Environ Geol (2006) 51: 333–340
DOI 10.1007/s00254-006-0329-7

ORIGINAL ARTICLE

Ali Gürel

Adsorption characteristics of heavy metals in soil zones developed on spilite

Received: 18 February 2006
Accepted: 4 May 2006

A. Gürel
Department of Geology Engineering,
Niğde University, Niğde, Turkey
E-mail: agurel_1999@yahoo.com

Abstract Various soil zones such as Bw, C1, and C3 are developed on spilite. Montmorillonite, vermiculite and chlorite is moderately occurred in the C1 and C3 soil zones, in contrast montmorillonite and vermiculite are absent in Bw soils whereas illite and sesquioxide are relatively increased. The high cation exchange capacity (CEC) of montmorillonite and vermiculte and moderate CEC of chlorite and illite resulted in the high adsorption of heavy metals. The adsorption of the heavy metals on spilite soil zones was studied at different concentrations and pH levels. Heavy metals like lead, cadmium, and copper were selected for adsorption studies considering their contribution as toxic metals in the environment. The initial solute concentrations ranged from 7.0×10^{-3} to 1.0×10^{2} mg/L. The sorption behavior of Cd^{2+}, Pb^{2+}, and Cu^{2+} on soil zones of spilite was investigated using the batch equilibrium technique at 25°C. The characteristics of the adsorption process were investigated using Scatchard plot analysis (q/C vs. q) by the batch equilibrium technique at 25°C. In the adsorption of heavy metals, deviation from linearity in the plot of q/C versus q was observed, indicating the presence of multi-model interaction and non-Langmuirean behavior. When the Scatchard plot showed a deviation from linearity, greater emphasis was placed on the analysis of the adsorption data in terms of the Freundlich model, in order to construct the adsorption isotherms of the metal(s) at particular concentration(s) in solutions. The adsorption behavior of these metal ions on spilite soil zones is expressed by the Freundlich isotherms. Adsorption constants and correlation coefficients for the Cd, Pb, and Cu on spilite soil zones were calculated from Freundlich plots.

Keywords Heavy metals · Adsorption · Clay minerals · Spilite · Scatchard analysis · Freundlich isotherm

Introduction

Heavy metal contamination of groundwater is a major environmental concern. The contamination is primarily due to improperly disposed industrial wastes. Environmental constraints have forced the metal plating industry to reduce their emissions to water systems, otherwise mass usage of metals could cause severe environmental problems. Therefore, recovery of heavy metals from wastewaters and industrial wastes has become a very important environmental issue. These metals, which find many useful applications in our life, are very harmful if they are discharged into natural water resources. The prevalence of contamination from both natural and anthropogenic sources has increased concern about the health effects of chronic low-level exposures. Heavy metals like cadmium; lead and copper were selected for adsorption studies considering their contribution as toxic metals in the environment.

There are many processes, such as solvent extraction, ion exchange, adsorption and complexing that can be used for the removal of metals from wastewaters. Solvent extraction, ion exchange and activated carbon adsorption are the most commonly used processes for this purpose. These processes can be selective but solvent extraction produces liquid organic secondary waste, which may cause problems. The value-adding step in the process industry is often found in the separation and purification of products. Adsorption process has an important share in this step. There are many materials, both from nature and from synthesis, that have adsorption capacity. The most important commercial adsorbents are activated carbon, zeolites, activated alumina and silica gel. Wastewater containing relatively low concentrations of heavy metals is usually treated with ion exchange resins to remove heavy metals but this involves expensive resins. Owing to their cation exchange properties, ion-exchange resins, activated carbon, etc., can be used to remove heavy metals from wastewater but they are often very expensive to be utilized on a large scale (Suraj et al. 1998; Maliou et al. 1992; Mazidji et al. 1992). Furthermore, because of regeneration costs of activated carbon and ion exchange resins, researchers are encouraged to look for other types of adsorbents. Clay suspensions are powerful adsorbents and are much cheaper than common adsorbents like activated carbon to remove heavy metals from industrial wastewaters. So far, the adsorption and interaction of inorganic and organic pollutants with clay components has been widely investigated (Suraj et al. 1998; Lawrence et al. 1998; Ghosh and Bhattacharyya 2002). Bentonite clays were used for the removal of polyethyleneimine (Öztekin et al. 2002), pesticide (Bojemueller et al. 2001) and sodium dodecylbenzene sulfonate (Rodriguez-Sarmiento et al. 2001); kaolinite was used for the adsorption of cadmium, copper (Suraj et al. 1998) and Cd–cysteine complexes (Benincasa et al. 2002) from aqueous solution and methylene blue from a local deposit. The clay minerals in soil can act as a natural scavenger in removing color from the contaminated water (Ghosh and Bhattacharyya 2002). However, the studies on heavy metals and spilite and its soil zone interaction are scarcer.

In the present study, the adsorption of heavy metals on spilite and its soil zones, which are relatively widely distributed in the environment as well as their adsorption models, have been investigated, and the adsorption parameters of the clays are reported. In an attempt to investigate the mechanism of this process, Scathard analyses (Scatchard 1949) were used to determine the type of binding (specific or non-specific). The basic objective of the study is to contribute to the understanding and modeling of the equilibrium of adsorption processes.

