Environmental Engineering and Management Journal

December 2019, Vol. 18, No. 12, 2605-2611
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

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ADSORPTION OF Fe, Mn AND Cd IN CARBONATE-RICH CLAYEY SOILS AND ASSESSMENT OF ENVIRONMENTAL EFFECTS

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Abstract

Aim of the study is to determine Fe, Mn and Cd adsorption in the carbonate-rich clayey soils and to assess their environmental impacts. Soil samples represented a carbonate-rich clayey soil (Isaoren), carbonate-rich soil (Maşuk) and clayey soil (Aşık) was obtained from three different villages in Sanliurfa, southeast of Turkey. Adsorption studies were carried out with batch method. The maximum Fe, Mn and Cd adsorption was found on Isaoren, Maşuk and Aşık soils with Kf (empirical Freundlich constant) values of 16.63, 2.18 and 1.01, respectively. While the carbonate content of soil showed a higher affinity than clay for Fe and Mn; the clay was found more accelerate efficacious than the carbonate on the Cd adsorption. Because of Fe and Mn adsorption on the soil, uptake of these nutrients by plants reduces, and Fe-Mn deficiency occurs with the yield losses. In this manner, unused mobile nitrate ions in soil solution from fertilizer leaches easily through the ground water. Both problem of the soil salinity decreasing the crop yield and the excessive irrigation accelerating the nitrate infiltration in the area support this phenomenon. As a conclusion, carbonate-rich clayey soils can prevent the Cd leaching into the groundwater but may trigger the nitrate contamination.

Key words: heavy metal, iron deficiency, manganese, nitrate contamination

Received: January, 2019; Revised final: April, 2019; Accepted: May, 2019; Published in final edited form: December, 2019

1. Introduction

Iron (Fe) is not included in the composition of the chlorophyll molecule but is one of the elements required for chlorophyll formation in green plants. It is an important micronutrient and soil properties can affect the iron availability. In general, total iron increases with the increase in cation exchange capacity (CEC) and the content of clay and silt. Complexing iron with soil organic matter can lead to increased plant availability and microbial waste materials can provide additional iron to plant paths. Similarly, exchangeable iron and diethylenetriaminepentaacetic acid (DTPA) extractable iron, which is adsorbed to inorganic regions, increases with increasing soil organic matter, but decreases with higher soil pH and calcium carbonate content. (Jelic et al., 2011; Pak, 2011).

Manganese (Mn) deficiency in plants is also often seen in plants grown on calcareous, high-pH soils. Iron or Mn deficiency in calcareous soils is much more common problem, especially in irrigated and semi-arid regions. Calcareous soils are carbonate-rich soils with high Ca^{++} concentration and pH in soil solution. In the case of manganese deficiency in cotton, a slight discoloration occurs in young leaves. If the Mn deficiency is more severe, the discoloration increases, the leaf surface covers the spots of whitish yellow. Decrease in product quantity is unavoidable even if deficiency is mild.

Cadmium (Cd) is a persistent heavy metal that has toxicological effects on ecosystems due to its high mobility and easily transformation from soil to plants (Vaverkova et al., 2018; Xu et al. 2013). Accumulation of Cd in soil is due to coal combustion, inadequate battery recycling practices, frequent use of

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phosphate fertilizers and pigment production. Even at a low concentration (<1 mg kg^{-1}), Cd in the soil also poses serious threats to living organisms as accumulating in the edible parts of crops, which initiates Cd toxicity in humans via the food chain (Adriano 2004). The excessive presence of Cd in soil poses great risks and hazards to human health (Liu et al., 2015). Inorganic and organic materials applied as heavy metal soil amendments can effectively reduce the bioavailability of Cd in soil and prevent Cd uptake into plants (Zhang et al., 2018).

Adsorption is an important issue in soil that affects the availability of micronutrients to plants or deficiency of micronutrients and leaching of toxic elements to groundwater. The aim of the study is to determine Fe and Mn adsorption as two microelements for plants and the adsorption of Cd in carbonate-rich clayey soils as toxic metal and to assess the adsorption phenomena of three elements through their environmental impacts.

