

Determination of solid waste sorption capacity for selected heavy metals in landfills

A. Suna Erses^a, Mohammad A. Fazal^b, Turgut T. Onay^{a,*}, William H. Craig^b

^a *Institute of Environmental Sciences, Bogazici University, 34342 Bebek/İstanbul, Turkey*

^b *School of Mechanical Aerospace and Civil Engineering, University of Manchester, PO Box 88, Manchester M60 1QD, UK*

Received 29 April 2004; received in revised form 18 February 2005; accepted 26 February 2005

Available online 31 March 2005

Abstract

The adsorption process is largely a surface-action phenomenon. In this study, sorption capacities for heavy metals on a solid waste matrix were investigated. Five heavy metals (iron, copper, zinc, nickel and cadmium) were chosen because of their availability in any landfill site. The conditions during all the experimental runs were pH 7.0, temperature 32 °C and suppressed microbial degradation. For adsorption isotherm (Freundlich and Langmuir) calculations, fixed quantities of heavy metal ions were mixed with variable quantities of solid waste. The ratio of mass of adsorbate per unit mass of adsorbent was changed five times, by changing only the adsorbent amount. The results showed that the time required to reach equilibrium varied from metal to metal but all reached equilibrium within the first 32 h. The relative potential of sorption of the individual metals and mixed metals on the solid waste matrix is $Fe > Zn > Cu > Ni > Cd$. The sorption capacity of domestic solid waste matrix for heavy metals is quite significant and this property might prove helpful for the in situ removal of heavy metals in landfill operation. © 2005 Elsevier B.V. All rights reserved.

Keywords: Solid waste; Landfill; Heavy metals; Sorption; Equilibrium time; Adsorption isotherm; Freundlich isotherm; Langmuir isotherm

1. Introduction

Sanitary landfill is the most common method of disposal of solid waste all over the world and is the oldest and the most popular ultimate disposal option often enabling the reclamation of derelict land to be achieved. It also has the advantages of flexibility and reliability and it is quite easy to predict the future costs of direct landfill. As well as municipal solid waste, commercial and industrial wastes, which may contain hazardous substances, such as heavy metals, organic solvents, radioactive wastes etc. are also received by landfills in many countries [1]. Batteries, paints, dyes and inks in paper, pesticides and fertilizers in yard waste are examples of household and commercial wastes, which contain high quantities of heavy metals. Incineration ash is another type of waste that is disposed to landfills. High amounts of heavy metals are

present in this and could severely affect the overall processes occurring in a landfill environment.

Leachates are liquid wastes produced at all landfill sites as water percolates through refuse which contains significant amounts of heavy metals and other contaminants and these cause a potential pollution problem for surface and groundwaters. The characteristics of leachate change over time, as do the decay processes within the waste body. As a landfill ages there is a change from a relatively short initial aerobic period of activity to a longer-time anaerobic decomposition period that has two distinct sub-phases: an acidic phase followed by a methanogenic phase. Leachate may be removed from the base of the waste mass for immediate treatment or disposal or may be recycled within the waste mass to accelerate decay and defer treatment and disposal costs.

In the acidic phase leachates are generally “young” and have high levels of organic pollutants and volatile fatty acids (VFAs). The high concentration of VFAs results in pH values as low as 4 [2], and this acidic environment promotes increased concentrations of heavy metals in leachate [3]. The

* Corresponding author. Tel.: +90 212 3597257; fax: +90 212 2575033.
E-mail address: onayturg@boun.edu.tr (T.T. Onay).

concentration of heavy metals is a function of the complex formation with organics, the pH and the carbonate species. The concentration increases with low pH and decreases with increasing concentrations of carbonate species. In the methanogenic phase, methane-forming bacteria degrade the VFAs and reduce the organic strength of the leachate. The decrease in the VFAs concentration causes a rise of pH to 7 or greater [4].

The potential leachate treatment methods are biological [5] and physico-chemical [6,7], the latter being more appropriate for “old” leachate than “young” leachate [8]. One important process occurring inside the landfills is the adsorption of heavy metals onto the waste. However, there are no quantitative data about heavy metal sorption potential of domestic refuse in literature due to both the heterogeneity of received refuse and the absence of standard procedures for the determination of sorption characteristic of specific wastes [9]. This study sets out to investigate the physical behavior of solid waste with heavy metals at pH 7 to reflect typical methanogenic phase conditions.

The main objective of this research was to investigate the sorption kinetics of each metal (iron, copper, zinc, nickel and cadmium) and hence the potential for adsorption of heavy metals onto solid waste matrix, under one particular set of physical conditions. This objective was achieved under a range of fixed environmental conditions; initial concentration of metal solution that was fed on the solid waste matrices, pH of the whole mixture and temperature in the system appropriate to the methanogenic phase of the solid waste decomposition and suppressed micro-biological degradation of the solid waste. The variable condition was the amount of solid waste matrix that was prepared in laboratory. Thus, the research was able to identify the dominant physical removal processes with solid waste.

2. Sorption isotherms

Sorption is a physical and/or chemical process in which a substance is accumulated at an interface between phases. The overall rate of sorption of metals on a solid waste matrix depends on composition (density, surface area) of the solid waste, concentration of adsorbate (metal ion) in solution, solid waste to solution ratio, contact time history of the solute concentration with the solid waste, solution sampling procedure, pH, temperature and biodegradable characteristics of the solid waste.

A number of different equations can be used to predict theoretical adsorption capabilities for different adsorbents. For this study, the Freundlich isotherm and Langmuir isotherm equations have been used to predict adsorption capabilities of metals on the solid waste matrix.

2.1. Freundlich isotherm

Freundlich isotherm is the oldest and most widely used adsorption equation for solid–liquid system. The empirically

derived Freundlich isotherm can be defined as follows [10]:

$$\frac{x}{m} = K_f C_e^{1/n} \quad (1)$$

where x/m is unit of adsorbate added per unit of adsorbent (mg/kg), C_e is equilibrium concentration of adsorbate in solution (mg/L). K_f and n can be determined experimentally by determining the degree of adsorption x/m at different concentrations C_e . The information can then be plotted using the following equation.

