IOSR Journal of Agriculture and Veterinary Science (IOSR-JAVS)
e-ISSN: 2319-2380, p-ISSN: 2319-2372. Volume 10, Issue 12 Ver. II (December 2017), PP 57-62
www.iosrjournals.org

Effects of Rivers Slop and Soil Depth on Total Copper Concentration in Some of Central Provinces of Iraq

[1]Raid Shaalan Jarallah, [2]Bahaa Hussein Fadel Al-mayaly *
University of Al-Qadisiyah
College of Agriculture Department of soil science and water resources
Corresponding Author: Bahaa Hussein Fadel Al-mayaly

Abstract: *Aiming to study the soil depth and rivers slop effects on total copper concentration in Middle Euphrates River Region that represent in the mesopotamia plain, soil pedon samples of cultivated territory that adjacent to rivers were taken. The seregions are located in provinces of: Karbala, Babylon, Najaf, Diwaniyah, and Al-Muthana. Teen soil pedons were taken of areas that adjacent to the main Euphrate River, the Al-Hilaa, and the AL-Daghara Rivers in these provinces. Soil pedons of areas that on the banks or close to the main Euphrates River were taken of counties of Twarije, Kufa, Gamas, and Al-Samawa. In the same way, soil pedons of Missaib, Hashmiah, Diwaniyah, and Rumitha are adjacent to the Hilla River and soil pedons of Al-Daghara and Affak belongs to the area of Al-Daghara River. Results showa reduction in total copper concentration for all of the tested soil pedons directly related with the depth. Total copper concentration values are the highest at the surface layer and reduce as going depth except for soils of Al-Samawa and Al-Rumitha as aresult of polluted with dranges water and sewage that added to the rivers. Aggregate copper concentration values are fluctuated between 5.710 mg.kg^{-1} and 41.139 mg.kg^{-1}in all of the studied soils.*

Keywords*: Soil copper, Soil pedon, River slop, copper reduction, total copper.*

Date of Submission: 15-12-2017 Date of acceptance: 31-12-2017

I. Introduction

Total soil content of copper is between (5 and 50) ppm. It could be reached 100 ppm sometimes. (1), (2). found that the total soil content of copper is fluctuated between 55- 70 mg.kg^{-1} of soil, and most of which is found in composition of primary metal crystals. Copper concentration in soil solution is very little; it is no more than ($1*10^{-8}$) to ($60*10^{-8}$) molar. Copper an element that is not easy to move in the soil since it is strongly associated with the soil separators. It concentration is higher as going up closer to the surface and gets reduced as going depth (3), (4), (5). Organic matter is one of the factors that affecting copper concentration. More than 98% of the soluble copper is strongly attached to organic materials forming organic complexes that are unavailable to plants. These complexes reduce the movement of copper down. Therefore, it is stayed in and close to the surface of the soil body. Soil copper forms are divided to:

- Soluble copper in soil solution, which is the least quantity of copper forms compared to other.
- Copper exchangeable on surfaces of clay minerals and organic maters, which is available to plants. It is in balance with soil solution copper.
- Fixed copper, which is fixed between crystalline metal plates.

The highest concentration of soil copper is found in crystalline plates of the elementary and secondary metals . Cu_2S, $CuFeS_2$, Cu_2O, $Cu(OH)_2CO_3$, $CuSiO_3.2H_2O$, and $Cu(OH)_6SO_4$ are the most important minerals that contain copper. This study was conducted to find out the existence of copper in different levels of cultivated soils in central the Euphrates River in Iraq and the role of depth and rivers declivity on its concentration. A few studies have been conducted in this area of Iraq about copper forms and their levels in calcareous soils.