2. Material and methods

2.1. Study area and soil sampling

Soil samples were obtained from Aşık (37°13'44"N 38°42'55"E), İsaören (37°16'35.3"N 38°40'20.2"E) and Maşuk (37°14'04"N 38°45'57"E) villages in Şanlıurfa, southeast of Turkey (Fig. 1). Soils were heavy-textured and dark-colored as found ones in arid and semi-arid regions. They contain smectite type clay and low level of organic content. Their most significant feature was cracking, as a result of buckling during the droughty period. Vertisols are the predominant soils in the region. The villages' climate is semi-arid with almost no precipitation in the summer periods. The mean annual precipitation, atmospheric temperature and evaporation were about 284.2 mm, 18ºC and 1884 mm, respectively (Yeşilnacar and Güllüoğlu, 2007).

Surface soil samples (Fig.2) were taken from 0-20 cm depth and placed in polyethylene containers and transported to the Harran University, Environmental Engineering laboratory. Certain properties of the soil samples used in this study are presented in Table 1.

2.2. Chemicals and analysis

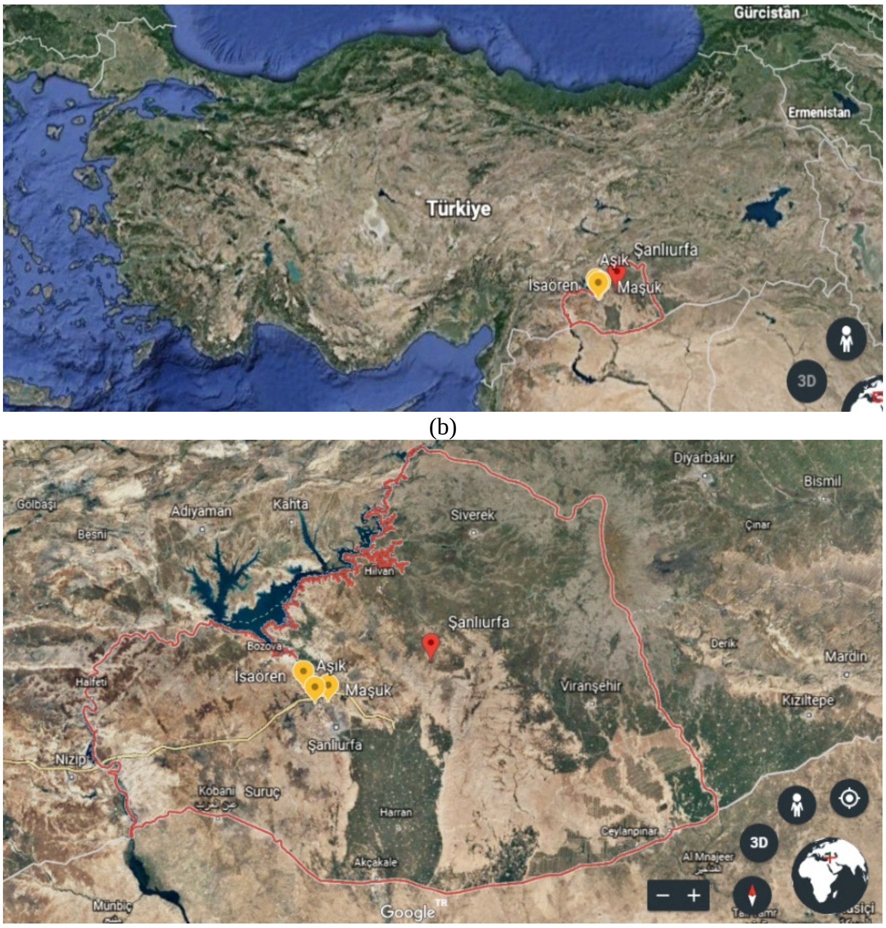
Stock solutions were prepared from $Fe(NO_3)_3.9H_2O$, $Mn(NO_3)_2$ and $Cd(NO_3)_2.4H_2O$ in 1 L of deionized water. They were further diluted to get the desired concentration for practical use. Analytical grade chemicals were provided by Merck with a chemical purity of 99%. All solutions were stored at 4ºC. Solutions of 0.1 M HCl and 0.1 M NaOH were used for pH adjustment.

All samples were filtered using 0.45 μm syringe filters and the filtrates were immediately measured for Fe, Mn and Cd in an inductively coupled plasma (ICP) mass spectrometer (Perkin Elmer Optima 5300 DV model). The differences between the initial and the equilibrium metal concentrations determine the amount of metal that is adsorbed by the soil.