Geology and soil development

Geology

Samples were obtained from Harz forest drainage basin of Söse dam of Germany, which covers an area of about 50 km^2. Country rocks of this area were slightly metamorphosed and Devonian-Carboniferous in age. Major lithologies were progressing upward, as follows:

Alluvium Consisted of loose gravel, silt, and clay minerals.

Sedimentary sequence Consisted of alternating layers of greywacke, clayey schist, and layered chert. These were deposited during upper Devonian and Carboniferous and were composed of coarse-grained, brown colored greywacke, clayey schist, and reddish chert layers.

Spilite Composed of albite, chlorite, calcite, augite, quartz, and hematite and was about 500 m thick which occurred in gray to light gray colors. It is considered to be middle Devonian in age.

Clayey schists Represents the oldest rocks of the study area that are lower Devonian in age. They may reach up to 200 m in thickness and have prevalent red colors. These are composed mainly of chlorite, quartz, illite, microcline, albite, and hematite. The red coloration of the clayey schists is due to hematite pigment as stated by Eren and Kadir (1999).

Description of soil profile

For this investigation, soil profile developed on spilitic country rocks in Harz forest drainage basin of Söse Dam (Germany) has been selected for sampling.

These soils can be considered as brown podzols (Soil Survey Staff, 1962, zonal soils, conifer forest) developed under climatic regime of 1,300 mm annual rainfall of which is 550 mm annual evaporation and 750 mm percolation and runoff (Matschullat et al. 1990; Gürel 1991; Matschullat et al. 1994).

Eight soil zones have been distinguished on spilite in Harz forest drainage basin of Söse Dam (Germany), the names of the soil zones have been adapted from Soil Survey Staff (1998, Fig. 1).

Zones including O, E, EB, and Bw (up to 85 cm) were developed on the highly altered parent rock. Zones BC, C1, C2, and C3 (up to 220 cm) were highly altered in which clays washed out from the overlying zones were redeposited.

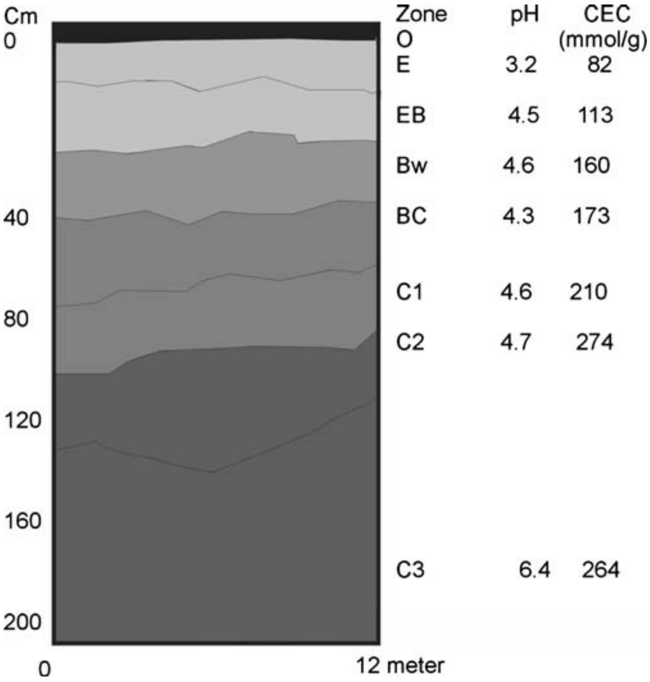

Fig. 1 Spilitic rock section and soil profile developed on it occurring in Kehrzug district of Harz forests, Germany

Organic matter having the thickness of 10–15 cm lies over mineral matter (O, organic zone). E and EB soil zones have been developed under this organic zone. Due to strong wash of the basic ions the colors of the soils in these zones have grayed. Bw and BC zones developed on spilite are rather thick and they locally reach up to 85 cm in depth. The colors of these zones range from brown to light brown (Munsell color, 7.5 YR 4/4 ve 10 YR 5/3). E, EB, Bw, and BC zones are thicker than 85 cm and they include fine components of grain sizes up to 2 mm, but the conglomerate are also present sporadically. C1 soil zone is formed of strongly weathered spilitic blocks with which large amount of fine grain soil of brown color (Munsell color, 7.5 YR 5/2) occurs. The zone C1 sharply passes into the zone C2, containing coarse-grained spilite conglomerates, C2 zone takes place under the C1 prevalent dark brown color. Intergranular spaces are filled with fine-grained material washed out from the overlying zones. C3 soil zone starts from 180 cm and includes partly weathered spilite. Volume of fine-grained material is significant low in comparison with overlying zones.

Experimental

Geological and mineralogical measurements

Four samples, representative of the partly altered spilite and various soil zones developed on spilite (partly altered spilite and Bw, C1, C3 soil zones), were analyzed with respect to their mineralogical, chemical and adsorption characteristics.