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

In a plot of the above equation, $\log K_f$ will be the intercept of the line when C_e is 1 mg/L, and it indicates the adsorption capacities of the solid waste, $1/n$ is the gradient assuming a linear relationship.

2.2. Langmuir isotherm

Langmuir [11] proposed the first isotherm model which assumed monolayer coverage of the adsorbent surface. The most commonly used expression of the Langmuir equation for describing adsorption data for solid–liquid systems is

$$\frac{x}{m} = \frac{K_L M C_e}{1 + K_L C_e} \quad (3)$$

where x is the amount or concentration of the solute adsorbed in mg, m is the mass of the adsorbent in kg, C_e is the equilibrium concentration of the solute in mg/L, K_L and M are constants. The linearized expression of this equation is

$$\frac{1}{x/m} = \frac{1}{K_L M C_e} + \frac{1}{M} \quad (4)$$

This equation is called the “Double-Reciprocal Langmuir Equation” and more suitable for situations in which the distribution of equilibrium concentrations tends to be skewed towards the lower end of the range of the equilibrium concentrations. An EPA report [12] concluded that the Langmuir constant or affinity parameter (K_L) is related to the bonding energy between the adsorbed ion and the adsorbent, but that specific functional relationship is uncertain. Kinniburgh [13] noted that K_L is best estimated from the slope of the adsorption isotherm at very low concentrations. The constant M is accepted as the adsorption maximum of the adsorbent with respect to the specific solute and is interpreted as the maximum amount or concentration that an adsorbent can retain.

3. Materials and methods

3.1. Solid waste preparation

Composition of the synthetic solid waste was taken according to the average of a typical municipal solid waste

composition (food waste 76%, paper 12%, plastic 4%, textiles 4% and yard waste 4%) determined for five districts in Istanbul [14].

About 5 kg of solid waste was prepared in the laboratory. As adsorption is a surface area phenomenon, it was considered necessary to increase the surface area of solid waste by shredding it into small pieces as near as possible to about a centimeter at any side. The solid waste was heated at 105 °C for 24 h to evaporate all moisture and to kill microorganisms. Moisture content of this solid waste was 71%. Finally, the waste was cooled and kept dry until use.

3.2. Standard solution preparation

In these experiments, de-ionized water taken from a standard laboratory was used throughout. Tap water and/or distilled water could not be used since they may contain inorganic salts and organic components that may affect sorption capacity and interfere with the spectrophotometric determination of the metals concentration [15]. Initial metal concentration for individual solutions was taken as 40 mg/L for iron, 20 mg/L for copper, 20 mg/L for zinc, 20 mg/L for nickel and 2 mg/L for cadmium using the highest availability to be found at any landfill site in Turkey according to The Turkish Hazardous Waste Control Regulation [16]. These solutions were prepared in the laboratory by using $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ salt, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ salt, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ salt, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ salt and $\text{CdSO}_4 \cdot 2.5\text{H}_2\text{O}$ salt. A mixed solution was prepared by using the same concentrations of each metal ion simultaneously.

3.3. Solid waste:solution ratio

The term solid waste to solution ratio refers to the ratio of the mass of the adsorbent to the mass of liquid. The solid:solution ratio of the ASTM procedure D4646 is 1:20 [17], whereas EPA [12] suggests that the solid:solution ratio may or may not have a profound effect on sorption data and recommends the use of samples with a ratio varying from 1:4 to 1:10,000 to enable direct comparison of sorption data. For each time and each metal case, 650 mL of solution was taken to conduct the experiment. Arbitrarily 50, 90, 130, 170 and 210 g samples on a wet weight basis of solid waste were used as adsorbent matrix. The ratio varied for this experiment from 1:13 to 1:3 for 50–210 g of solid waste mass.

3.4. Measurement of equilibrium time

The equilibrium time in batch-sorption experiments is the time interval in which the system reaches chemical equilibrium and the concentration of the products and reactants cease to change with respect to time.

$$\frac{\partial C}{\partial t} = 0 \quad (5)$$

The EPA [12] have suggested that the equilibrium time should be defined as the minimum time needed to establish a rate of change of the solute concentration in solution equal to or less than 5% per 24-h interval. This definition is an operational definition of equilibrium and is equivalent to a steady state. Cast as an equation it may be written as

$$\frac{\Delta C}{\Delta t} \leq 0.05 \text{ per 24-h interval} \quad (6)$$

Jones et al. [18] have suggested a less rigorous approach based on the minimum time needed to establish a rate of change of the solute concentration equal to, or less than, 10% during a 6-h period.

3.5. Laboratory procedure

Generally, two types of experimental techniques were used to generate batch-sorption data: (i) constant solid:variable solution method, mixing a range of aqueous solutions—containing progressively decreasing solute concentrations—with a fixed mass adsorbent, in all instances and (ii) variable solid:constant solution method, mixing batches of the same solute concentration, with progressively increasing amount of adsorbent.

The amount of adsorbate by weight was kept constant at all times and the amount of solid waste matrix was varied. A 1 L plastic bottle was used for each experiment. A measured amount (50, 90, 130, 170 or 210 g) solid waste and 650 mL of solution of any one ion (iron, copper, zinc, cadmium nickel or mixed) were added to this bottle. Continuous shaking was provided using a heated water bath mechanical shaker. The temperature was maintained constant at 32 °C. The initial pH was set at 7.0 using NaOH or HCl and the change of pH was monitored. Conductivity of the solution was measured at different times. The combination of all runs and measurements (pH, electrical conductivity (EC) and temperature inside the bottle) during a single test is tabulated in Table 1.

Degradation of organics within the waste by microbial action can cause an increase of acidity in the solution which causes a drop in pH and sorption capacity of metals from the solution on solid waste. Sodium azide (NaN_3 0.2% arbitrarily) was used to suppress the biological activity [19]. The experiments were conducted using translucent plastic bottles to prevent photo-degradation of the solid waste matrix.

To determine equilibrium time and concentration, 10 mL samples were taken at 0.5, 1, 3, 5 h intervals until reaching 11 h in 1 day. After 9 h overnight, samples were taken again at 20, 22, 24, 26, 28, 30 and 32 h intervals. Equilibrium concentration of the solution was then used for isotherm calculations.