Table 1. Characteristics of soils from study area

Soil characteristics	***Aşık***	***İsaören***	***Maşuk***
Soil depth (cm)	20.00	20.00	20.00
Water saturation (%)	74.00	74.00	70.00
Electrical conductivity (EC) x10^3 (milli Siemens/ centimeter) (mS/cm)	0.87	0.78	0.50
$CaCO_3$ (%)	5.70	27.00	27.00
pH	7.46	7.32	7.25
Organic matter (%)	1.06	1.30	1.33
Texture of soil	Clay	Clay	Clay loam
% Clay	63.44	61.44	39.44
% Silt	19.28	21.28	29.28
% Sand	17.28	17.28	31.28
P_2O_5 (kg/m^2) x 10^{-3}	3.04	5.10	4.20
K_2O (kg/m^2) x 10^{-3}	360.00	126.00	84.00

(a)



(b)

(c)

Fig. 1. Location views of Aşık, Isaoren and Maşuk villages: (a) in the world (b) in Turkey (c) in region

Fig. 2. Soil samples of Aşık (A), İsaören (B) and Maşuk (C)

Air-dried, sieved (<2 mm) soil samples were treated for determination of basic soil properties. Particle size distribution was assigned using Bouyocuos hydrometer method. The organic matter content was determined using modified Walkley-Black (wet combustion) method. Lime (carbonate) content was determined using calsimetric method (Tüzüner et al., 1990).

Soil pH and electrical conductivity (EC) were measured in a 1:1 (w/v) soil to deionized water solution mixture by a Jenway Model 370 pH meter and a portable Hach-Lange HQ40d conductometer, respectively.

2.3. Batch experiments

Adsorption isotherms of Fe, Mn and Cd on three soils were obtained by batch equilibration method. Preliminary experiments to determine the equilibrium time and the optimum adsorbent (soil) dosage were carried out at room temperature (25 °C). Soils (0.25 g) were mixed with 25 mL of metal solutions (10 g/L) on a reciprocating shaker (150 rpm). Then the reaction mixture was centrifuged at 8000 rpm for 5 min; the supernatant was filtered through 0.45 μm syringe filter and analyzed for metals in ICP mass spectrometer. All experiments were executed with controls-with only metal in tube (no soil) and blanks with the same amount of soil in tube (without metal). All reported results constituted the mean of duplicate measurements. The adsorption data were analyzed for each soil sample using linearized forms of the Langmuir and Freundlich isotherms (Sparks, 1995).

3. Results and discussion

3.1. Soil samples

Characteristics of the soil samples used in this study were presented in Table 1. Soil organic matter, carbonate rate, clay content and pH are the most important constituents in the adsorption phenomena. The organic matter content and pH of the soils were similar. However, Isaoren and Maşuk soils were carbonate-rich samples (27%) while Aşık soil has low carbonate content (5.7%). Aşık and Isaoren soils contained higher amount of clay compared to Maşuk soil. Isaoren is a material representing the carbonate-rich clayey soil. Calcareous vertisol soil is characterized by its high pH and $CaCO_3$ content, which made the heavy metals to be oxidized and adsorbed onto soil.

3.2. Fe, Mn and Cd adsorption in the soils

3.2.1. Equilibrium time

Adsorption phenomenon exhibited an immediate rapid adsorption within 10 min. Metal adsorption leveled off 20 min for Cd and 40 min for Fe and Mn (Fig. 3). The rapid sorption was followed by a slow sorption of metals in the soils.

Because the changes in metal concentration were rather small after equilibrium period, 20 min for Cd and 40 min for both of Fe and Mn was used in the remaining adsorption studies. Resmi et al. (2012) specified that rapid adsorption followed by a steady stage is due to reduction in the driving force after a long period of operation.

3.2.2. Adsorbent (soil) dosage

The effect of adsorbent (soil) dose on the metal adsorption is shown in Fig. 4. The percentage of Mn and Cd adsorption increased with the increase in the amount of the soil and it was obviously due to the enhanced active sites with an increase in adsorbent dosage. Fe exhibited a rapid adsorption for the initial soil dosage and no significal change was observed with the increasing soil doses. Amount of 2 g/L for Fe, 30 g/L for Mn and 30 g/L for Cd was fixed as optimum soil dosage and it was used in the remaining adsorption studies.

