Zinc(II) Sorption Characteristics of Soils in Predominant Smectite, Illite and Kaolinite Clay Minerals

K. Yilmaz*, K. Saltali, E.U. Güzel and H. Dikici

Department of Soil Science, Kahramanmaras Sutcu Imam University,
46060 Kahramanmaras, Turkey
Fax: (90)(344)2191526; Tel: (90)(344)2191523; E-mail: kyilmaz@ksu.edu.tr

The purpose of the present study was to evaluate the adsorption behaviour of zinc in soils dominated with smectite, illite and kaolinite. The linear Langmuir model is more suitable for the adsorption of Zn ions onto the soils since it had higher coefficient of determination value compared with that of the linear Freundlich model. The maximum sorption capacity of illite for Zn ions was determined from the Langmiur equation and found to be 11.38, 10.23 and 8.50 mg g^{-1} for smectite, illite and kaolinite soils, respectively. The dimensionless equilibrium parameter or separation factor (R_L) approaches zero as the C_o (initial concentration) value is increased, indicating that the adsorption of Zn(II) ions onto the clay fractions is less favourable. The Dubinin-Redushckevich (D-R) model was also applied equilibrium data to identify the type of sorption (chemically or physically) of Zn ions onto the soils. The bonding energies for ion-exchange mechanism (E, kJ mol^{-1}) calculated from D-R parameter β (the activity coefficient related to mean adsorption energy) was found as 11.9, 10.6 and 10.1 kJ mol^{-1} for smectite, illite and kaolinite soils, respectively. The calculated E value in these soils indicated that the type of sorption of Zn ions onto the soils was predominantly chemical in nature according to typical ranges of bonding energy. From the obtained results, it can be concluded that the Zn ions adsorption on soils rich in smectite was higher compared with the adsorption on the other soils.

Key Words: Adsorption isotherms, Soil, Zinc, Smectite, Illite, Kaolinite.

INTRODUCTION

Zinc is one of the minor plant nutrition elements. Its deficiencies retard plant growth. The concentration of Zn in soil solution and its availability are governed by the adsorption mechanisms of Zn by the soil constituents. Depending on the environmental conditions, Zn adsorption in soils depends on some soil chemical and mineralogical characteristics such as pH, clay content, type and mineralogy, organic matter, cation exchange capacity (CEC), carbonates anhydrous oxides, which all affect Zn uptake by plants[1]. The adsorption of Zn is strongly influenced by the types and contents of the clay minerals and Shuman[2] obtained that soils high in clay had higher adsorptive capacities. Reddy and Perkins[3] found the bentonite and illite clays

adsorbed higher Zn than that of kaolinite clay. Farah *et al.*[4] also reported that the retention of Zn ions was in the order of montmorillonite > illite > kaolinite.

Adsorption and desorption characteristics of elements by soils or clays are frequently studied by adsorption isotherms such as Langmiur, Freundlich, Temkin and Dubinin-Redushckevich (D-R). The adsorption isotherms also reveal specific relationships between sorbate and adsorbent. The D-R model also reveals sorption type (chemical or physical) depending on the nature of adsorbent and adsorbate[5,6]. The prediction of specific relationships of trace metals in soils with different clay minerals and characteristics is a useful tool for metal uptake by plants and environmental protection[7].

The aim of this study is to investigate the adsorption characteristics of Zn ions onto the soils high in smectite, illite and kaolinite.

EXPERIMENTAL

The soils selected were dominated by smectite, illite and kaolinite. Soil pH and was determined in soil saturation paste[8]. Cation exchange capacity (CEC) was determined by Richards[9]. The total carbonate contents were measured using a Scheibler Calcimeter. Organic matter was determined by the Walkley-Black wet oxidation method[10].