Collected samples were monitored by using the Perkin-Elmer atomic adsorption spectrophotometer. Before using the spectrophotometer all samples had to be prepared in a standard way to break down their complex bonds. The standard method, EPA method 3010A was used for sample preparation.

Table 1
Combination of all runs

Metal ion	Solution condition	Amount of solid waste (g)	Number of runs	Measurements
Fe, 40 mg/L	Individual	50, 90, 130, 170, 210	5	pH, EC, $T^{\circ}\text{C}$
Cu, 20 mg/L	Individual	50, 90, 130, 170, 210	5	pH, EC, $T^{\circ}\text{C}$
Zn, 20 mg/L	Individual	50, 90, 130, 170, 210	5	pH, EC, $T^{\circ}\text{C}$
Ni, 20 mg/L	Individual	50, 90, 130, 170, 210	5	pH, EC, $T^{\circ}\text{C}$
Cd, 2 mg/L	Individual	50, 90, 130, 170, 210	5	pH, EC, $T^{\circ}\text{C}$
Fe, Cu, Zn, Ni, Cd	Mixed	50, 90, 130, 170, 210	5	
Reference tests	No feed metals	50, 90, 130, 170, 210	5	
Total number of runs			35	

3.6. Evaluation of procedures and equipment

For the evaluation of procedures and equipment, 10 samples were taken from a single test bottle containing 90 g solid waste matrix with mixed metals solution at one arbitrary time (repetitive measurements). All samples were then prepared for standard testing and the concentration of each metal was obtained from each of the samples. Standard deviation for each metal from the data of 10 samples was calculated. The standard deviation for Fe was 1.848 mg/L, for Cu 0.590 mg/L, for Zn 0.315 mg/L for Ni 0.714 mg/L and for Cd 0.039 mg/L. The obtained results from all 10 samples for five metal ions gave a precision (percentage of deviation from the average point) for procedures and equipment in the range of 3.39–5.65%.

3.7. Reference experiment

Five reference experiments were conducted for the five different amounts of solid waste matrix (50, 90, 130, 170 and 210 g) to determine metal concentrations that were present within the laboratory prepared solid waste matrix. De-ionized water was used with the addition of NaN_3 to suppress biological degradation under a constant initial pH of 7.0. The amount of NaN_3 was taken as 1.3 g for the 650 mL of de-ionized water used in each case. The working environment was the same as previously described. The objective was to determine the effect of NaN_3 on the solid waste matrix, the rate of desorption of metals from the solid waste matrix, and subsequent re-adsorption, during the experimental runs. The

results were then used as reference or control data and were subtracted from the measured concentrations of feed ion at different times in the main test series.

Sorption at the solid/solution interface is an “innately mathematical” process [20] in the sense that for sorption to occur, desorption of some antecedent species must also occur. Sparks [21] has noted that this effects exchange equilibrium in batch systems, but not in flow systems. In this respect, desorption behavior of the solid waste matrix was taken into consideration for each case and these values were subtracted from the measured experimental data.

4. Results and discussion

Batch sorption studies were conducted to investigate the sorption capacities of Fe, Cd, Cu, Zn and Ni on solid waste within a range of 50–210 g and to establish the equilibrium time of accumulation. For each of the metal ions, significantly rapid increase of sorption was observed within the first few hours and a steady equilibrium was already reached in 32 h. As an example, Fig. 1 shows equilibrium time of 11 h and equilibrium concentration of 10.63 mg/L for Cu ion using 170 g solid waste matrix.

Solid waste has different components each representing a different percentage of the total; not all of these components have metal ions within them, some of them have. Metals are coming out from them in contact with water at the same time as those components, which do not have any metal ion, are

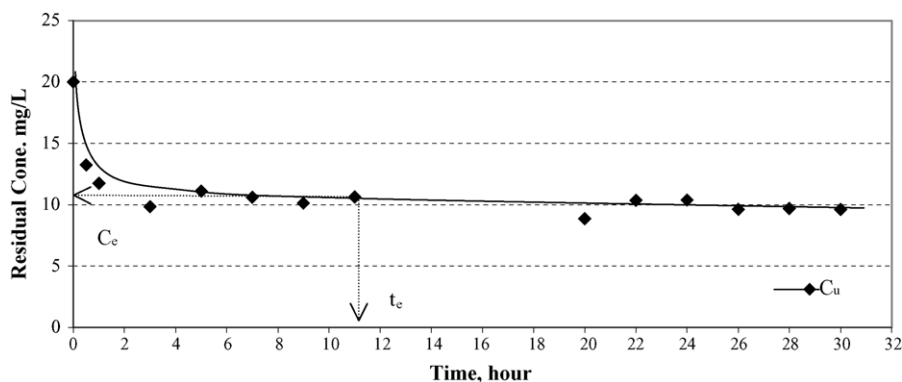


Fig. 1. Change in residual Cu ion concentration.

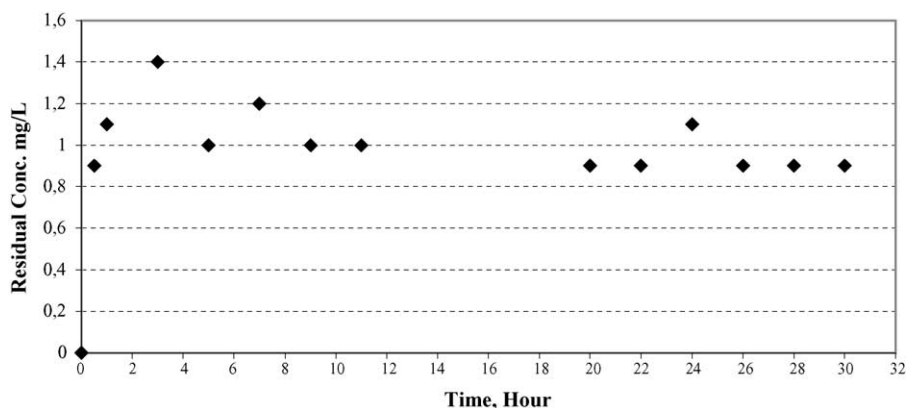


Fig. 2. Time dependent concentration of Zn ion from 170 g of the solid waste mass.

adsorbing these metals. In some cases, desorption rate is higher than adsorption rate within the solid waste and vice versa. This depends on the amount of solid waste that does not have metal ions and concentration of heavy metal within the solid waste. Hence, before the results of sorption experiments were evaluated, a number of runs was conducted to investigate the desorption of metals from solid waste in de-ionized water and subsequent re-adsorption. The results indicated that desorption concentrations of each metal were approximately 1 mg/L. As an example, Fig. 2 shows the desorption of Zn ion from 170 g of the solid waste matrix with different times.