3.2.3. Adsorption isotherms

The Freundlich and Langmuir adsorption constants are given in Table 2. Mn adsorption isotherms fitted well with both the Freundlich and Langmuir models ($R^2 \geq 0.95$). Cd adsorption gave a better fit to the Langmuir model ($R^2 \geq 0.99$) while Fe adsorption was better matched to the Freundlich model ($R^2 \geq 0.92$). The maximum Fe and Mn adsorption was found on Isaoren and Maşuk soils with Kf values of 16.63 and 2.18 respectively. Carbonate contents of both soils were higher than Aşık soil and carbonate content showed a higher affinity than clay for both metals.

CaCO3 is considered an important factor on the higher Fe and Mn adsorption of the soils. Cd adsorption was found maximum on Aşık soil with Kf and Qo values of 1.01 and 2.83 respectively. Aşık soil has higher clay (63%) and lower CaCO3 (6%) content than the other ones.

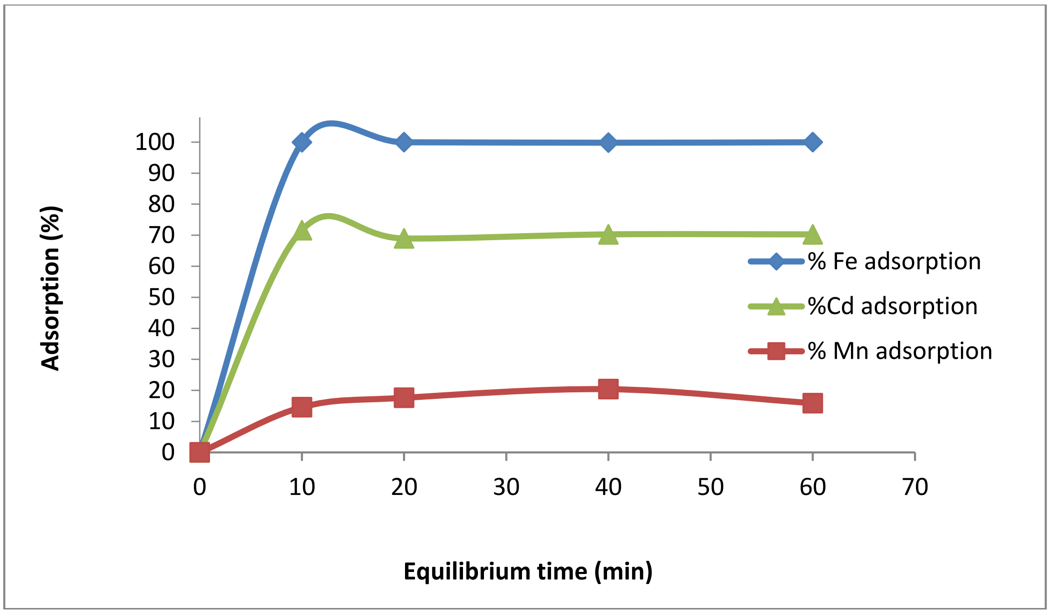


Fig. 3. Equilibrium time for Fe, Mn and Cd adsorption on soil
(Temperature: 25 °C, Adsorbent dosage: 10g/L, Shaking rate: 150 rpm,
Initial metal concentration: 100 mg/L, pH: 6.82 (Fe + soil), 6.92 (Mn + soil), 8.11 (Cd + soil))

