

Rate process of potential toxic elements reactions in Arid region

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Abstract: Kinetics of reactions in soil and aquatic environments is of extreme importance to understand the fate of reactions take place in soil ecosystems. Most of the chemical processes that occur in these ecosystems are dynamic, and a knowledge of the mechanisms and kinetics of these reactions is fundamental. Moreover, to properly understand the fate of applied fertilizers, pesticides, organic and inorganic pollutants in soils with time, and to thus improve nutrient availability and the quality of our groundwater, one must study kinetics. This review article represents different mechanisms take place in Arid region in order to put the best management practices should be applied to minimize the hazards of these inorganic pollutants.

Keywords: Potential toxic elements, kinetics, arid region

INTRODUCTION

There is an ever increasing awareness and concern about the environment and the extent of the interrelationships between the three basic resources; land, water and air. A seemingly for removed input into one of these resources can be detrimental to another. Because of the immensity of the environment and the heretofore relatively low rate of use, interests have generally been centered on other aspects of daily activities [1]. Recently, a considerable degree of worldwide concern has been developing regarding the effects of heavy metals on the environment.

Because soils are heterogeneous, numerous studies have focused on the interaction of several heavy metals with different soil constituents. Thus, an accurate description of the complex interactions of heavy metals in soils is a prerequisite to predict their behaviour in the contaminated soils. Specifically, to predict the fate of heavy metals in soils, one must account for retention and release reactions of the various species in the soil environment. Heavy metals in soils can be involving in a serious of complexed chemical and biological interactions including oxidation-reduction, precipitation and dissolution, volatilization, and surface and solution phase complexation [2].

Many soil chemical processes are time-dependent. To fully understand the dynamic interactions of metals, pesticides, industrial chemicals, plant nutrients and heavy metals with soils and to predict their fate with time, knowledge of the kinetics of these reactions is important.

Considering the above facts, the objectives of this review article is to reviewing the recent directions toward heavy metal kinetic reactions in contaminated soils and the most factors affecting these reactions. More specifically, the objectives are to declare the hazardous of heavy metals, their injury effects on plant growth and the critical levels of the pollutants in soils through detecting the recent studies represent mechanism of heavy metal sorption/release in soil surfaces using kinetic studies and the effects of some soil properties on heavy metal sorption/release reactions in different soils.

Main source of heavy metals in soils

From a purely physical point of view, heavy metals are elements with a density higher than 6 g/cm³. However, from a soil scientific point of view, a more sound approach is reached when chemical characteristics and their natural appearance are also included. Heavy metals such as Pb, Cd, Cu, Zn and Ni, these elements have comparable chemical characteristics and are essential for most organisms. The concern comes from the fact that the magnification of very small amounts of these elements have resulted in adverse effects on biosystem [3].

Although heavy metals are ubiquitous in soil parent materials, the major anthropogenic source of metals to soils and the environment are:

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- **Metalliferous mining and smelting**

Metals utilized in manufacturing are obtained from either the mining of ore bodies in the earth's crust. Ores are naturally occurring concentrations of minerals with a sufficiently high concentration of heavy metals [4].

- **Agricultural and horticultural materials**

Agricultural practices constitute very important non-point sources of metals which make significant contributions to their total concentrations in soils. The main sources are:

- a) Impurities in fertilizers: Cd, Pb, Zn
- b) Sewage sludge: especially Cd, Ni, Cu, Pb, Zn
- c) Manures from intensive animal production especially poultry: Cu, Zn

Table 1. Ranges of heavy metals concentration of fertilizers used (mg/kg)

Metal	Phosphate fertilizer	Nitrate fertilizer	Farmyard manure	Composted reuse
Cd	0.1-170	0.05-8.5	0.1-0.8	0.01-100
Cu	1-300	-	2-172	13-3580
Ni	7-38	7-34	2.1-30	0.9-270
Pb	7-225	7-27	1.1-27	1.3-2240
Zn	50-1450	1-42	15-566	82-5894

- **Sewage sludge**

The accumulation of heavy metals in soil such as Pb, Cu, Ni and Cd and their uptake by crops and/or their migration to the ground water, represent one of the major hazards to the use of sewage sludge as fertilizers [5].

- **Waste disposal**

The disposal of industrial wastes can lead to soil pollution with heavy metals with various ways. The landfilling of municipal solid wastes can lead to several metals including Cd, Cu, Pb, and Zn being dispersed into soil, groundwater and surface waters in leachates if the landfill is not managed properly. Incineration of wastes can also lead to the emission of metal aerosols [Cd, Pb] if appropriate pollution control equipment is not installed [4].

Essential soil process that acquired of heavy metals bioavailability in soils

Sorption kinetics of Heavy Metals by Soils and their constituents

Many of soil chemical processes are time-dependent. To fully understand the dynamic interactions with soils of metal, pesticides, industrial chemicals, sludge and manures as sources of heavy metals and to predict their fate with time, knowledge of the kinetics of these reactions is important [6].