II. Materials and Methods

Soil pedons were determined in cultivated soils close to the main Euphrates River and its branches (Hilla and Al-Daghara rivers) in provinces of Karbala, Babylon, Najaf, Diwaniyah, and Al-Muthana. 10 soil pedons were made in the mentioned provinces as followed: Soil pedons of adjacent area to the main Euphrates River were digged on counties of Twarije, Kufa, Gamas, and Al-Samawa, soil pedons of Missaib, Hashmiah, Diwaniyah, and Rumitha were done onsoils that are close to the Hilla River, and soil pedons of Al-Daghara and

* Part of MSc thesis for the second author

Affak are belongs to the area of Al-Daghara River. Soil specimens were taken of each diagnostic pedon level for laboratory examinations. Assessments of physical characteristics were done according to the following mentioned methods and their values are in the tables (1, 2, and 3). Soil minutes volumes test was done by the pipette method to assess soil separators according to Day method (6). Virtual density was estimated by Core Sampler method (6). In the same way, chemical characteristics were estimated according to the following methods and their values are in the tables (4, 5, and 6). Electric connectivity in an extract soil to water (1:1) was measured by an Electrical Conductivity Bridge device (7). Potential of hydrogen (pH)of an extract soil to water (1:1) was assessed by using pH-Meter device (7). Exchange capacity of positive ions were measured by ammonium acetate method 1.0 molar at (pH=7) (8). Soil organic matter was estimated by using the method of wet digestion by titrationit with ammonium ferrous sulphate according to Wikelly black methods (7). Gypsum was estimated by acetone sedimentation method (9). Carbone minerals were estimated by using Cacimeter device that based on calculation of Carbon dioxide that resulting of hydrochloric acid reaction 3N, which diluted with carbonates (10). Positive soluble ions of K^+, Na^+, Mg^+, Ca^+ in extraction (1:1). Ca^+ and Mg^+ were estimated by the titration method by using Na_2 EDTA (11).Using a flame photometer device, K^+ and Na^+ were assessed (9). Negative soluble ions, carbonate and bicarbonate were measured by titration with On the other hand, chloride measured by titration with of $AgNO_3$(11). Carbonates were measured by using fogmethod with $BaCl_2$, then using the Spectrophotometer (6).

Total copper concentration assessed through digesting each soil sample by mixture of hydrofluoric and acids according to (10), then measuring it leachate using the atomic absorption device.

Statistical analysis: Data was statistically analyzed (12) computing program.

Table (1) Some of the physical characteristics of the soils that were taken of the main Euphrates River adjacent soils.

	Location	Depth Cm	Soil Separators mg. kg^{-1}			Soil texture	Bulk Density Mg. m^{-3}
			Silty	Loam	Clay		
1	Twarije	0-32	220	420	360	Clay loam	1.40
2		32-62	220	540	240	Silty loam	1.38
3		62-86	290	540	260	Loamy	1.42
4		86-120	310	440	250	Loamy	1.43
5	Kufa	0-31	210	440	350	Clay loam	1.39
6		31-60	180	370	450	Silty clay loam	1.42
7		60-120	270	450	280	Loamy	1.42
8	Gamas	0-49	240	510	250	Silty loam	1.38
9		49-90	240	385	375	Clay loam	1.42
10		90-115	320	430	250	Loamy	1.43
11	Al-Samawa	0-33	190	340	470	Clay	1.39
12		33-58	160	415	425	Silty clay	1.38
13		58-99	215	430	355	Clay loam	1.41
14		99-120	225	405	370	Clay loam	1.42

Table (2) Some of the physical characteristics of the soils that is adjacent to the Hila River.

	Location	Depth Cm	Soil Separators mg. kg^{-1}			Soil texture	Bulk Density Mg. m^{-3}
			Silty	Loam	Clay		
1	Missaib	0-39	250	300	450	Clay	1.41
2		39-64	165	410	425	Silty clay	1.40
3		64-98	165	440	395	Silty clay loam	1.40
4		98-125	166	450	384	Silty clay loam	1.41
5	Hashmiah	0-34	280	460	260	Loamy	1.40
6		34-62	205	440	355	Silty loam	1.42
7		62-115	300	470	230	Loamy	1.43
8	Diwaniyah	0-35	166	450	393	Silty clay loam	1.39
9		35-69	168	460	372	Silty clay loam	1.40
10		69-130	220	410	370	Clay loam	1.42
11	Rumitha	0-49	190	405	405	Silty clay	1.38
12		49-72	170	410	420	Silty clay	1.39
13		72-100	170	445	385	Silty clay loam	1.40

Table (3) Some of the physical characteristics of the soils that is adjacent to the Al-Daghara River.