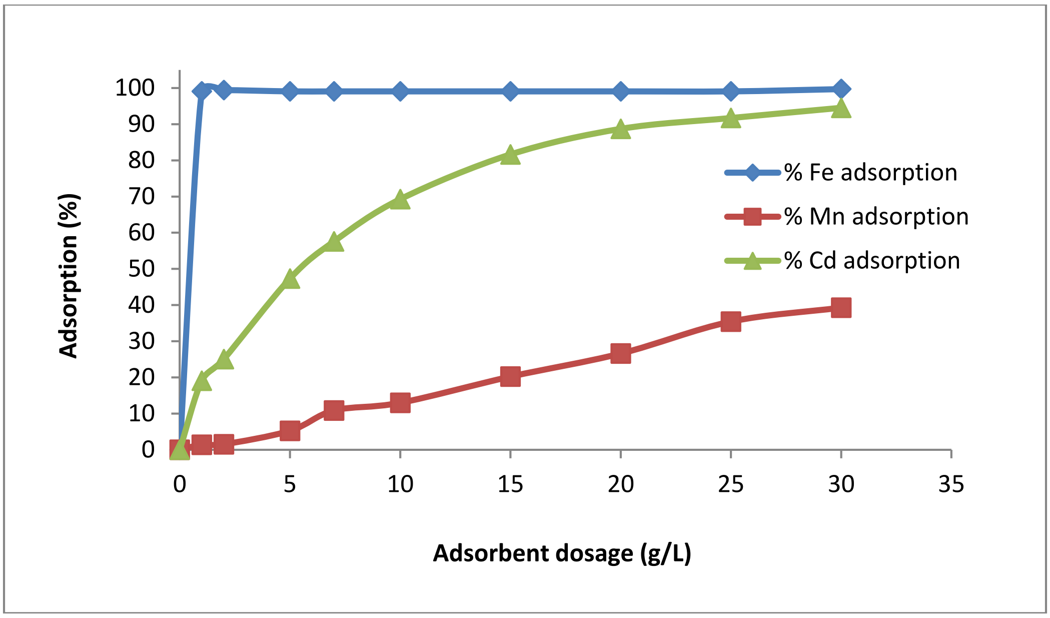


Fig. 4. Effect of adsorbent dose on the metal adsorption of soil
(Temperature: 25 °C, Contact time: 40 min for Fe and Mn, 20 min for Cd, Shaking rate: 150 rpm,
Initial metal concentration: 100 mg/L, pH: 6.66 (Fe + soil), 6.68 (Mn + soil), 8.11 (Cd + soil))

Therefore, it is thought that the clay was more efficacious than the carbonate on the Cd adsorption. High clay content resulted in the high Cd adsorption on the soil due to the interaction of negatively charged sites (Liu et al., 2018) and cationic species. Consequently, the adsorption of elements on the soil is extremely relevant to the soil characteristics.

3.3. Environmental effects of Cd accumulation/leaching and excess nitrate in soil

High Fe and Mn adsorption with the high soil pH and calcium carbonate content allow the deficiency of micronutrients in plants and decrease in product quantity in time. If there is no restriction on the application of nitrogen fertilizer despite the loss of product, excess nitrate levels in the soil will be unavoidable. Irrigation in the area will accelerate the nitrate leaching to groundwater (Spalding et al., 2001; Chilundo et al., 2018). Irrigation will also prompt the Cd movement in the soil leading to groundwater contamination The distribution and availability of heavy metals in soils is important when assessing the environmental quality of an area, since increased concentrations in soil, water and plants pose a serious threat to human and animal health (Jelic et al., 2011; Shaheen and Iqbal, 2018). The application of pesticides and especially phosphate fertilizers are important sources of Cd contamination in soil (McCauley et al., 2009; Lombi et al., 2000). In present study, high Cd adsorption is thought to be an essential factor that determined the amount of cadmium available for leaching and uptake. Whereas leaching poses a threat to groundwater quality, accumulation may have an adverse effect on soil biological processes (Jami Al-Ahmadi et al., 2018). Thus, it is of paramount importance to give an accurate description of the sorption process when the environmental impact of cadmium contamination of soil needs to be assessed (Boekhold, 1990). It is suggested that Cd adsorption on the soil will allow Cd accumulation on the plants while reducing its leaching to groundwater. According to data from our unpublished studies, Cd concentration in the groundwater was found below the detection limit in the region. Cadmium is a biotoxic heavy metal and can be enter the human food chain. However mobile characteristic of Cd and excessive irrigation in agricultural soils constitute also a risk for groundwater contamination.

Some metals in the soil such as Fe and Mn are essential for plant growth and their availability amounts in plant could be significantly affected by the soil properties. Generally loss of plant yield occurs if they are deficient or adsorbed onto inorganic sites in the soil. Extractable iron decreases with higher soil pH and calcium carbonate content. Similarly, manganese deficiency is often seen in plants grown on calcareous soils with higher soil pH (Jelic et al., 2011). Our adsorption results showed that Fe and Mn adsorption on soil increased with clay and $CaCO3$ contents of the soil. In this case iron and manganese deficiency may be expected in plants because of their adsorption to specific sites of the soil components. It is supposed that an important environmental problem will arise at this stage. Loss of yield in plants reduces nitrate uptake from the soil.