The soil samples for mineralogical analysis were pre-treated with 1 N NaOAC, adjusted to pH 5, to remove carbonates and with 30 % H_2O_2 to remove organic matter and with sodium dithionite-citrate-bicarbonate to remove Fe-Si-Al-oxides. Soils were then adjusted to pH 9.5 with 1 M Na_2CO_3 for dispersion. Wet sieving separated the sand fraction and clay and silt fractions were separated by sedimentation and decantation[11]. Diffractograms were obtained from Mg and K saturated clay slides by scanning from 3 to 13 2θ, with nickel-filtered CuKα radiation using a Philips X-ray diffractometer[11]. The diffraction intensity of the clay minerals was determined by calculating the peak areas. Vermiculite minerals were determined by the differences between magnesium and potassium saturated clay slides at the 10 Å peak. The multiplication factors determined by Yilmaz[12] were used for quantitative clay analysis.

A 0.4 g air-dried soil samples were placed as duplicates in 33 mL centrifuge tubes and were mixed with 20 mL of solution containing 0, 10, 25, 50, 75, 100, 150, 200 and 250 mg mL^{-1} Zn. The stock solution of trace metals (1000 mg L^{-1}) were obtained by dissolving metal salts (ZnCl$_2$). Then the tubes were shaken for 24 h at 21 °C until the suspensions reach equilibrium. The samples were centrifuged and the clear supernatant was carefully taken to determine the trace metal concentrations of the solution phase and filtered through Whatman 42 filter paper. The trace metals in the filtrates were analyzed by a flame atomic adsorption spectrophotometer (AAS, Perkin-Elmer analyst 3100 model).

The average value of the duplicate analysis was used to calculate the amount of trace metals in solution. The differences between the amount of added trace metals

and recovered in the solution was considered as retained by the soils according to eqn. 1.

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (1)$$

where q_e is the amount of adsorbed Zn ion (mg g^{-1}), C_o and C_e are initial and equilibrium concentrations of Zn ion in solution (mg L^{-1}), respectively. V is the solution volume (L) and m is the soil weight (g).

Linear Langmuir, Freundlich and Dubinin-Redushckevich (D-R) isotherms were used to evaluate Zn adsorption data. The goodness of fit was evaluated by the determination coefficient (R^2) as reported by Mesquita and Vieira e Silva[13].

RESULTS AND DISCUSSION

Soil characteristics: The physical and chemical characteristics of investigated soils were given in Table-1. Soil pH, CEC (cmol kg^{-1}), CaCO$_3$ (%) and organic matter (%) contents ranged from 6.31 to 7.76, 19 to 68, 1.2 to 18.1 and 0.52 to 3.46, respectively. The smectite, paligorskite, illite, kaolinite and vermiculate % contents ranged from 7.45 to 15.15, 0.00 to 15.78, 3.50 to 15.60, 2.58 to 16.88, 1.28 to 3.05, respectively.

TABLE-1
PHYSICAL AND CHEMICAL PROPERTIES OF THE SOILS

| Soil | pH | CEC (cmol kg^{-1}) | % | | | | | | |
			CaCO$_3$	Organic matter	Smectite	Paligorskite	Illite	Kaolinite	Vermikulite
Smectitic soil	7.70	68	5.8	0.63	15.15	4.85	3.50	2.58	1.28
Illitic soil	7.76	40	18.1	0.52	9.65	0.00	15.60	7.29	1.60
Kaolinitic soil	6.31	19	1.2	3.46	7.45	15.78	15.08	16.88	3.05

(a) Smectitic soil: Smectite dominate clay mineral; (b) Illitic soil: Illite dominate clay mineral
(c) Kaolinitic soil: Kaolinite dominate clay mineral.