Adsorption has been one of the hallmarks, and because of environmental concerns, it will continue to be a major research emphasis. Adsorption can be defined as the accumulation of a substance or material at an interface between the solid surface and the bathing solution. It is strictly a two dimensional process and does not include three-dimensional process such as surface precipitation, coprecipitation, and diffusion into the crystal [7].

In addition, It determine the quantity of plant nutrients, metals, pesticides, and other organic chemicals that are retained on soil surfaces and, therefore, is one of the primary processes that affects transport of contaminants in soils. Sorption also affects the electrostatic properties of suspended particles and colloids. The electrostatic properties affect coagulation and settling [8,9].

Unfortunately, the expression adsorption still used rather than sorption, even when they have not definitively ruled out the possibility of precipitation and diffusion phenomena.

The forces involved in adsorption can range from weak, physical, van der Waals Forces [e.g., physisorption] and electrostatic outer-sphere complexes [e.g., ion exchange] to chemical interactions [Fig 1]. Chemical interaction can include inner-sphere Complexation that involves a ligand exchange

mechanism, covalent bonding, hydrophobic bonding, hydrogen bonding, hydrogen bridges, and orientation effects^[10]. Inner-Sphere complexes can be either monodentate or bidentate [Figure 1].

As the amount of a metal cation or anion sorbed on a surface [surface coverage] increases to a higher surface coverage, a surface precipitates can form [fig 1]. When the precipitate consists of chemical species derived from both the aqueous solution and dissolution of the mineral, it is referred to as a coprecipitate. There is a continuum between surface Complexation [adsorption] and surface precipitation^[11].

At low surface coverages surface complexation tends to dominate. As surface coverage increases nucleation occurs and results in the formation of distinct entities or aggregates on the surface. As surface loading increases further, surface precipitation becomes the dominant mechanism.

Diffusion of ions through crystalline solids is extremely slow at 25°C so that the term solid diffusion should generally be interpreted to mean transfer through micropores, faults, or interfaces of the solid rather than through the lattice itself^[12].

To aware about adsorption, it should be several different mechanisms can be involved in the adsorption of metal ions, including cation exchange, specific adsorption, co-precipitation and organic Complexation.

- **Cation exchange**

Most heavy metals exist mainly as cations in the soil solution, and their adsorption therefore depends on the density of negative charges on the surfaces of the soil colloids. Ion exchange refers to the exchange between counter-ions balancing the surface charge on the colloids and the ions in the soil solution. It has the following characteristics: It is reversible, diffusion controlled, stoichiometric and, in the most cases there is some selectivity or preference for one ion over another by the adsorbent^[13].

- **Specific adsorption**

Specific adsorption involves the exchange of heavy metals cations and most anions with surface ligands to form partially covalent bonds with lattice ions. It results in metal ions being adsorbed to a far greater extent than would be expected from the CEC of a soil. Specific adsorption is strongly pH dependent and is related to the hydrolysis of the heavy metal ions. **Brummer, et al.**^[14] give the order for increasing specific adsorption as" Cd [pK = 10.1] < Ni [pK = 9.9] < Zn [pK= 9.0] << Cu [pK = 7.7] < Pb [pK = 7.7]. Heavy metals ions can also diffuse into minerals such as goethite, Mn oxides, illites and some other minerals. The relative rate of diffusion of the metal ions into minerals increases with pH up to a maximum which is equal to the pK value for the situation when $M^{2+} - MOH$ on the mineral surface. Above this pH the $MOH^+ > M^{2+}$ and the relative diffusion rate decreases. For example, the maximum relative diffusion rates for Ni and Zn decreases in the order Ni > Zn > Cd and can be related to their ionic diameters [Ni = 0.69 nm, Zn = 0.74 nm and Cd = 0.97 nm]. Adsorption of metals by goethite therefore comprises three different steps: first, surface adsorption; second, diffusion into goethite particles and third, adsorption and fixation at positions within the mineral particles.

- **Co-precipitation**

Co-precipitation is defined as the simultaneous precipitation of a chemical agent in conjunction with other elements by any mechanism and at any rate. The types of mixed solid commonly formed include clay minerals, hydrous Fe and Mn oxides and calcite in which isomorphous substitution has occurred. In addition to co-precipitation, replacement of Ca^{2+} cations by Cd^{2+} can also occur in the surface layer of calcite when it comes into contact with solutions containing Cd^[15].

- **Insoluble precipitates of heavy metals in soils**

When the physico-chemical conditions and concentrations of appropriate ions are sufficiently high, many metals can form insoluble precipitates which could play a role in controlling their solubility in the soil solution.