Salinity as another important problem in the soil is also accelerating yield loss (Bilgili et al., 2017; Flowers and Flowers 2005; Kendirli et al., 2005; Munns and Gilliham 2015). The nitrogen fertilizer added to the soil cannot be consumed by the plant and eventually nitrate leaching to groundwater occurs due to its mobile ion nature and excessive irrigation in the area (Chilundo et al., 2018).

Table 2. Freundlich and Langmuir isotherm constants for metal adsorption on soils

	Freundlich constants					***Langmuir constants***				
Soil	***K_f (mg/g)***	***log K_f***	***1/nf***	***n***	***R^2***	***Q_0 (mg/g)***	***$1/Q_0$***	***B (L/mg)***	***$1/Q_0*b$ (g/L)***	***R^2***
	Cd									
İsaören	0.67	-0.18	0.60	1.67	0.8	2.75	0.36	2.39	0.15	0.99
Maşuk	0.74	-0.13	0.42	2.38	0.8	2.46	0.41	1.99	0.20	0.99
Aşık	1.01	0.01	0.42	2.38	0.7	2.83	0.35	17.16	0.02	0.99
	Fe									
İsaören	16.63	1.22	2.34	0.43	0.95	0.45	2.22	9.58	0.23	0.85
Maşuk	4.09	0.61	1.83	0.55	0.92	0.62	1.62	9.34	0.17	0.69
Aşık	9.20	0.96	2.38	0.42	0.95	0.41	2.42	7.34	0.33	0.65
	Mn									
İsaören	1.56	0.19	0.46	2.16	0.99	3.13	0.32	0.20	1.57	0.95
Maşuk	2.18	0.34	0.46	2.16	0.98	2.59	0.39	0.15	2.53	0.97
Aşık	1.35	0.13	0.47	2.14	0.99	3.21	0.31	0.29	1.07	0.95

Thus, the nitrate pollution in groundwater (Yesilnacar and Gulluoglu 2008) and salinity in soil (Bilgili et al., 2018) were important environmental problems in the region. High nitrate levels in groundwater samples from different wells in 2016 (Yesilnacar and Gulluoglu, 2008) and salinity problems (Atasoy, 2008) were determined in the region. NO_3-N concentrations in the wells were generally between 5 and 30 mg/L; but in two wells 30 mg/L was exceeded. High Fe and Mn adsorption phenomena is thought to indirectly affect the increase in nitrate concentration in soil and with the influence of excessive irrigation, leaching nitrate will induce the groundwater pollution.

4. Conclusions

Cd adsorption gave a better fit to the Langmuir model ($R^2 \geq 0.99$) while Fe adsorption was better matched to the Freundlich model ($R^2 \geq 0.92$). Mn adsorption isotherms fitted well with both the Freundlich and the Langmuir models ($R^2 \geq 0.95$). The maximum Fe, Mn and Cd adsorption was found on Isaoren, Maşuk and Aşık soils with Kf values of 16.63, 2.18 and 1.01, respectively. While the carbonate content of soil showed a higher affinity than clay for Fe and Mn, the clay was found more efficacious than the carbonate on the Cd adsorption.

It is suggested that Cd adsorption on the soil will allow Cd accumulation on the plants while reducing its leaching to groundwater. High Fe and Mn adsorption with the high soil pH and calcium carbonate allow the deficiency of micronutrients in plants and decrease in product quantity in time. Salinity is another important problem in the soil accelerating the yield loss.

Loss of yield in plants reduces the nitrate uptake from fertilizer and nitrate leaching to groundwater occurs due to its mobile ion nature and excessive irrigation in the area. Consequently, carbonate-rich clayey soils can prevent the Cd leaching through the groundwater but may trigger the nitrate contamination.

Acknowledgements

This study was funded by the Scientific Research Projects of Harran University (HUBAK projects no: 14177 and 15106). The author thanks to Prof. Dr. M. Irfan Yesilnacar for his advice.

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