The amount of heavy metals adsorbed by solid waste (x/m , mg/kg) as a function of the equilibrium concentrations of heavy metals (C_e , mg/L) was determined by linear sorption isotherms in Fig. 3. As can be seen from the figure, the sorption of heavy metals generally exhibited an S-type isotherm characterized by an initially small slope that increases with adsorptive concentration. Zinc and nickel in mixed heavy metal solution and nickel in individual solution exhibited a L-type isotherm characterized by an initial slope that does not increase with the concentration of adsorptive in the solid. However, the behavior of sorption is not completely clear and can not be concluded from the figures because S-type sorption may be returned to an L-type after maximum saturation in later stages.

The slope of isotherms increased particularly for Fe and Zn, indicating high sorption affinities for these heavy metal ions. The maximum metal sorption $(x/m)_{\max}$ by solid waste was obtained at low solid waste amount and high residual concentrations, and was 205 mg/kg for Fe, 125 mg/kg for Zn, 100 mg/kg for Cu, 38 mg/kg for Ni, 18 mg/kg for Cd. In the metal mixture, $(x/m)_{\max}$ was 145 mg/kg for Fe, 126 mg/kg for Zn, 100 mg/kg for Cu, 42 mg/kg for Ni, 16 mg/kg for Cd. A smaller amount of Fe was adsorbed from the heavy metal mixture compared to the sorption from a single ion solution. There was no vital change in the sorption of other metals. This sorption sequence is confirmed by a number of studies exist in literature. Veeresh et al. [22] investigated the capacity of metal accumulation (Cd, Ni and Pb) in three soils of India and concluded that sorption capacity in all the

soils decreased in the order: Pb \gg Ni > Cd. Accumulation of metals Cu, Co, Ni, Pb, Cd and Zn by gellan gum (GG) gel beds was also studied by Lazaro et al. [23] and maximum metal uptake sequence was Pb > Cu > Ni \approx Zn = Co > Cd. On the other hand, removal rates of heavy metals rose by increasing the amount of solid waste (Fig. 4). Both individual and mixed heavy metal solutions indicated same removal trend except zinc; Cd > Fe > Zn > Cu > Ni for individual and Cd > Zn > Fe > Cu > Ni for mixed solution. The maximum removal rates of initial metal concentrations were obtained at high solid waste and low residual concentrations and were 81% for Cd, 72% for Fe, 64% for Zn, 49% for Cu and 27% for Ni of individual solution and were 88% for Cd, 84% for Zn, 70% for Fe, 60% for Cu and 29% Ni. Removal rates and sorption affinities of these heavy metals were not compared to each other because of the different initial concentrations of feed metal solution prepared according to the amounts given in the Turkish Hazardous Waste Control Regulation [16]. Removal efficiency of cadmium was much higher than other metals and reached to 81–88% for both solutions. This might be related to low concentration of cadmium (2 mg/L) in solution. However, from the view point of sorption, cadmium uptake by solid waste was the lowest. When the heavy metals (Ni, Zn and Cu) having the same concentration were compared, sorption and removal of Ni for both individual and mixed solution was lower than Zn and Cu. On the other hand, Zn was the highest of the three. The affinity sequence can be related to large atomic weight and ionic radius of the heavy metals. Atomic weights (g) and ionic radius (picometers) are 65.39 and 134 for Zn; 63.55 and 128 for Cu; 58.70 and 124 for Ni, respectively [24].

The mathematical description of sorption isotherms was determined by the application of Freundlich and Langmuir equations. In Fig. 5, the sorption of individual and mixed heavy metals are shown by plotting Freundlich adsorption isotherms. As described in Eq. (2). K_F , the sorption capacity, can be determined from the intercept and $1/n$, indicating to the degree of non-linearity between the capacity of adsorbent and equilibrium solute concentration, from the slope of its linear form. K_F and n values were calculated

