MODELOWANIA MATEMATYCZNEGO NA POTRZEBY OGÓLNEJ OCENY TOKSYCZNOŚCI ODPADÓW ZAWIERAJĄCYCH METALE

Wydział Technologii i Inżynierii Chemicznej, Uniwersytet Technologiczno-Przyrodniczy im. J.J. Śniadeckich, Bydgoszcz

Abstrakt: Próby wstępnej oceny ogólnej toksyczności odpadów, zawierających w swoim składzie metale, w tym przede wszystkim ciężkie, wykonano za pomocą wielomianowego, statycznego i zarazem prognostycznego modelu matematycznego. Ogólną toksyczność wyznaczono dla próbek odpadów, w których metale były oznaczone metodą toksycznego ługowania TCLP (*Toxicity Characteristic Leaching Procedure*). Kierunkowe współczynniki (a, b, c, …, n) do równania ogólnej toksyczności postaci $y(x_1, x_2, x_3, \ldots, x_n) = ax_1 + bx_2 + cx_3 + \ldots + nx_n$ dobierano metodą średniej ważonej, biorąc pod uwagę zawartość poszczególnych metali oraz ich właściwości toksykologiczne. Poszukując kryterium oceny, przyjęto, że zawartość form wymywanych metali o stężeniach toksycznych w odpadach może być zagrożeniem dla komponentów biosfery wówczas, gdy wartość ogólnej toksyczności spełnia zależność $y(x_1, x_2, x_3, \ldots, x_n) \geq 1$. Bezwzględną wartość toksyczności ogólnej (y) wyznaczano, sumując oznaczone doświadczalnie poszczególne szczątkowe stężenia pierwiastków, zaznaczając ich udział ważony w ogólnej puli toksyczności. Na podstawie obliczeń dla przyjętego modelu ogólnej toksyczności wytypowanych odpadów i weryfikacji modelu względem kryteriów toksyczności zdefiniowanych w metodyce TCLP stwierdzono zbieżność uzyskanych wyników.

Słowa kluczowe: ocena ogólnej toksyczności, modelowanie matematyczne, metale o stężeniach toksycznych