Desorption

While most studies in environmental soil chemistry have focused on the adsorption or sorption of ions and molecules on soils, the desorption process is also extremely important. To predict the fate and mobility of contaminants in contaminated soils and to develop sound and cost-effective remediation

strategies, information on desorption is required. For example, if it is found that the contaminants is strongly bound to the soil and little if any desorption occurs, or if the desorption process is extremely slow, movement into groundwater may not be a problem. However, depending on the use of the soil, the "persistence" of the contaminants in the soil may present a problem for crop production. On the other hand, if desorption is effected easily, the contaminant could become mobile and contaminate water supplies. However, its ease of desorption could be an advantage in using remediation techniques such as leaching to decontaminate the soil.

RESIDENCE TIME EFFECTS

Recent studies have demonstrated that desorption of trace metals from soil constituent surfaces is slower than adsorption and that desorption becomes more difficult with time ^[16, 17]. The slow process has been related to mechanisms such as recrystallization of metals into the mineral structure, diffusion into micropores, surface precipitation, change in surface complex, and solid state diffusion into the crystal matrix. Ainsworth et al.^[18] examined the residence time effect of Co^{2+} , Cd^{2+} , and Pb^{2+} adsorption to hydrous ferrous oxide [HFO]. The researchers found that after hours of aging 18% of the total Cd^{2+} and 30 % of the total Co^{2+} could not be desorbed as pH was decreased. Furthermore, the total quantity of both Cd^{2+} and Co^{2+} that could not be desorbed increased with an increase in residence time. In contrast essentially all of the Pb^{2+} was desorbed as pH decreased regardless of residence time ^[18]. Eick et al. ^[16] examined the influence of residence time on desorption of Pb^{2+} from goethite. Rate coefficients for desorption decreased as residence time increased at all sorption densities investigated. Although these results were not statistically significant, it was deemed unlikely that experimental error would consistently produce the observed trends. These researchers suggested that diffusion within micropores may be responsible for the observed trends.

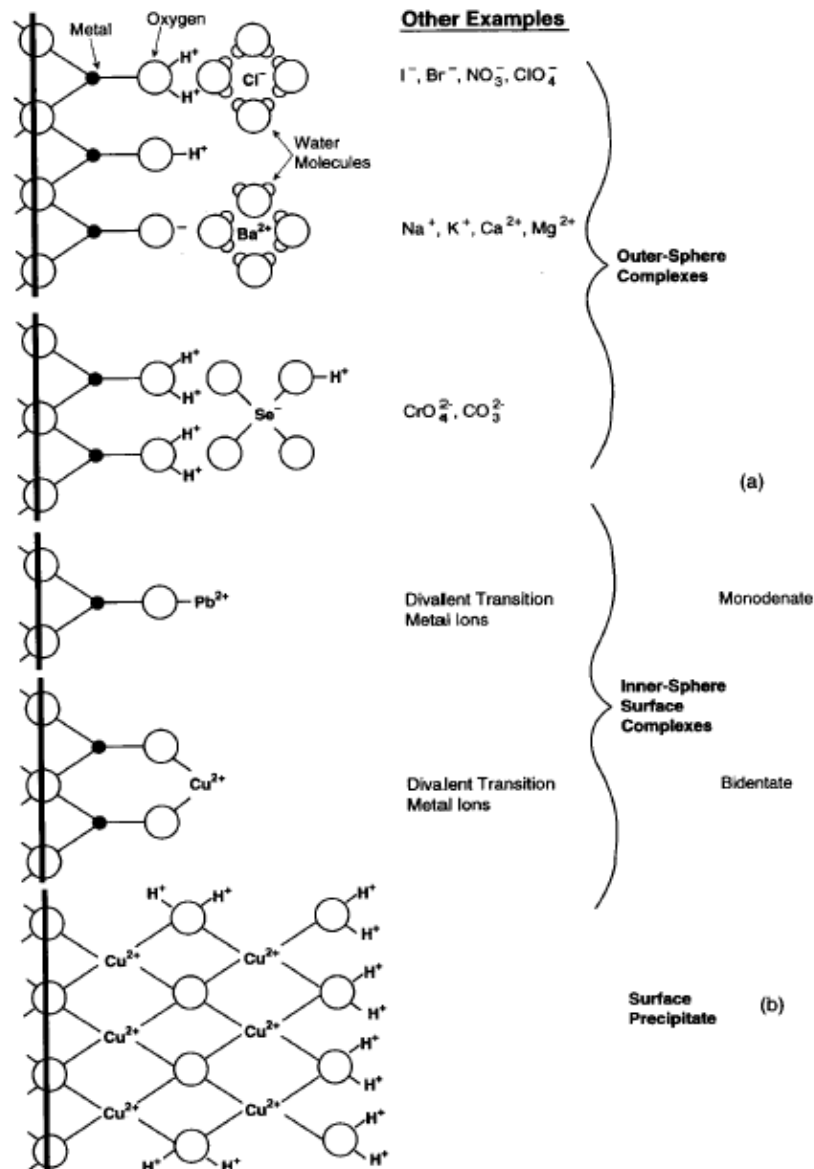


Figure 1. Possible sorption complexes at the mineral/water interface. [a] Surface complexes formed between inorganic ions and hydroxyl groups of an oxide surface [17]; [b] precipitation phenomena [9].