Adsorption isotherms: The adsorption isotherms reveal the specific relation between the concentration of sorbate and its sorption degree onto the adsorbent surface. The adsorption capacities of the soils (a: smectitic soil, b: illitic soil and c: kaolinitic soil) for Zn(II) ions were evaluated using the Langmuir, Freundlich and Dubinin-Redushckevich (D-R) isotherm models. Linear langmuir models is as follows[14].

$$\frac{C_e}{q_e} = \frac{1}{kb} + \frac{C_e}{b} \qquad (2)$$

where C_e is the equilibrium concentration of the sorbent in solution (mg L^{-1}), q_e is the adsorbed amount of the sorbent (mg) by per unit mass of adsorbent (g), b is maximum adsorption capacity (mg g^{-1}) and k represent adsorption energy coefficient

(L mg^{-1}). The C_e/q_e plotted against C_e yields a straight line with determination coefficient as shown in Fig. 1a,b,c, indicating that the equilibrium data fitted well into the Langmuir model as also reported by Shuman[11] and Krishnasamy *et al.*[15]. The b (mg g^{-1}) values were calculated from the slope of the linear plot, whereas k (L mg^{-1}) values were found from the intercept of the linear plot (Table-2). As shown in Table-2, the maximum adsorption capacity (b) for smectitic soil was higher than that of the other soils. This was the reason with higher simectite and lime content of the simectite soil. Since, b value is a measure for the total binding sites for zinc(II) adsorption, the clay mineral type, clay content and lime content increase zinc(II) adsorption[1]. Krishnasamy *et al.*[15] also reported that clays dominant in illite and montmorillonite elevated the maximum adsorption capacity of zinc.
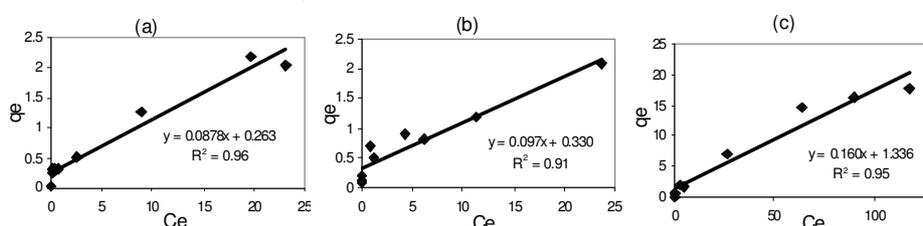

Fig. 1.   Linear Langmuir isotherms of the adsorption of Zn(II) ions on the soils (adsorbent dosage: 0.4 g; pH: 7; Temperature: 21 ºC)

TABLE-2
LANGMUIR AND FREUNDLICH PARAMETERS OF THE SOILS

Soil	Langmuir parameters			Freundlich parameters		
	b	k	R^2	K$_f$	1/n	R^2
Smectitic soil	11.38	0.333	0.96	2.36	0.436	0.85
Illitic soil	10.23	0.294	0.91	0.85	0.551	0.86
Kaolinitic soil	8.50	0.120	0.95	0.51	0.520	0.92

Comparisons of the k values showed the following affinity trends: smectitic soil > illitic soil > kaolinitic soil. The magnitude of adsorption energy coefficient (k) can be considered to be the measure of the degree of availability or suitability of the adsorption sites[16]. Thus, for higher k values of smectitic and illitic soils, it is possible that the relatively large numbers of adsorption sites are readily available for zinc adsorption. The k value of kaolinitic soil is lower than the others, indicating a lower affinity of zinc adsorption

On the other hand, the dimensionless equilibrium parameter or separation factor, R$_L$, based on the further analysis of Langmuir equation can be given by

$$R_L = \frac{1}{1 + K_L C_o} \tag{3}$$

where C_o (mg L^{-1}) is the initial concentration of adsorbate. The R$_L$ parameter is considered as more reliable indicator of the adsorption. There is four probabilities for the R$_L$ value; for favourable adsorption, $0 < R_L < 1$, (ii) for unfavourable adsorption,

$R_L > 1$, (iii) for linear adsorption, $R_L = 1$, (iv) for irreversible adsorption, $R_L = 0$[17-19].