The mineralogical composition of these soil samples was determined by using X-ray powder diffraction (Philips PW 1010/98 diffractometer with graphite-filtered Cu Kα radiation). Semi-quantitative of relative rock-forming mineral was obtained by using the external standard method of Brindley (1980), whereas the relative abundance of clay mineral fractions was determined using their basal reflections and the mineral intensity factors of Moore and Reynolds (1989). The infrared spectra of soil samples mixed with KBr were recorded on Perkin Elmer 1725X spectrophotometer, operating in the range 4,000–400 cm^{-1}.

Chemical compositions of major and trace elements of the soil zones were determined by X-ray fluorescence (XRF) using a Philips PW 1400 spectrometer. Mineralogical and geochemical features of spilite and soils developed on spilite are given in Tables 1 and 2.

pH measurements: 10 g of soil samples representing each zone of the soil profiles was added to 25 ml of 0.01 M $CaCl_2$ prepare suspensions on which pH measurement were carried out by a conventional pH meter.

Determination of cation exchange capacity (CEC): 1 N NH_4Cl peculation liquid was used to acquire amount in μmol/100 g as described by Mewis et al (1984) to determine the CECs.

Adsorption experiments

In all of the soil zones used in this work, sample fraction (< 2 mm) was separated by sieving. The adsorption experiments were carried out using the batch equilibrium technique at different pH values. Constant pH was maintained by the addition of small amounts of dilute NaOH or HNO_3. For each experiment, 5 g of soil zones was weighed and placed in plastic centrifugal tube then 15 mL of metal ion solution (7.0×10^{-3}–1.0×10^{2} mg/L) was added. The tubes were shaken overnight at 25°C and centrifuged at 10,000 rpm for 30 min. The metal concentration in the supernatant was determined by using Hitachi model 3210 atomic absorption spectrophotometer. To study the effects of pH on the adsorption of metal ions, the initial pH values were adjusted and tests were carried out in a water bath at 25°C.

Results and discussion

Mineralogy and geochemistry

Spilitic parent rocks are composed of mainly feldspar associated with moderate amount of chlorite and accessory quartz and augite (Table 1). In contrast feldspar and

Table 1 Mineral species and their abundances in spilite and soil profile developed on spilite

Minerals	Cation exchange capacity (mval/100 g)[a]	Soil zones			
		Bw	C1	C3	Spilite
Quartz	10–30 (in solution)	+ + + +	+ +	+	Acc
Feldspar	–	+ +	+ +	+ +	+ + + + +
Illite[b]	10–40	+ + +	+ +	+ +	–
Vermiculite[b]	10–40	Acc	+	+	–
Montmorillonite[c]	80–120	Acc	+ +	+ +	–
Chlorite[b]	20–50	+	+ +	+ +	+ + +
Kaolinite	3–15	Acc	+	+	–
Calcite	–	–	–	–	+
Augite	–	–	–	–	+
Others[b](Sesquioxides)	10–25	+	Acc	Acc	Acc

Location: Spilite, Harz forests, Germany; XRD and IR–spectrometry measurements, + relative abundance of mineral, *acc* accessory
[a]Patchineelam (1975), [b]minerals with high adsorption

chlorite decreased significantly to moderately in the soil zones. Source rock minerals excluding quartz were either decreased in abundance or completely depleted in the soil due to natural and anthropogenic acid generation. Calcite and augite contents of the parent rock were small amount to accessory, respectively. Both of these minerals are absent in the soil zones. Table 1 is representing the Patchineelam (1975) cation exchange capacity (mval/100 g) of some of clay and sequioxide minerals. It is found that montmorillonite and vermiculite have the highest CEC. Montmorillonite, vermiculite, chlorite, and illite occurred moderately, while kaolinite poorly in the C1 and C3 soil zones, and these minerals decreased upward and appeared as accessory in Bw zone soils, whereas illite and sesquioxide are relatively increased in the upper acidic soil zones similar to that is reported by Tarah (1989).

Decreases of chlorite of the host rock upward of the soil zone and partly increase of illite and montmorillonite indicate that illite and montmorillonite are pedogenically formed from chlorite. Presence of Al-hydroxide in highly acidic soil zones resulted in dissolution and degradation of primary chlorite (chlorite of the host rock) to montmorillonite (Shröder and Dümmler 1962; Tarrah 1989; Gürel 1991). In addition, pedogenic processes during the Quaternary period under appropriate paleoclimatical conditions resulted in alteration of basic units such as spilite and liberation of ions causing precipitation of montmorillonite in basic environmental condition. Association of calcite with smectite and vermiculite indicate that these minerals are precipitated in an alkaline environmental condition, which is different from the present lower pH condition (Table 1).

Major element oxide contents of soil samples collected from spilite and soil profile are shown in Table 2. SiO_2, Na_2O, MgO, CaO, and P_2O_5 contents are decreased in soil comparing to source rock contents, Fe_2O_3 is constant, whereas, Al_2O_3, and LOI contents relatively increased due to increase of alteration products such as montmorillonite, illite, vermiculite and kaolinite relative to partly altered spilite.