Two important studies, which exhibit residence time effects for adsorption/desorption of Cd^{2+} [18] and Co^{2+} McLaren et al. [19], examined the kinetics of cadmium and cobalt desorption from iron oxides [goethite and ferrihydrite] and manganese oxides [hausmannite and cryptomelane]. In comparing adsorption/desorption between Mn oxides and Fe oxides, Mn oxides sorbed larger amounts of Cd^{2+} and Co^{2+} than Fe oxides.

After one week of adsorption Mn oxides sorbed between 0.190-0.51 $\mu\text{mol m}^{-2}$ of Cd^{2+} while Fe oxides adsorbed between 0.06-0.21 $\mu\text{mol m}^{-2}$. Similar results were seen at one week for Co^{2+} adsorption. After 14 weeks of adsorption time Mn oxides sorbed between 0.20-0.50 $\mu\text{mol m}^{-2}$ of Cd^{2+} while Fe oxides adsorbed between 0.04-0.10 $\mu\text{mol m}^{-2}$. For iron oxides, goethite sorbed greater amounts of Cd^{2+} and Co^{2+} than did ferrihydrite on a surface-area basis [19] examined the kinetics of Cd^{2+} and Co^{2+} desorption from soil clay fractions using the same techniques and models of [21]. In particular they investigated how an increase in sorption period would influence the quantity and rate of desorption. The two clay fractions from Craigieburn and Wakanui regions had similar organic C contents but differed in their dominant mineralogy with the Craigieburn clay containing a higher concentration of short range order and crystalline Fe materials, than the Wakanui clay. No substantial differences were seen in the concentrations of Cd^{2+} and Co^{2+} adsorbed between clay fractions, or at the different sorption

periods used [1wk and 12-16 wk]. This was attributed to the similarity in the organic C content of both clay fractions ^[19].

Kinetic methodologies

Chemical reaction of heavy metals on soil components are rapid, occurring on a millisecond time. For such rapid reaction, one of the most important aspects of any kinetic study is the method employs to measure rate parameters. An array of techniques can be employed to measure the rates of soil chemical reactions. These can broadly classified as methods for slower reactions [>15 s], which include batch and flow techniques, and rapid techniques that can measure reactions on milliseconds and microsecond time scales ^[22, 23].

Batch technique

In the simplest traditional batch technique, an adsorbent is placed in a series of vessels such as centrifuge tubes with a particular volume of adsorptive. The tubes are then mixed by shaking or stirring. At various times a tube is sacrificed for analysis, i.e., the suspension is either centrifuged or filtered to obtain a clear supernatant for analysis. There is a number of disadvantages to traditional batch technique. Often the reaction is complete before a measurement can be made, particularly if centrifugation is necessary, and the solid: solution ratio may be related as the experiment proceeds. Too much mixing may cause abrasion of the adsorbent, altering the surface area, while too little mixing may enhance mass transfer and transport processes. Another major problem with all batch techniques, unless a resin material is used, is that products are not removed.

Flow or miscible displacement Techniques

These techniques have been used to lesser extent to investigate the kinetics of reactions in soils and clay minerals ^[24]. Flow technique are increasingly being recommended over batch method to study sorption/desorption phenomenon on colloids, particularly if one wishes to relate kinetic studies to solute transport under field conditions.

An Electrical Stirred Flow Unit [ESFU] was designed to be use in kinetic studied ^[29]. The kinetic part of this apparatus was modified to take specific volume from the kinetic part at specific time of stirring containing the precise concentration of the studied ion. This volume could be changed using valves and solenoid valve. Moreover, there is a possibility to change the time of having the kinetic solution by the timer. The diagram of the apparatus presented in Figure 1. ^[22].

Relaxation method

Many soil chemical reactions are very rapid, occurring in millisecond and microsecond time scale. These include metal and organic sorption-desorption reactions, ion exchange process, and ion association reaction. Chemical relaxation methods must be used to measure very rapid reaction. These techniques are fully outline and described in ^[9].