Fig. 2 shows the variation of separation factor, R_L with initial concentration of the Zn ions in the solution. As it can be seen from the curves, the R_L parameter lied between 0 and 1, representing that the adsorption of Zn ions by soils is favourable. Fig. 2 also indicates that the R_L value approaches zero as the C_o value is increased and it means that the adsorption of Zn(II) ions onto the soils is less favourable and soluble Zn compounds are converted to less soluble forms, probably due to precipitation and/or crystallization of Zn(II) ions at high initial concentrations[1].
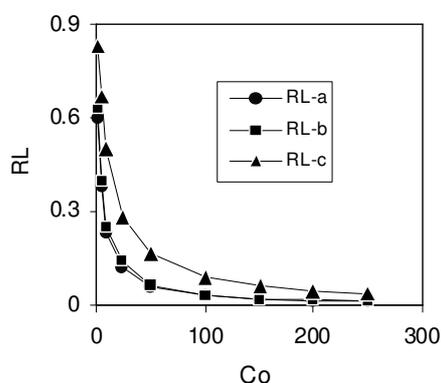

Fig. 2. Variation of separation factor (R_L) as a function of initial Zn(II) concentrations

The adsorption data were also applied to the Freundlich model expressed as follows[20];

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (4)$$

where K_f is the measure of the adsorption capacity of the adsorbent, $1/n$ is a constant relating to adsorption intensity or surface heterogeneity. The coefficient of determination (R^2) values of the linear plot of Freundlich isotherm was shown in Fig. 3 smectitic soil (a), illitic soil (b), kaolinitic soil (c). Freundlich parameters, K_f (mg g^{-1}) and $1/n$ (L g^{-1}) and coefficients of determination (R^2) values were presented in Table-2.

Fig. 3 showed the Freundlich isotherms obtained for the sorption of Zn(II) ions onto the soils and also the Freundlich parameters, K_f and $1/n$, can be seen at Table-2. A high value of the intercept, K_f, is indicative of a high adsorption capacity[21,22]. The K_f value of the Freundlich equation (Table-2) indicated that smectitic soil has high adsorption capacity for Zn ions compared with the other soils. The magnitude of $1/n$ value generally range from 0 to 1 and it is a measure of exchange intensity or surface heterogeneity and the value of $1/n$ smaller than 1 pointed out the favourable removal conditions[5,6,21]. However, for the Freundlich model the R^2 values compared with that obtained from the Langmuir model, it can be remarkably noted that the Langmuir model is better conformed to the equilibrium data.
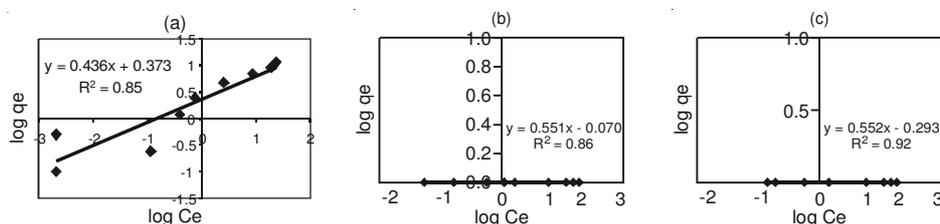
Fig. 3.   Linear Freundlich isotherms of the adsorption of Zn(II) ions on the soils
(adsorbent dosage: 0.4 g; pH: 7; Temperature: 21 ºC).