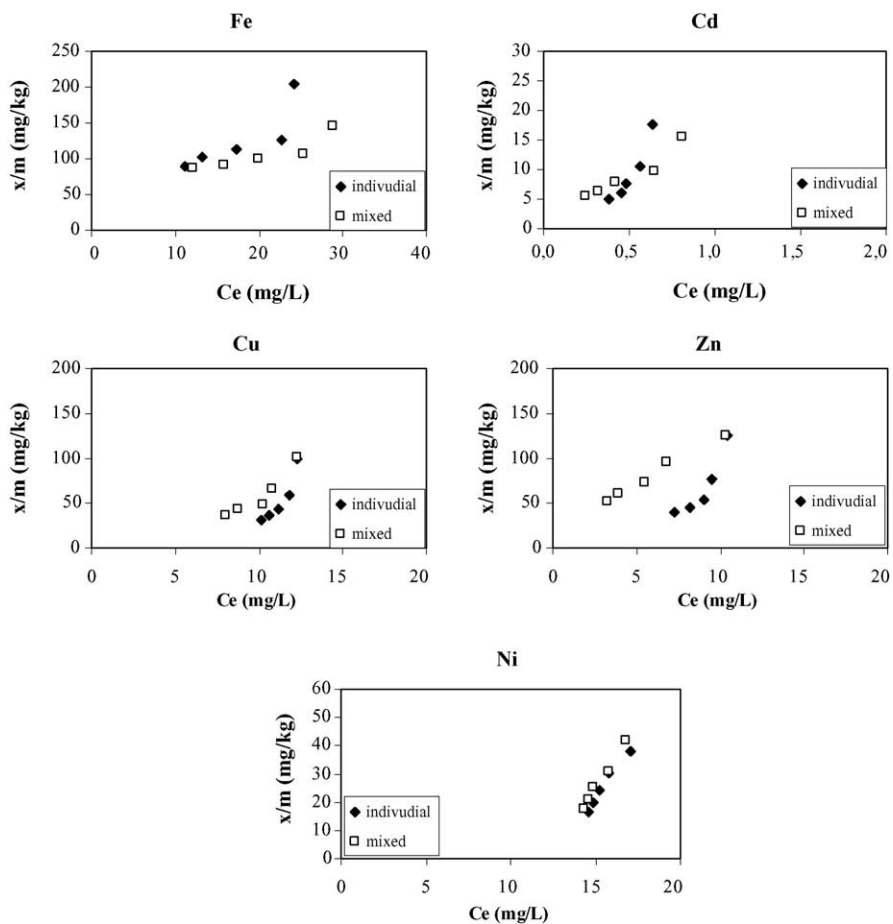


Fig. 3. Linear sorption isotherms for Fe, Cd, Cu, Zn and Ni ions from individual and mixed solution.

using the least squares method and tabulated in Table 2. The K_F value of Cd for individual solution, calculated as $47.28 \text{ mg}^{1-1/n} \text{ L}^{1/n}/\text{kg}$, was found to be highest among metals. The lowest K_F values, on the other hand, were observed for Cu ion of individual solution and Ni ions of both individual and mixed solutions, which were about 3.07×10^{-5} , 1.92×10^{-5} and $2.62 \times 10^{-5} \text{ mg}^{1-1/n} \text{ L}^{1/n}/\text{kg}$, respectively. The nonlinearity ($n < 1$) of isotherms in most cases was observed in this study (Table 2). The values of n ranged from

0.169 to 1.951. Potential of adsorption for individual metal on solid waste matrix using Freundlich constant K_F was in order of: $\text{Cd} \geq \text{Fe} > \text{Zn} > \text{Cu} \geq \text{Ni}$ and for mixed metals, $\text{Fe} \geq \text{Zn} \geq \text{Cd} > \text{Cu} > \text{Ni}$.

A second common model is the sorption isotherm equation developed by Langmuir, which describes the formation of a monolayer of solute molecules on the adsorbent surface. Fig. 6 shows the sorption of individual and mixed heavy metals by plotting Langmuir adsorption isotherms. The processes

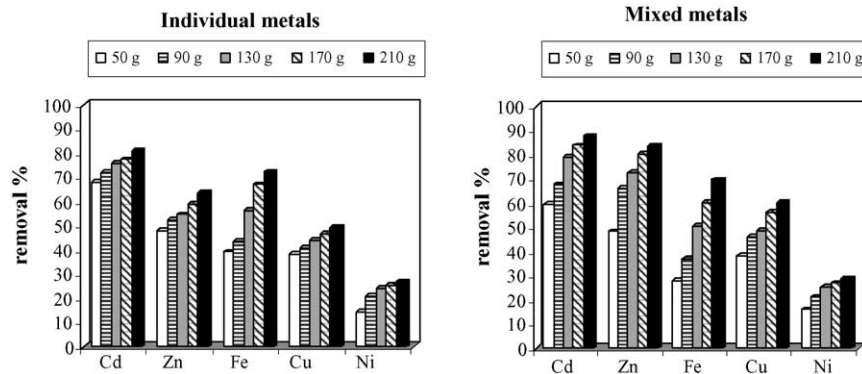


Fig. 4. Removal rates of heavy metals for individual and mixed solutions.