Table 2 Major element contents of spilite and soils developed on spilite (in wt %)

Major element oxide	Bw	C1	C3	Spilite
SiO_2	46.9	48.5	46.9	51.3
Al_2O_3	19.8	20.4	–	13.4
Fe_2O_3	11.3	10.4	12.5	11.9
MgO	4.5	2.6	–	3.0
CaO	0.3	1.7	–	5.0
Na_2O	0.3	1.7	–	2.2
K_2O	4.9	5.6	–	6.0
TiO_2	2.0	1.9	2.7	1.9
P_2O_5	0.3	0.3	–	0.4
MnO	0.4	0.3	–	0.1
LOI	8.5	6.6	–	5.0
C	0.3	0.001	–	0.01
Total	99.2	100.0	–	100.2

Introduction to adsoption isotherms

The adsorbed amounts of heavy metals on soil zones have been determined as a function of the metal concentration in the supernatant (Cs) at the equilibrium state and controlled temperature (25°C). The concentration of metals in the solid phase was calculated as:

$$q = (C_0 - C)V/W \tag{1}$$

where C_0 and C denote the initial and equilibrium concentrations of the heavy metals in the aqueous phase, V is the volume of the aqueous phase and W is the dry weight of the soil zones.

Adsorption isotherms

The metal adsorption data was analyzed using the method developed by Scatchard. The Scatchard linearisation [$q/C_e = f\ (q)$] has been used to interpret the isotherms and the results are presented in Fig. 2, which shows the adsorption characteristics assessed from the Scatchard plot. In the adsorption of heavy metals, deviation from linearity in the plot of q/C–q was observed, indicating the presence of multi-model interaction and non-Langmuirean behavior. Particularly in the adsorption on C1, divergence from the Scatchard plot was evident, consistent with the participation of secondary equilibrium effects in the adsorption process. The presence of more than one inflection point on a plot based on Scatchard analysis usually indicates the presence of more than one type of binding site (Uçan and Ayar 2002; Ayar et al. 2003). Scatchard analysis of the results from the experiments in this study indicated the possibility of more than one type of binding site for all the heavy metal adsorption. When the Scatchard plot showed a deviation from linearity, greater emphasis was placed on the analysis of the adsorption data in terms of the Freundlich model.

The Freundlich exponent n between 0.96 and 1.00 indicates favorable adsorption for which $0 < n < 1$. The Freundlich constant k is appreciable for all the soil zones in general agreement with strong adsorption. The C1 soil zone had the largest value of k followed by the C3 soil zone for Pb^{2+} at pH 3.5. The C1 soil zone had the lowest k-value for Cd^{2+} at pH 3.5. As shown in Figs. 3, 4 and 5 the adsorption isotherms of uptake metals could be expressed as Freundlich isotherms. Metal adsorption constants and correlation coefficients for the Cd^{2+}, Pb^{2+}, and Cu^{2+} on the soil zones were calculated from Freundlich plots and are given in Table 3.

The effect of pH on heavy metals uptake by the spilite soil zones is displayed in Figs. 3, 4 and 5. A small increase in cadmium uptake on soil zones was noticed with an increase in pH. A significant increase in lead uptake on soil zones was noticed as the pH decreased to 3.5 and increased to 6. And the lead adsorption showed a minimum between pH 3.5 and pH 6.0. Probably this pH range includes the value of point of zero charge for the spilite surface. However, the tendency for increasing adsorption at pH values below 3.5 is difficult to explain because of the electrical nature of the spilite soil zones surface, which is still somewhat uncertain, but evidence suggests an electrostatic interaction between clay surface and the high positive charged metal ions took place at the low pH values. The effect of pH on copper uptake by the spilite is