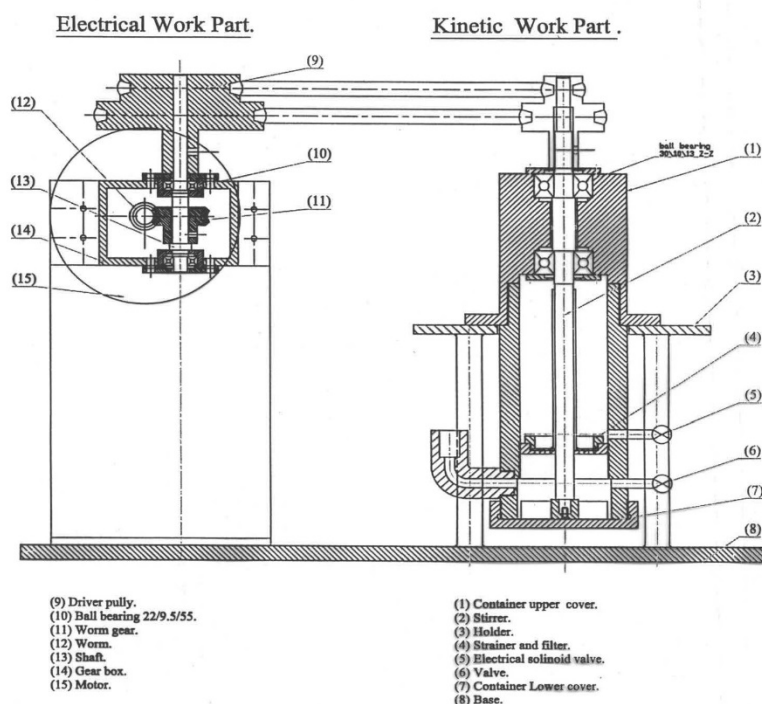


Figure 2. Electrical stirred flow unit used in kinetic study

KINETICS OF Heavy Metals ADSORPTION/DESORPTION REACTIONS

Many equations have been used for the analysis of adsorption/desorption kinetics on soil surfaces. Some of the most commonly used equations for the analysis of adsorption/desorption kinetics are first-order, second order, and zero order reactions [22]. The chemical kinetics of adsorption/desorption reactions on soil surfaces are concerned with three processes: [1] the rates of chemical reactions, [2] how the rate responds to changes in conditions or presence of a catalyst, and [3] the mechanism of the reaction [23]. The first stage in investigating the rate and mechanism of a reaction is to determine the overall stoichiometry of the reaction, and to identify any side reactions with time after the reaction are initiated, which is done experimentally.

• Some of kinetic models describing adsorption/desorption reactions

A. Order models

First order reactions have been used extensively to model both adsorption and desorption of trace metals from soil and soil constituent surfaces [22]. The first order reaction, can be written as

$$-\ln [A] + \ln [A_0] = kt \quad (\text{Equation 1})$$

where $[A_0]$ is the concentration of species A at time zero, k being the first order rate constant, t being time, and $[A]$ as the concentration of species A at a given time. While first-order models have been used widely to describe the kinetics of chemical reactions, a number of other simple kinetic models also have been employed like Second-order equations, Zero-order equations and Fractional order equations.

B. Elovich equation

The Elovich equation was originally developed to describe the kinetics of heterogeneous chemisorption of gases on solid surfaces. In soil chemistry, the Elovich equation had been used to

describe the kinetics of sorption and desorption of various inorganic materials on soils [24]. It can be expressed as:

$$q = 1/\beta \ln \alpha\beta + 1/\beta \ln t \quad (\text{Equation 2})$$

where:

q = the amount of sorbed /unit mass

α = a constant related to the initial rate of K adsorbed in $\text{mg K kg}^{-1}\text{min}^{-1}$

β = a constant in $\text{mg kg}^{-1}\text{soil}$

t = time

C. Parabolic diffusion model

From [22]:

$$F_d = kt^{1/2} \quad (\text{Equation 3})$$

where F_d is the fraction of metal desorbed [$1 - \text{Pbt} / \text{Pb}_0$], $t^{1/2}$ is the square root of time in seconds, and k is the diffusion rate coefficient [s^{-1}]. If the reaction is diffusion controlled then a graph of F_d versus $t^{1/2}$ should be linear with a slope of k . [17] used the parabolic diffusion equation to describe desorption of Pb^{2+} from goethite at different surface loading with a filter flow method. Eick et al. [16] found at a sorbent concentration of 2.5 g/L the proportion of Pb^{2+} desorbed varied inversely with surface coverage. The parabolic diffusion equation best described the desorption of Pb^{2+} from goethite at all surface coverage investigated in contrast to a shell progressive particle diffusion equation, and single and two first order equations. This suggested that the reaction was transport or diffusion controlled [17]. Other models used to describe adsorption/desorption reactions on soil constituent surfaces include a two-constant rate equation [26].