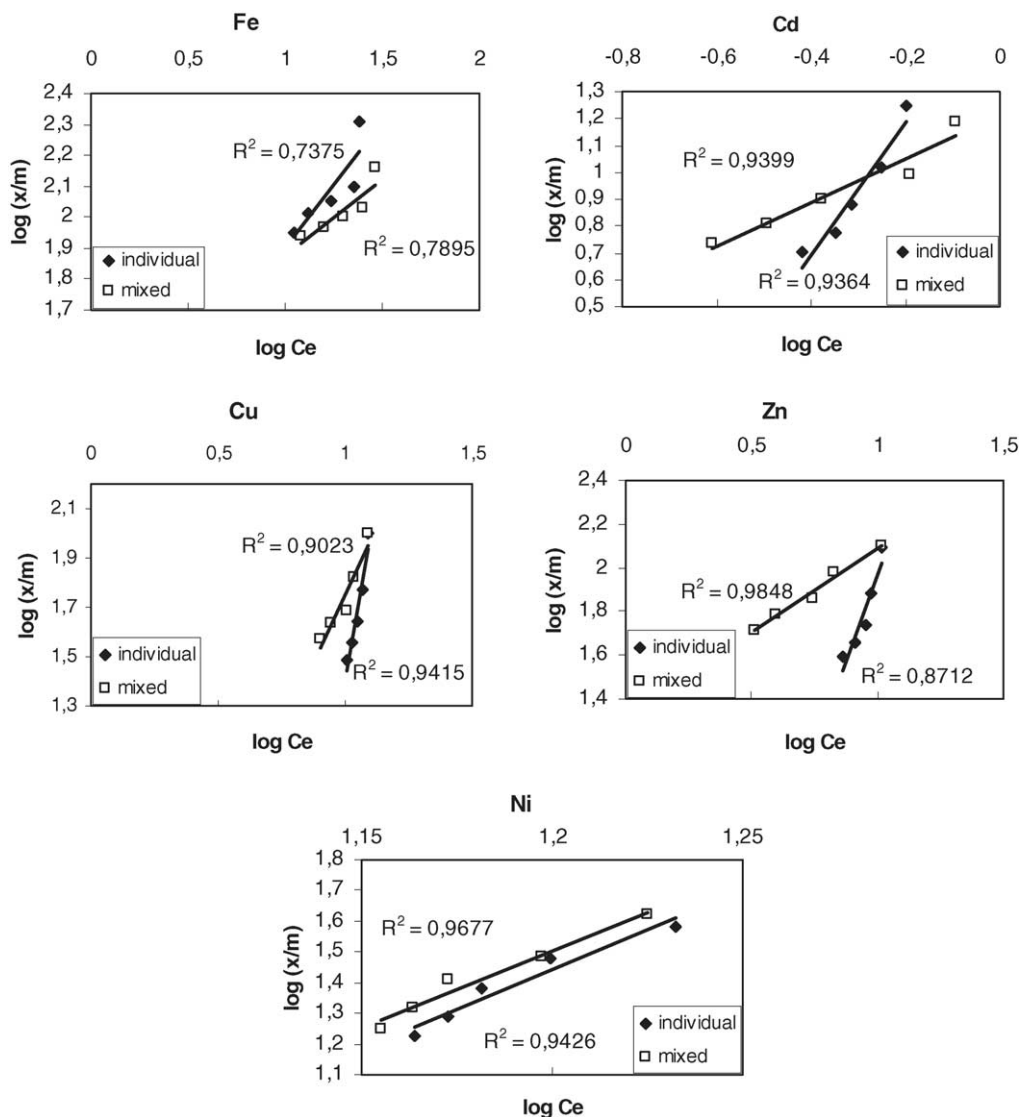


Fig. 5. Freundlich isotherm for Fe, Cd, Cu, Zn and Ni ions from individual and mixed solution.

were linearized by the double-reciprocal Langmuir equation because better fits were obtained with this model. K_L (L/kg) is a constant related to the energy or net enthalpy of adsorption, M (mg/kg) (the adsorption maximum) is the amount

of solute adsorbed per unit weight of adsorbent in forming complete monolayer on the surface. K_L and M values were also calculated using the least squares method and given in Table 3. K_L values were highest for Cd in both individual

Table 2
Freundlich isotherm constants for individual and mixed solution

Solution	Heavy metals	K_F ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{kg}$)	n	r^2
Individual metal ion solution	Fe	12.46	1.241	0.74
	Cd	47.28	0.408	0.94
	Cu	3.07×10^{-5}	0.169	0.94
	Zn	0.067	0.318	0.87
	Ni	1.92×10^{-5}	0.195	0.94
Mixed metal ions solution	Fe	22.84	1.951	0.79
	Cd	16.22	1.238	0.94
	Cu	0.39	0.462	0.90
	Zn	20.69	1.289	0.98
	Ni	2.62×10^{-5}	0.197	0.97

Table 3
Langmuir isotherm constants for individual and mixed solution

Solution	Heavy metals	K_L (L/kg)	M (mg/kg)	r^2
Individual metal ion solution	Fe	0.023	431.6	0.79
	Cd	1.103	6.608	0.97
	Cu	0.094	10.59	0.99
	Zn	0.073	32.90	0.92
	Ni	0.055	6.019	0.90
Mixed metal ions solution	Fe	0.052	189.6	0.78
	Cd	0.760	33.55	0.95
	Cu	0.050	55.28	0.93
	Zn	0.055	337.9	0.98
	Ni	0.051	6.573	0.92

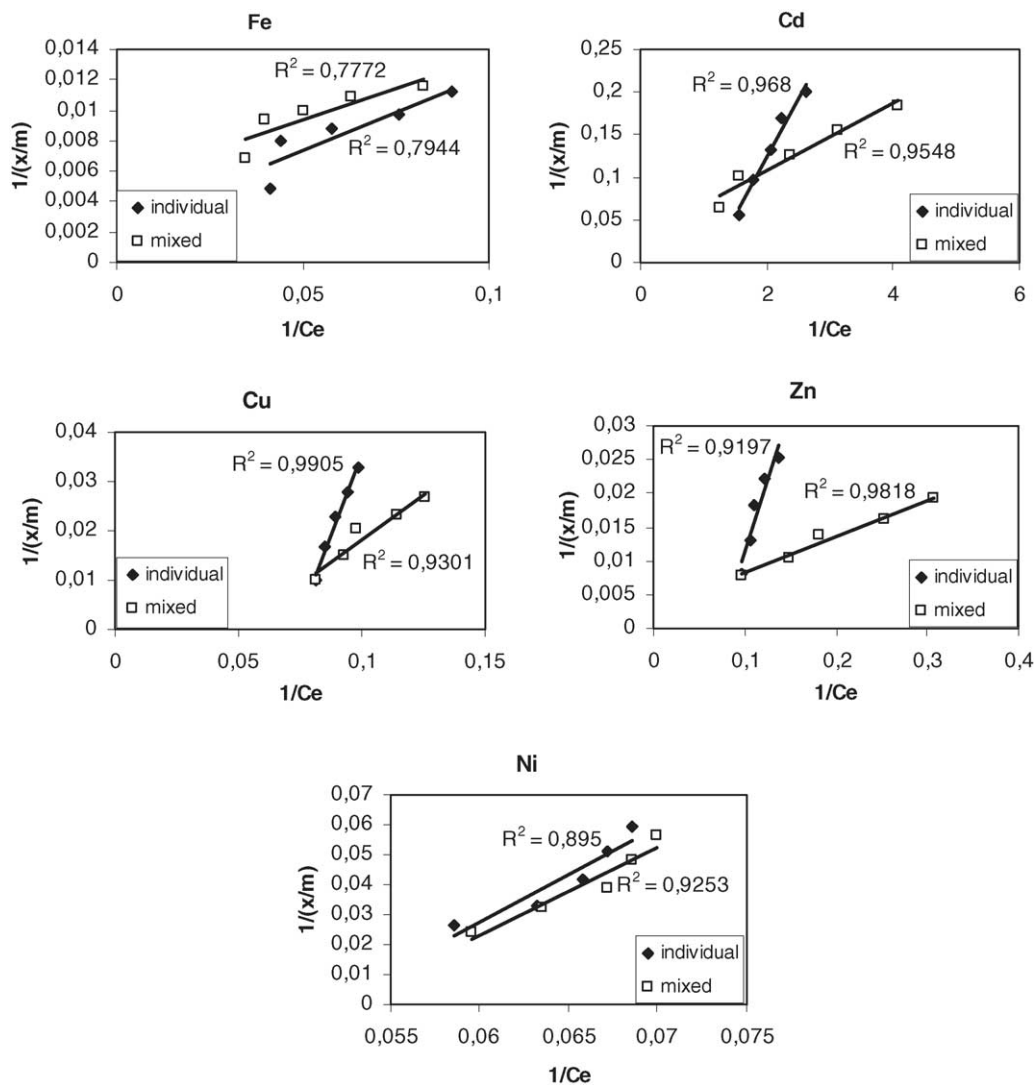


Fig. 6. Langmuir isotherm for Fe, Cd, Cu, Zn and Ni ions from individual and mixed solution.