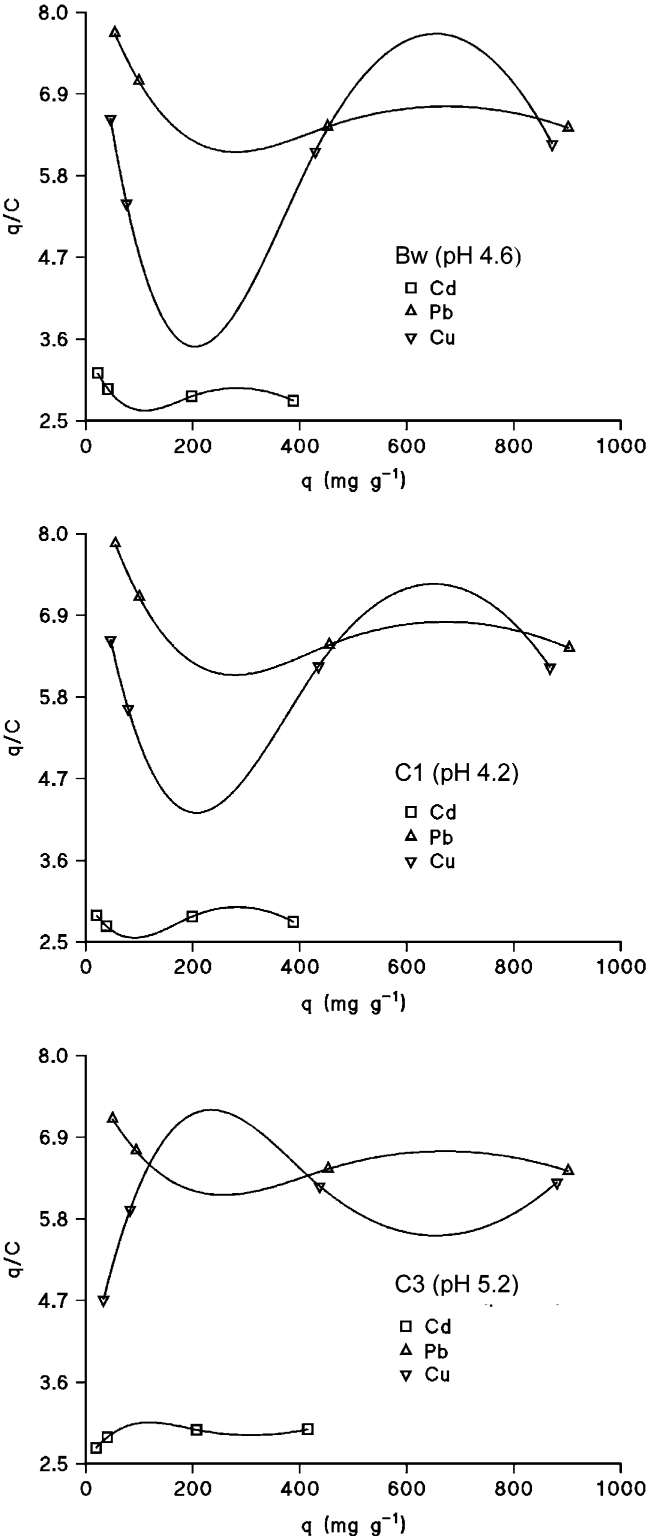

Fig. 2 Scatchard plot of cadmium, lead, and copper on soil zones

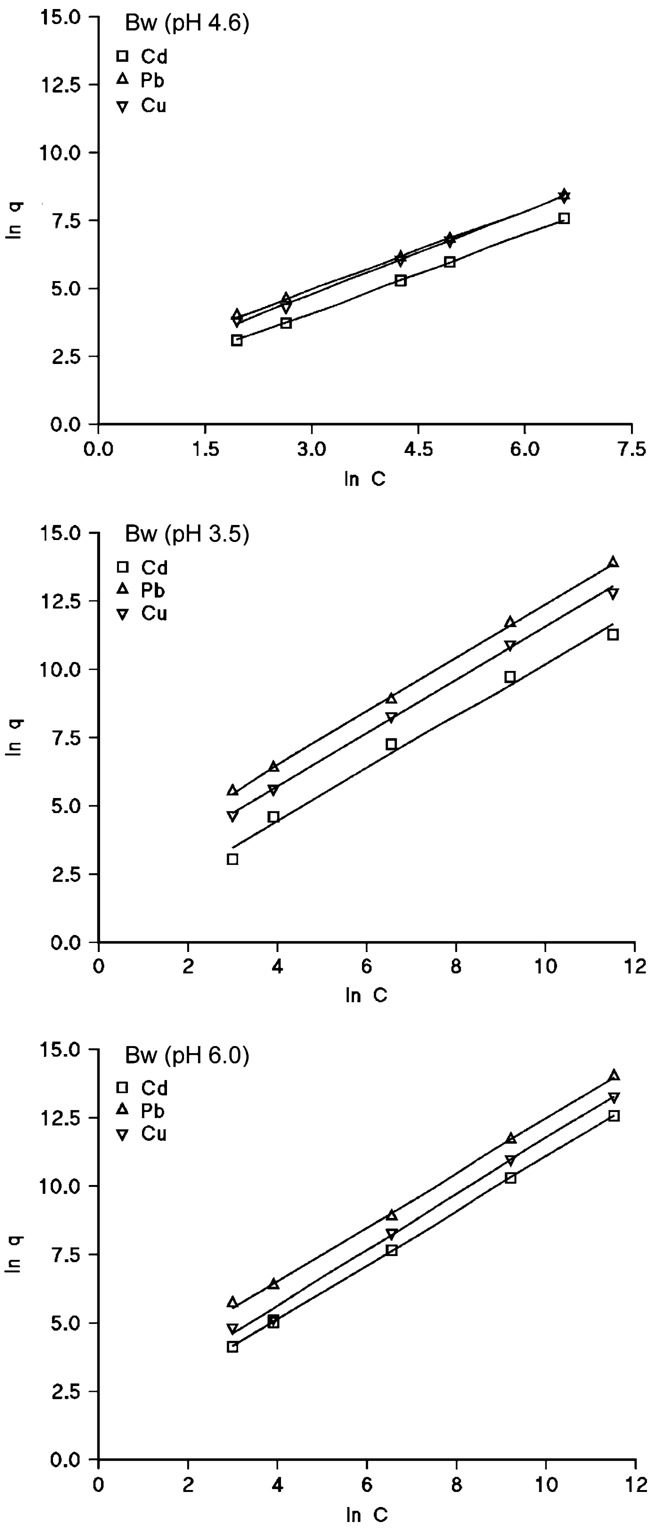

Fig. 3 Freundlich sorption isotherms of heavy metals on Bw as function of pH

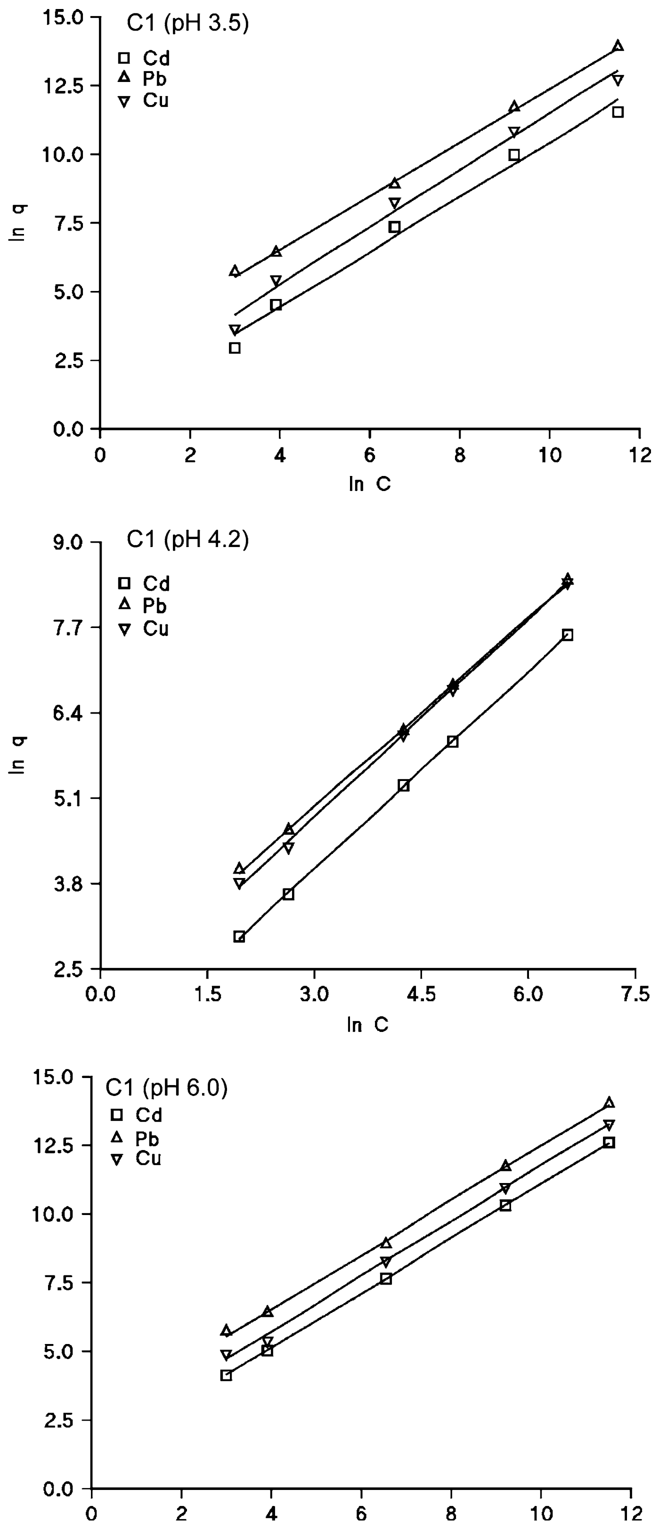

Fig. 4 Freundlich sorption isotherms of heavy metals on C1 as function of pH

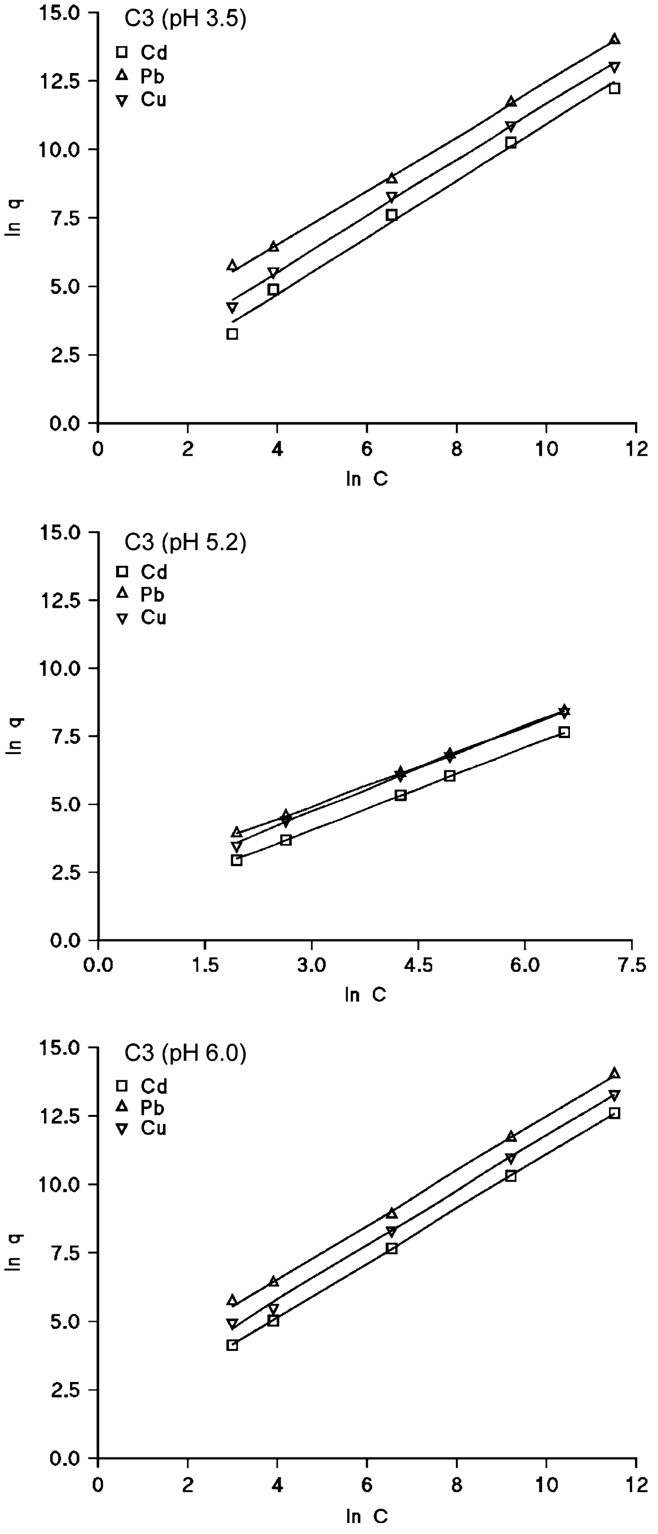

Fig. 5 Freundlich sorption isotherms of heavy metals on C3 as function of pH

Table 3 Freundlich isotherm parameters of metals on soil zones developed on spilite

Soil zone heavy Metal		pH	Freundlich constants N	K (mg g^{-1})	R^2
Bw	Cadmium	3.5	0.96	1.92	0.987
		4.6	0.97	3.19	0.999
		6.0	0.99	3.13	0.999
	Lead	3.5	0.99	12.43	0.999
		4.6	0.96	7.92	0.999
		6.0	0.99	13.33	0.998
	Copper	3.5	0.97	6.49	0.998
		4.6	1.00	5.93	0.998
		6.0	1.00	4.53	0.996
C1	Cadmium	3.5	1.00	1.51	0.986
		4.2	1.00	2.77	0.999
		6.0	1.00	3.10	0.999
	Lead	3.5	0.97	14.30	0.998
		4.2	0.96	8.17	0.999
		6.0	0.98	13.60	0.998
	Copper	3.5	1.00	2.94	0.987
		4.2	1.00	6.05	0.999
		6.0	1.00	5.53	0.997
C3	Cadmium	3.5	1.00	1.80	0.992
		5.2	1.00	2.69	0.999
		6.0	1.00	3.10	0.999