Major factors effects kinetic reactions and uptake of some heavy metals in soils

In natural attenuation processes heavy metal in soils undergoes to both forward [adsorption] and backward [desorption] reactions, these processes occur as mechanisms of pollutant accumulation and pollutant dilution in the soil system. In addition, Inorganic chemicals are passively taken up by plants from soil water, with the additional possibility of active uptake in the case of required nutrients, such as copper and zinc.

There are different factors effects the heavy metals bioavailability in soil; this review article will represent some of these major factors.

Soil pH

Although various soil parameters can effects the availability of heavy metals in soils, soil pH becomes the first factors effecting on the bioavailability of heavy metals in soils [27]. Soil pH is the major factor determining the availability of Cd in soils because it affects all adsorption mechanisms and the speciation of metals in the soil solution. Cadmium uptake is inversely related to soil pH. Lead sorption in clay usually increases with increasing pH, decreasing soil/solution ratio, and decreasing ionic strength [16]. The dominant mechanisms of Pb sorption in soils vary with pH: cation exchange at low pH [$\sim 2-4$], precipitation at high pH [> 6], and combination of both at intermediate pH [$\sim 4-6$]. Complexation and solid-state diffusion may also play important roles in Pb sorption. At intermediate pH [$\sim 4-6$], Pb sorption in clay minerals is very sensitive to pH. The difference between the Pb sorption isotherm at uncontrolled pH with an average value and that controlled at the specific pH is poorly documented and deserves a careful study. In addition, the associated anions on Pb sorption need to be investigated because of the complexity of Pb hydrolysis and complexation [16]. **Selim and Sparks** [27] reported that the X ray Absorption fine Structure data indicated that the mechanism of Pb [II] sorption to the SiO_2 surface was pH-dependent. At $\text{pH} < 4.5$, a mononuclear inner-sphere Pb sorption complex with ionic character dominated the Pb surface speciation. Between $\text{pH} 4.5$ and $\text{pH} 5.6$, sorption increasingly occurred via the formation of surface-attached covalent polynuclear Pb species, possibly Pb-Pb dimers, and these were the dominant Pb complexes at $\text{pH} 6.3$.

Soil Type

Clay minerals are major soil components with large surface areas, cation exchange capacities, and various binding sites. Numerous studies have been reported on the sorption of Pb by clay minerals [17, 29] and a few spectroscopic studies involving Pb sorption in clays have been reported [11]. These works indicated that Cd content in plants is inversely proportional to increasing of sorption capacity factors represented by the CEC of the soils. Zaghoul and Abou Seeda, [23], studied the kinetics of Lead release characteristics in some Egyptian soils using different kinetic models, they reported that in alluvial soil, Pb undergoes to several factors reducing its mobility in soil system. Pb was found to be positively correlated with organic carbon and clay content; these factors are important for retention of Pb in surface soil colloids. These parameters differ from one soil to the other being higher in sandy soil [*Typic psammets*] and the least in alluvial soil [*Typic torrerts*], while in calcareous soil [*Typic calcids*] was in between. The decreasing order of the capacity factors namely; b^{\setminus} , α , b , and k for the above named equations respectively, take the increasing order:

Alluvial > calcareous > sandy soils.

Organic matter

Soil organic matter plays a significant role in affecting the availability of heavy metals in soils. Selim and Sparks [28] reported that high organic matter content in soils with other soil factors related to this important factor like CEC, led to tend to favor the adsorption of heavy metals. In natural to alkaline conditions favor the precipitation of new solid phases. In contrast the data of Zaghoul [30] showed that the presence of organic matter in soil led to act as remediation material and favor to another kinds of materials used to remediate the Pb polluted soils. Alloway [15] reported that the presence of organic matter in heavy metals contaminated soils absorbs heavy metals by forming complexes.

Effects of other elements in soils

Uptake of Cd by soybeans related to the sorptive capacity of soil. Lead has been widely observed to increase cadmium uptake; for example, the addition of both lead and cadmium increased the foliage content of each contaminant in American sycamore over the uptake values observed with a single metal added. Lead has also increased the uptake of cadmium in rye and fescue, and in corn shoots. However, only low-level and inconsistent synergistic and antagonistic effects among cadmium, lead and other heavy metals in uptake by little bluestem and black-eyed Susan plant species. A better regression may have been obtained in this study if soil lead were included as a variable [30]. Relative excesses of Cu, Ni, Mn and P can reduce the uptake of Cd by plants. The situation with Zn is less clear and appears to depend on the Cd content of the soil. Zn less been found to have an antagonistic effect of Cd uptake in soils with low Cd concentrations [32], and either a synergistic or a nil effect with relatively high Cd contents [15].

Metal concentrations in soils

The effect of concentrations of heavy metals in soils was reported by several researchers. Alloway [15] reported that there are significant multiple regression models between nickel in wheat and soybean and soil metal concentrations. Because nickel is hyperaccumulated by some plants in remediation studies, it was expected that the distribution of uptake factors would be bimodal and that regressions would be different at high nickel concentrations from those at lower concentrations in soil. This expected effect was not observed, perhaps because hyperaccumulating plants are tested only in soils with very high nickel levels.