and mixed solution. This can be explained that the sites responsible for cadmium adsorption at low concentration are characterized by much higher energies than those at higher concentrations. The M values were firstly higher for Fe and then for Zn in both solutions indicating their high adsorptive capacities. Potential of sorption for individual metal on solid waste matrix in terms of Langmuir constant M was in the order of: $Fe > Zn \geq Cu > Cd \geq Ni$ and for mixed metal, $Zn > Fe > Cu \geq Cd > Ni$. However, when M values of solid waste are compared to the values of other sorbents in literature, it can be concluded that the sorption capacity of solid waste is low. Yavuz et al. [25] studied the removal of Mn(II), Co(II), Ni(II) and Cu(II) from aqueous solution using a raw kaolinite and found that the sorption of these metals on kaolinite conformed to the linear form of Langmuir adsorption equation. Langmuir M constants for each metal were found as 0.446 mg/g for Mn, 0.919 mg/g for Co, 1.669 mg/g for Ni, 10.787 mg/g for Cu at 25 °C, respectively. On the other hand, Ho et al. [26] investigated a new sorbent

system (tree fern) for Zn(II), Cu(II) and Pb(II) removal from aqueous solutions. The experimental results were analyzed by using Langmuir, Freundlich and Redlich-Peterson equations and correlation coefficients for fitting the Langmuir and Redlich-Peterson equations were significantly better than the coefficients for Freundlich equation. According to the evaluation using the Langmuir equation, the maximum sorption capacities of metal ions onto tree fern were 7.58 mg/g for Zn, 10.6 mg/g for Cu and 39.8 mg/g for Pb.

When the coefficient of determination (r^2) is used as a criterion for this study, copper, nickel, cadmium and zinc sorptions fit the Langmuir plot. Copper, nickel, cadmium and zinc sorption isotherms also agreed with the Freundlich model. However, the general trend observed in sorption profiles in Figs. 5 and 6 revealed that the sorption data were better interpreted with the Langmuir equation. On the other hand, iron behaved inconsistently. This may be explained by the presence of complex-forming ligands in the solid waste which complicates the prediction of relative metal cation sorption

affinity. For iron sorption equilibrium in both Freundlich and Langmuir models, correlation coefficients were lowest ($r^2 < 0.80$).

The effect of isotherm shape can be used to predict whether a sorption system is “favorable” or “unfavorable” [26]. According to Hall et al. [27], the essential features of the Langmuir isotherm can be expressed in term of a dimensionless constant separation factor or equilibrium parameter K_R , which is defined by the following relationship:

$$K_R = \frac{1}{1 + K_L \times C_0} \quad (7)$$

where K_R is a dimensionless separation factor, C_0 is initial concentration (mg/L) and K_L is a Langmuir constant (L/mg). The parameter K_R indicates the shape of the isotherm accordingly: $K_R > 1$ (unfavorable); $K_R = 1$ (linear); $0 < K_R < 1$ (favorable) and $K_R = 0$ (irreversible). The values of K_R for both individual and mixed metal solutions were approximately the same (0.99). The K_R values indicate that sorption is favorable for all metals and reaches to linearity.

The ionic strength of the solution has both direct and indirect effects on sorption data. The extent of these effects depends on the concentration, composition and change of the ionic constituents. Atkins [28], Bohn et al. [29], Bolt and Buggenwert [30], Garrels and Christ [31], Stumm and Morgan [32] have discussed the effect of ionic strength on sorption data and they concluded that ionic strength may affect sorption in two ways: by changing solute activity, and by changing the thickness and properties of the diffuse electrical double layers associated with colloidal particles. With the help of the shielding effect of neighboring ions, the activity of most solutes tends to decrease as the ionic strength of the solution increases. Griffin and Jurinak [33], describe a linear relationship between ionic strength and electrical conductivity,

$$IS = 0.0127 \times EC \quad (8)$$

where IS is ionic strength in moles per litre and EC is electrical conductivity in milisiemens per centimeter. In the study, conductivity data generally showed increasing trend. As an example, conductivity of Zn in individual solution with 170 g of the solid waste matrix increased from 4.82 ms/cm at 0 h. to 4.92 ms/cm at 20 h. The ionic strengths were calculated using electrical conductivity measured during the experiment and as proportional to conductivity, ionic strength showed increasing trend; from 0.061214 to 0.062484.

The ionic strength of each individual and mixed metal solution changes slightly with time during the experimental run, that can be attributed to the changes in pH. It has been observed that although the initial pH was always 7.0, it dropped gradually and remained steady after 5–7 h at pH level of 6.5–6.7 for different amounts of the solid waste matrix and ions.

It should be noted that, in order to determine the sorption capacity of the solid waste matrix for heavy metals, an attempt was made to stop the biological degradation using

NaN_3 . However, high temperature, continuous shaking and breakdown of metallic salt in solution may cause the drop in pH from 7.0 to near 6.5.

The effect of temperature on sorption data was linked to the thermodynamics of the sorption process. The experiment was conducted at a constant temperature of 32 °C by using a mechanical shaker with hot bath. Inside temperature of the test bottles fluctuated between 32 and 33 °C throughout the test period for both individual and mixed metal solution experiments without showing any significant variation.