	Lead	3.5	0.98	13.87	0.998
		5.2	0.98	7.24	0.999
		6.0	0.98	13.74	0.998
	Copper	3.5	1.00	4.26	0.997
		5.2	1.00	4.71	0.998
		6.0	1.00	5.99	0.998

negligible. A significant change is not observed on copper adsorption with the change in pH.

Conclusion

Various soil zones such as Bw, C1, C3 are developed on spilite. Montmorillonite, vermiculite, chlorite and illite occurred moderately and kaolinite poorly in the C1 and C3 soil zones, and these minerals decreased upward and appear as accessory in Bw zone soils, whereas illite and sesquioxide are relatively increased in the upper acidic soil zones. The heavy metals are strongly adsorbed on the adsorbent particles such as montmorillonite and vermiculite, which have the highest CEC. The adsorption experiments reveal that soil zones may be quite effective in removing lead ions from the aqueous medium. The high affinity type of interactions between metals and soil zones is attributed to the electrostatic interaction between the clay particles in ambient basic suspensions. Hence the spilite soil zone samples can be suggested as an alternative to adsorb heavy metals from aqueous pollutants. The high adsorption capacity of the soil in the study area is due to relatively high cation exchange capacity of the partly altered spilitic rocks and clay minerals (montmorillonite and partly chlorite vermiculite and illite) play an important role in the substitution of heavy metals, which have similar charge or/and diameters. Relative depletion of the soluble elements such as Na, K, and Ca downward results in the acidity of the environmental condition, where Al, Fe, and Mg are relatively gained. Increase of pH can also increase effective CEC due to removal of some interlayer material as secondary precipitation reactions take place.

In this study, all experiments were carried out using by batch method. Adsorption equilibria of cadmium, lead and copper on soil zones were studied in terms of the adsorption isotherm. The adsorption behaviors of metal ions on the soil zones were expressed by the Freundlich isotherm but were not expressed by the Langmuir isotherms. The results of this investigation have provided further insight into the nature of the adsorption process of heavy metals with spilite and its soil zones.