Plant species

As with most inorganic chemicals, the uptake of zinc by plants has been observed to vary with plant species; for example, some plants hyperaccumulated zinc. In addition, Plant species and varieties differ widely in their ability to absorb, accumulate and tolerate heavy metals, [15] showed that lettuce, spinach, celery and cabbage tended to accumulate relatively high concentration of Cd, while potato tubers, maize and French bean accumulate only small amount of Cd.

Table 2. Relative metal accumulations (Cd and Pb in edible portions; Cu, Ni and Zn in leaves). Based on data from ^[15]

Metal	High accumulations	Low accumulation
Cd	Lettuce, Spanish, celery, cabbage	Potato, maize, French bean
Pb	Kale, ryegrass, celery	Potato, maize
Cu	Sugar beet, certain barley cvs	Leek, cabbage, onion
Ni	Sugar beet, ryegrass, mangold, turnip	Maize, leek, barley, onion
Zn	Sugar beet, mangold, spinach	Onion, potato, leek, tomato

SUMMARY

During the last decade, observation of high concentrations levels of trace elements in air, water, soil and plants have been recorded. In general, inorganic contaminants enter soil as a result of human activities. The heavy metals arsenic, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium, and zinc are the most hazardous of these substances. Although many of these heavy metals are needed in small quantities by plants and animals, they may enter soils in great enough quantities to pose risks to the health of plants, animals, and humans. Heavy metals are persistent, and their negative effects in soil are long-lasting. For this reason, their levels in soils must be controlled.

A voluminous amount of research has examined the adsorption of trace metal cations on soils and soil constituent surfaces. However, less research has examined the rate of these reactions in soils. It is important to realize the occurrence and behaviour of heavy metals in the soil since it is a sink for metal contaminants.

This review article aims to focus on the toxicological effects of some heavy metals occurred in soils from different sources in the environment. In the beginning, the review article was exposed to the major sources of pollution by heavy metals in soils like fertilizers as an important source of heavy metals in soil and the contribution of different fertilizers to add heavy metals in soils.

Also, the review was exposed to the hazardous of heavy metals to some plant species through its reactions in soils, i.e. adsorption, desorption, exchange and precipitation and introduced the recent methodologies applied in the kinetics studies of heavy metals reaction in soils and the models used to describe the kinetic data.

The data of kinetics of heavy metals sorption and release from different soils and the most effective factors affect the heavy metals bioavailability such as pH, type of soil, the effect of other metals in soils and different soil constituents that influenced the rate of heavy metals released from the soils was also reported. The information of this review article will give a valuable background to elevate the injury of these kind of pollutant.

REFERENCES

- [1] Saber, M; Hobballa, E.; Soad El-Ashery and Zaghoul, A. M. (2012) Decontamination of Potential Toxic Elements in Sewaged Soils by inorganic Amendments. *J. Agricultural Sci. Technology A* 2(11):1232-1244.
- [2] Zaghoul (2013) Evaluation of natural amendments in minimizing the hazards of potential toxic elements in contaminated soils technique. *Journal of Applied Sciences Research*, 9(11): 5930-5940, 2013.
- [3] Alloway, B. J. (1995) *Heavy Metals in Soils* (2nd Edition). Blackie Academic & Professional, London.
- [4] Yong, R. N (2001). *Geoenvironmental Engineering Contaminated soils, pollutant fate, and Mitigation*. CRC press, New York.
- [5] Figliolia A., MANGIONE D., LEITA L., BRAGATO G., DE NOBILI M., 1996. *Proceedings of the Third International Conference on the Biogeochemistry of Trace Elements*. Paris..
- [6] Sparks, D.L. 1999. Kinetics and mechanisms of chemical reactions at the soil mineral/water interface. p. 135-192 *In* D.L. Sparks (ed). *Soil Physical Chemistry*, 2nd edition. CRC Press, Boca Raton, FL.
- [7] Sparks, D.L., A.M. Scheidegger, D.G. Strawn, and K.G. Scheckel. 1999. Kinetics and mechanisms of metal sorption at the mineral-water interface. p. 108-135. *In* D.L. Sparks and T.J. Grundl (eds.) *Mineral-Water Interfacial Reactions*. ACS Symp. Series 715, Am. Chem. Soc., Washington, DC.