The equilibrium data were also applied to the Dubinin-Redushckevich (D-R) model to determine the type of adsorption, physical or chemical processes[6,17,23]. The linearized form of the D-R isotherm is as follows:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{5}$$

where q_e is the amount of adsorbate adsorbed on per unit weight of adsorbent (mol L^{-1}), q_m represent the maximum adsorption capacity (mol g^{-1}), β is the activity coefficient related to mean adsorption energy (mol^2 J^{-2}) and ε is the Polanyi potential. The Polanyi potential is described using the following equation:

$$\varepsilon = RT\ln(1 + 1/C_e) \tag{6}$$

where R is the gas constant (J mol^{-1} K^{-1}), T is temperature (K) and C_e is the equilibrium concentration of the Zn(II) ions (mol L^{-1}). The mean adsorption energy (E; kJ mol^{-1}) is as follow:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{7}$$

This adsorption potential is independent of the temperature, but it varies depending on the nature of adsorbent and adsorbate. The value of mean adsorption energy gives information about chemical and physical sorption.

As seen Fig. 4, for smectite, illite and kaolinite soils, the β and q_m values calculated from the slope and intercept of the plot of ln q_e against ε^2 were found as -3.52 $\times$ 10^{-9}, -4.48 $\times$ 10^{-9}, -4.87 $\times$ 10^{-9} (mol^2 J^{-2}) and 4.95 $\times$ 10^{-4}, 3.42 $\times$ 10^{-4}, 3.16 $\times$ 10^{-4} (mol g^{-1}), respectively. The E values for smectite, illite and kaolinite soils were calculated as 11.9, 10.6 and 10.1 kJ mol^{-1} using eqn. 7. If the E value ranges from 1 to 8 kJ mol^{-1}, physical sorption is dominancy and from 9 to 16 kJ mol^{-1}, chemical sorption is dominant[5,6].

The E values indicated that the type of sorption of Zn ions onto the soils was predominantly chemical (specific) in nature. Dominant chemical sorption could be expected for soils (a) and (b) due to higher clay and lime contents. But, dominant chemical sorption for soil kaolinite may be attributed to ligand exchange between Zn ions and organic-inorganic ligands. Similarly, Borah *et al.*[24] also reported that specific adsorption was one of the main processes of Zn adsorption in kaolinite dominated soils. The chemically adsorbed Zn(II) ions in soils are usually very low
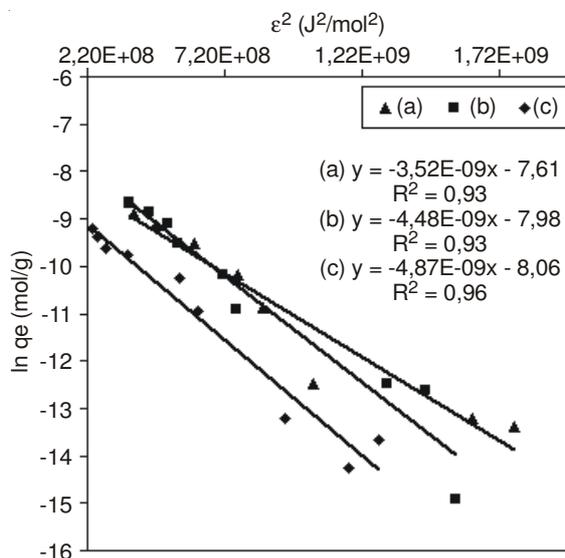
Fig. 4.   D-R isotherms plot of the adsorption of Zn(II) ions on the soils (adsorbent
          dosage: 0.4 g; pH: 7; Temperature: 21 ºC)

availability for the plants and they forms low solubility compounds with clay, lime and oxides in soils[2,25]. The higher q_m and E values were found in the smectitic soil > illitic soil > kaolinitic soil. Farah *et al.*[4] reported that the retention order for Zn ions was to be in order of montmorillonite > illite > kaolinite and Krishnasamy *et al.*[15] determined the Zn sorption by the clays was greatest in montmorillonite-dominated soils.

Conclusion

The adsorption data of all the soils were better described by the linear Langmuir model compared with the Freundlich model. The Langmuir b and k values were higher in smectitic soil compared with the other soils. Dubinin-Redushckevich (D-R) model also results pointed out the type of sorption of Zn ions onto the soils was predominantly chemical in nature, probably due to higher clay and lime contents. To decrease chemisorption (specific adsorption) and increase the availability of applied Zn to plants in these soils, Zn could be applied as a combined with organic compounds or in the form of Zn-chelates.