5. Conclusions

The main findings of these experiments are as follows:

- Domestic waste has a significant and potentially useful capacity for adsorbing and retaining heavy metals.
- All five metals reached equilibrium concentration within the first 32 h for all five cases either individually or in mixed solutions.
- Solid waste was good biosorbent of heavy metals with an experimental $(x/m)_{\max}$ of (mg/kg ww) 205 for Fe, 125 for Zn, 100 for Cu, 38 for Ni, 18 for Cd from individual solution and of 145 for Fe, 126 for Zn, 100 for Cu, 42 for Ni, 16 for Cd from mixed solution.
- Solid waste showed a high affinity for Zn when compared to an equimolar of Cu and Ni.
- The experimental results were analyzed by using both Freundlich and Langmuir equations and the correlation coefficients for fitting the Langmuir equation were better than the coefficients for Freundlich equation.

The sorption capacity of domestic solid waste matrix for heavy metals is a quite significant mechanism and this property might be successfully used for in situ heavy metal attenuation in landfills.

Acknowledgments

The authors would like to acknowledge Dr. John T. Turner, School of Engineering, University of Manchester and Dr. Orhan Yenigun, Institute of Environmental Science, Bogaziçi University for their help in this research and for time-to-time online advice. The financial support by the Research Fund of Bogaziçi University (Project No. 03Y101) is gratefully acknowledged.

References

- [1] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, *Water Res.* 37 (2003) 1619–1627.
- [2] G. Tchobanoglous, H. Theisen, S.A. Vigil, *Integrated Solid Waste Management*, McGraw-Hill Inc., 1993.
- [3] U. Förstner, C. Colombi, R. Kistler, in: E. Merian (Ed.), *Metals and Their Compounds in the Environment, Dumping of Wastes*, VCH Publishers, Inc., New York, 1991, pp. 333–355.

- [4] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.A. Christensen, *Crit. Rev. Environ. Sci. Technol.* 32 (4) (2002) 297–336.
- [5] H.D. Robinson, G. Grantham, *Water Res.* 22 (1988) 733–747.
- [6] J. Iza, P.J. Keenan, M.S. Switzenbaum, *Water Sci. Tech.* 25 (7) (1992) 255–264.
- [7] E.A. McBean, F.A. Rovers, G.J. Farquars, *Solid Waste Landfill Engineering and Design*, Prentice Hall PTR, Englewood Cliffs, NJ, USA, 1995.
- [8] P.A. Vesilind, W.A. Worrell, D.R. Reinhart, *Solid Waste Engineering*, Brooks/Cole, Thomson Learning, Inc., USA, 2002.
- [9] I.A. Watson-Craik, K.J. Sinclair, in: E. Senior (Ed.), *Co-disposal of Industrial Wastewaters and Sludges*, Microbiology of Landfill Sites, CRC Press, 1995, pp. 91–130.
- [10] H. Freundlich, *Kapillarchemie: eine Darstellung der Chemie der Kolloide und Verwandter Gebiete*, Leipzig, Akademische Verlagsgesellschaft, 1909, 591 p.
- [11] I. Langmuir, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [12] EPA, Technical Resource Document, Batch-Type Procedures for Estimating Soil Adsorption of Chemicals, Environmental Protection Agency, Washington, DC, USA, 1992.
- [13] D.G. Kinniburgh, *Environ. Sci. Technol.* 20 (1986) 895–904.
- [14] İ. Öztürk, O.A. Arıkan, İ. Demir, A. Demir, B. İnanç, G. Kanat, S. Yılmaz, *İstanbul Katı Atıkların Karakterizasyonu Ve Aerobik (Havali) Kompostlaşabilirliği- Ara Rapor*, İTÜ İnşaat Fakültesi, Çevre Mühendisliği, Bölümü, Nisan, 1997 (in Turkish).
- [15] M.S. Kouyoumdjiev, Kinetics of adsorption from liquid phase on activated carbon, Ph.D. thesis, Eindhoven University of Technology, 1992.
- [16] Turkish Hazardous Waste Control Regulation, Official Paper No. 22387, 1995.
- [17] American Society for Testing and Materials, 24-Hour Batch-type Measurement of Contaminant Sorption by Soils and Sediments, vol. 11.04, Annual Book of ASTM Standards, Water and Environmental Technology, Pennsylvania, 1987, pp. 163–167.
- [18] C. Jones, P. Mcgugan, A. Smith, S. Wright, *J. Hazard. Mater.* 2 (1977–1978) 219–225.
- [19] C. Oman, *Int. J. Environ. Anal. Chem.* 71 (1998) 73–85.
- [20] N. Persaud, P.J. Wierenga, *Soil Sci. Soc. Am. J.* 46 (1982) 482–490.
- [21] D.L. Sparks, *Adv. Agron.* 38 (1986) 231–266.
- [22] H. Veeresh, S. Tripathy, D. Chaudhuri, B.R. Hart, M.A. Powell, *Appl. Geochem.* 18 (2003) 1723–1731.
- [23] N. Lazaro, A.L. Sevilla, S. Morales, A.M. Marques, *Water Res.* 37 (2003) 2118–2126.
- [24] J.P. Sevenair, A.L. Burkett, *Introductory Chemistry*, Wm. C. Brown Communications Inc., Dubuque, 1997, pp. 166–173.
- [25] Ö. Yavuz, Y. Altunkaynak, F. Güzel, *Water Res.* 37 (2003) 948–952.
- [26] Y.S. Ho, C.T. Huang, H.W. Huang, *Process Biochem.* 37 (2002) 1421–1430.
- [27] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, *Ind. Eng. Chem. Fundam.* 5 (1966) 212–223.
- [28] P.W. Atkins, *Physical Chemistry*, W.H. Freeman and Company, New York, 1982.
- [29] H.I. Bohn, B.I. McNeal, G.A. O'Connor, *Soil Chemistry*, John Wiley and Sons, New York, 1979.
- [30] G.H. Bolt, M.G.M. Bruggenwert, *Soil Chemistry: A Basic Elements*, second ed., Elsevier Scientific Publishing Company, Amsterdam, 1978.
- [31] R.M. Garrels, C.L. Christ, *Solutions, Minerals and Equilibria*, Freeman, Cooper and Company, California, 1965.
- [32] W. Stumm, J.J. Morgan, *Aquatic Chemistry*, second ed., John Wiley and Sons, New York, 1981.
- [33] R.A. Griffin, J.J. Jurinak, *Soil Sci.* 116 (1973) 26–30.