- [8] Stumm, W. (1996). Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters. John Wiley & sons, New York.
- [9] Sparks, D.L., Editor. 1998. Soil physical chemistry, 2nd edition, CRC Press, Boca Raton, FL
- [10] Sparks, D.L. 1995. Kinetics of metal sorption reactions. p. 35-58. In H.E. Allen, C.P. Huang, G.W. Bailey, and A.R. Bowers (eds.). Metal speciation and contamination of soil. Lewis Publishers, Chelsea, Michigan.
- [11] Strawn, D. G. and D. L. Sparks. 2000. Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in the soil. *Soil Sci. Soc. Am. J.* 64:144-156.
- [12] McBride, M. (1994) Environmental chemistry of soils. Oxford Univ. Press, New York. NY.
- [13] Ogwada, R. A. and D. L. Sparks. (1986) Kinetic of ion exchange on clay minerals and soil. *Soil Sci. Soc. Am. J.* 50:1158-1162.
- [14] Brummer, G.W., J. Gerth, K and G. Tiller. 1988. Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. I. Adsorption and diffusion of metals. *Journal of Soil Sci.* 39:37-52.
- [15] Alloway, B. J. (1995) Heavy Metals in Soils (2nd Edition). Blackie Academic & Professional, London.
- [16] Eick, M. J., J.D. Peak, P. V. Brady, and John D. Pesek. 1999. Kinetics of lead adsorption/desorption on goethite: residence time effect. *Soil Sci.* 164: 28-39.
- [17] Hayes K. F. (1987) Equilibrium, spectroscopic, and kinetic studies of ion adsorption at the oxide-aqueous interface. Ph.D. thesis. Stanford University.
- [18] McLaughlin, M.J. and Singh, B.R. (1999) Cadmium in soils and plants. Kluwer Academic Publishers. Dordrecht/ Boston/ London.
- [19] McLaren, R.G., C.A. Backes, A.W. Rate, and R. S. Swift. 1998. Cadmium and cobalt desorption kinetics from soil clays. Effect of sorption period. *Soil Sci. Soc. Am. J.* 62:332-337.
- [20] Ainsworth, C. C., J. L. Pilon, P. L. Gassman, and W. G. Van der Sluys (1994) Cobalt, cadmium and lead sorption to hydrous iron oxide: Residence time effect. *Soil Sci. Soc. Am. J.* 58, pp. 1615-1623.
- [21] Backes, C. A., R. G. McLaren, A. W. Rate, and R. S. Swift. (1995) Kinetics of cadmium and cobalt desorption from Iron and manganese oxides. *Soil Sci. Soc. Am. J.* , 59, pp. 778-785.
- [22] Sparks, D. L. (1989) Kinetics of soil chemical process. Academic press, San Diego.
- Zaghloul, A.M. (2002) Kinetics of potassium adsorption in some soils of Egypt using Electrical Stirred Flow unit (ESFU). *Egyptian J. Soil Sci.*, 42, 463 – 471
- [23] Zaghloul, A.M and M. T. Abou-Seeda (2003). Lead release characteristics in some Egyptian soils in relation to their properties. *Egypt. J. Appl. Sci.*, Vol. 18 (11) 408-422.
- [24] Atkins, Peter (1996). The Elements of Physical Chemistry. W.H. Freeman and Company. New York, New York.
- [25] Sparks, D.L. 1999. Kinetics and mechanisms of chemical reactions at the soil mineral/water interface. p. 135-192 In D.L. Sparks (ed). *Soil Physical Chemistry*, 2nd edition. CRC Press, Boca Raton, FL.
- [26] Kuo, S., and Lotse , E. G. (1973). Kinetics of phosphate adsorption and desorption by hematite and gibbsite . *Soil Sci.* ,116: 400 - 406.
- [27] Strawn, D.G., A.M. Scheidegger, and D.L. Sparks. 1998. Kinetics and mechanisms of Pb(II) sorption and desorption at the aluminum oxide-water interface. *Environ. Sci. Technol.* 32:2596-2601.
- [28] Selim, H. M. and D. L. Sparks. 2001. Editors. Heavy Metals Release in Soils. Lewis Publishers, Boca Raton.
- [29] Bereket, G., A. Z. Aroguz, and M.Z. Ozel. 1997. Removal of Pb(II), Cd(II), Cu(II), and Zn(II) from aqueous solutions by adsorption on bentonite. *J. Colloid Interface Sci.* 187: 338-343.
- [30] Zaghloul, A.M. {principle investigator}(2000) Remediation of Heavy Metals in Some Egyptian Contaminated Soils through the Kinetic Studies. Project No.2/1/1/1/4/b. National Research Center (NRC), Dokki, Cairo, Egypt.
- [31] Kabata Penias, A. and Pendaris, H. (1992) Trace Elements in Soils and Plants. (2nd addition)CRC press, Boca Raton, Fla. Davis, B. E., Applied soil Trace Elements. Wiley, New York.
- [32] Zaghloul, A. M. and S. M. El-Ashry (2003) Zink for remediation of cadmium contaminated soils. *Egypt. J. of Appl. Sci.* Vol. 18 (11) 398-407.