Acknowledgments I am greatly indebted to anonymous reviewers for their critical reviews and suggestions, which resulted improvement of the manuscript. I am also extremely grateful to Prof. Dr. J. Schwarzbauer and Prof. Dr. G. Dörhöfer for their editorial comments and suggestions. I thank Dr. A. Ayar from the Niğde University, Assoc. Prof. Dr. S. Kadir from the Eskisehir Osmangazi University and Dr. E. Çiftçi from the Niğde University for their help in preparing the manuscript. In addition, I thank Prof. Dr. R. Mayer and Mrs. B. Köhne from the Kassel University for their help during this investigation.

References

Ayar A, Pekacar AI, Mercimek B (2003) Determination of binding constants of labile ligands in metal-ligand complexes containing carboxylic groups bound polymer by using breakthrough technique. Colloids Surf A 212:51–55

Benincasa E, Brigatti MF, Malferrari D, Medici L, Poppi L (2002) Sorption of Cd–cysteine complexes by kaolinite. Appl Clay Sci 21:191–201

Bojemueller E, Nennemann A, Lagaly G (2001) Enhanced pesticide adsorption by thermally modified bentonites. Appl Clay Sci 18:277–284

Brindley GW (1980) Quantitative X-ray analysis of clays. In Brindley GW, Brown G (eds) Crystal Structures of Clay Minerals, their X-ray Identification, vol 5. Mineralogical Society Monograph, London, pp 411–438

Eren M, Kadir S (1999) Colour origin of upper cretaceous pelagic red sediments within the Eastern Pontides, northern Turkey. Inter J Earth Sci 88:593–595

Ghosh D, Bhattacharyya KG (2002) Adsorption of methylene blue on kaolinite. Appl Clay Sci 20:295–300

Gürel A (1991) Veränderung im Stoffbestand der Verwitterungsdecke als Folge natürlicher Bodenbildungsprozesse und antropogener atmosphärischer Deposition. Berichte Forschungszentrums Waldökosysteme. Universität Göttingen, Reich A, Bd. pp. 82

Lawrence MAM, Kukkadapu RK, Boyd SA (1998) Adsorption of phenol and chlorinated phenols from aqueous solution by tetramethylammonium- and tetramethylphosphonium-exchanged montmorillonite. Appl Clay Sci 13:13–20

Maliou E, Malamis M, Sakellarides PO (1992) Lead and cadmium removal by ion-exchange, Wat Sci Technol 25:133–138

Matschullat J, Schneider J, Heitkamp U, Lessmann D, Siewers U, Rostai A, Malessa V, Andreae H (1990) Verbundforschung Fallstudie Harz. Berichte Forschungszentrums Waldökosysteme, Reich B, Bd. 19

Matschullat J, Heinrichs H, Schneider J, Ulrich B (1994) Gefahr für Ökosysteme und Wasserqualität. Springer, Berlin Heidelberg New York, pp 478S

Mazidji CN, Koopman B, Bitton G (1992) Chelating resin versus ion-exchange resin for heavy metal removal in toxicity fractionation. Wat Sci Technol 26:189–196

Meiwes KJ, König N, Khanna PK, Prenzel J, Ulrich B (1984) Chemische Untersuchungsverfahren für Mineralboden, Auflagehumus und Wurzeln zur Charakterisierung und Bewertung der Versauerung in Waldböden. Berichte der Forschungszentrum Waldökosysteme. Band 7, Universität Göttingen

Moore DM, Reynolds RC (1989) X-ray diffraction and the identification and analysis of clay minerals. Oxford University Press, Oxford, pp 332

Öztekin N, Alemdar A, Güngör N, Erim FB (2002) Adsorption of polyethyleneimine from aqueous solutions. Mater Lett 55:73–76

Patchineelam SR (1975) Untersuchungen über die Hauptbindungsarten und die Mobilisierbarkeit von Schwermetallen in fluviatilen Sedimenten. Dissertation Universität Heidelberg, pp 136

Rodriguez-Sarmiento DC, Pinzon-Bello JA (2001) Adsorption of sodium dodecylbenzene sulfonate on organophilic bentonites. Appl Clay Sci 18:173–181

Scatchard G (1949) The attraction of proteins for small molecules and ions. Ann New York Acad Sci 51:660–672

Schoeder D, Dümmler H (1962) Tonminerale in Böden Schleswig-Holsteins Zeitschrift Pflanzenernährung Düngung. Bodenkunde Weinheim 101:129–140

Suraj G, Iyer CSP, Lalithambika M (1998) Adsorption of cadmium and copper by modified. Appl Clay Sci 13:293–306

Tarrah J (1989) Verwitterungsbilanzen von Böden auf der Basis modaler Mineralbestände, Berichte des Forschungszentrums Waldökosysteme, Reiche A., Bd., pp 52:229

Uçan M, Ayar A (2002) Sorption equilibria of chlorinated anilines in aqueous solution on resin-bound cobalt ion. Colloids Surf A 207:41–47