REFERENCES

1. N. Kariman and G.R. Moafpouryan, *Com. Soil Sci. Plant Anal.*, **30**, 1721 (1999).
2. L.M. Shuman, *Soil Sci. Soc. Am. Proc.*, **39**, 454 (1975).
3. M.R. Reddy and H.F. Perkins, *Soil Sci Soc. Am. Proc.*, **38**, 229 (1974).
4. H. Farah, D. Hatton and W.F. Pickering, *Chem. Geol.*, **28**, 55 (1980).
5. Y.S. Ho, J.F. Porter and G. McKay, *Water, Air Soil Pollut.*, **141**, 1 (2002).
6. R. Donat, A. Akdogan, E. Erdem and H. Cetisli, *J. Colloid. Interface Sci.*, **286**, 43 (2005).
7. A. Kabata-Pendias and B.M. Mukherjee-Arun, Trace Elements from Soil to Human, Springer Pub. Springer-Verlag, Berlin, Heidelberg, p. 10 (2007).

8.   Soil Survey Staff, Soil Survey Manual. USDA. Handbook 18. Washington D.C., p. 437 (1993).

9.   L.A. Richards, Diagnosis and Improvement of Saline and Alkaline Soils, In: USDA Handbook 60, U S Government Printing Office, Washington (1954).

10. L.E. Allison and C.D. Moddie, Carbonate in eds.: C.A. Black *et al.*, Methods of Soil Analysis Part 2, Argonomy, American Society of Argon. Inc. Madison, Wisconsin USA, p. 1379 (1965).

11. M.L. Jackson, Soil Chemical Analysis, Advanced Course, Published By the Author, University of Wisconsin. Madison, USA, edn. 2 (1969).

12. K. Yilmaz, The Properties of Harran Plain Soils, Soil Science Department, Natural Applied Sciences Cukurova University, Adana, Turkey (Ph.D. Thesis) (1990).

13. M.E. Mesquita and J.M. Vieira e Silva, *Geoderme*, **106**, 219 (2002).

14. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).

15   R. Krishnasamy, K.K. Krishnamoorthy and T.S. Manickam, *Clay Res.*, **4**, 92 (1985).

16. M.R. Derici, A.R. Brohi, K. Saltali, M. Kilic and K. Kilic, CIEC Conference, Turkey, pp. 143-149 (1995).

17. E. Gonzales-Pradas, M. Villafranca-Sanchez, F. Canton-Cruz, M. Socias-Viciana and M. Fernandez-Perez, *J. Chem. Technol. Biotechnol.*, **59**, 289 (1994).

18. S.S. Gupta and K.G. Bhattacharyya, *Appl. Clay Sci.*, **30**, 199 (2005).

19. M. Sekar, V. Sakthi and S. Rengaraj, *J. Colloid. Interface Sci.*, **279**, 307 (2004).

20. H.M.F. Freundlich, *Zeitsch. Physik. Chem. (Leipzig)*, **57**, 385 (1906).

21. A. Demirbas, E. Pehlivan, F. Gode, T. Altun and G. Arslan, *J. Colloid. Interface Sci.*, **282**, 20 (2005).

22. K. Saltali, A. Sari and M. Aydin, *J. Hazard. Mater.*, **141**, 258 (2007).

23. M.M. Dubinin, E.D. Zaverina and L.V. Radushkevich, *Z. Fizich. Khim.*, **21**, 1351 (1947).

24. D.K. Borah, N.K. Banerjee and R.K. Rattan, *J. Indian Soc. Soil Sci.*, **38**, 27 (1990).

25. L.M. Shuman, *Soil Sci. Soc. Am. J.*, **40**, 349 (1976).