	Location	Depth Cm	Soil Separators mg. kg^{-1}			Soil texture	bulk Density Mg. m^{-3}
			Silty	Loam	Clay		
1	Al-Daghara	0-24	210	360	425	Clay	1.39
2		24-54	175	415	410	Silty clay	1.40
3		54-85	180	400	420	Silty clay	1.41

4		85-110	165	440	395	Silty clay loam	1.41
5	Affak	0-21	220	520	260	Silty loam	1.38
6		21-47	210	380	410	Clay loam	1.42
7		47-76	230	375	395	Clay loam	1.43
8		76-110	195	435	370	Silty clay loam	1.42

Table (4) Some of the chemical characteristics of the soils that is adjacent to the main Euphrates River.

	Location	Depth	EC ds.m^{-1}	PH	Soluble ions Cmolc.kg^{-1}								CEC ds.m^{-1}	Carbonates metals	O.M	Gypsum
					Ca^{+2}	Mg^{+2}	Na^{+2}	K^{+1}	SO_4^{-2}	Cl^{-1}	HCO_3^{-1}	CO_3^{-1}		Gm.kg^{-1}		
1	Twarije	0-32	4.50	7.78	1.40	1.05	2.46	0.033	0.60	1.70	0.53	Nill	27.83	239	11.61	4.16
2		32-62	2.99	7.71	0.9	0.65	1.65	0.032	0.42	0.99	0.20	Nill	33.12	221	9.20	4.38
3		62-86	3.49	7.80	0.92	0.91	1.94	0.029	0.48	1.10	0.30	Nill	23.36	235	7.41	1.13
4		86-120	2.578	7.75	0.81	0.55	1.61	0.030	0.40	0.97	0.21	Nill	22.67	216	7.00	2.26
5	Kufa	0-31	1.808	7.60	0.53	0.45	1.02	0.023	0.25	0.63	0.16	Nill	30.35	271	10.89	0.51
6		31-60	3.506	7.68	0.94	0.94	1.96	0.026	0.28	1.09	0.31	Nill	32.78	293	8.71	0.69
7		60-120	2.06	7.59	0.67	0.43	1.05	0.024	0.26	0.8	0.15	Nill	24.00	278	6.53	0.34
8	Gamas	0-49	2.224	7.80	0.87	0.82	1.79	0.020	0.38	1.22	0.27	Nill	33.54	255	11.23	0.90
9		49-90	3.154	7.72	0.84	0.78	1.75	0.062	0.37	1.20	0.26	Nill	30.06	286	8.37	0.49
10		90-115	2.46	7.85	0.78	0.53	1.26	0.031	0.29	0.89	0.20	Nill	23.81	269	7.15	0.81
11	Al-Samawa	0-33	2.57	7.65	0.82	0.56	1.63	0.030	0.40	0.97	0.22	Nill	41.31	292	15.30	3.43
12		33-58	4.00	7.59	1.38	0.87	2.13	0.035	o.58	1.37	0.34	Nill	37.53	262	12.08	2.81
13		58-99	3.20	7.63	0.91	0.89	1.76	0.017	0.37	1.20	0.26	Nill	33.19	230	9.18	2.23
14		99-120	2.05	7.60	1.24	0.92	2.38	0.029	0.53	1.50	0.34	Nill	34.40	246	7.30	0.87

Table (5) Some of the Chemical characteristics of the soils that is adjacent to the Hila River.

	Location	Depth	EC ds.m^{-1}	PH	Soluble ions Cmolc.kg^{-1}								CEC ds.m^{-1}	Carbonates metals	O.M	Gyps
					Ca^{+}_{2}	Mg^{+}_{2}	Na^{+}_{2}	K^{+1}	SO_4^{-2}	Cl^{-1}	HCO_3^{-1}	CO_3^{-1}		Gm.kg^{-1}		
1	Missaib	0-39	14.22	7.68	4.23	3.92	7.55	0.046	1.88	4.98	1.34	Nill	39.58	336	13.84	2.50
2		39-64	5.10	7.72	1.54	1.23	2.70	0.04	0.64	1.84	0.46	Nill	36.36	281	10.22	2.79
3		64-98	4.60	7.79	1.44	1.09	2.53	0.033	0.60	1.71	0.38	Nill	34.25	289	8.30	1.34
4		98-125	4.36	7.70	1.35	1	2.36	0.033	0.27	1.66	0.51	Nill	34.88	252	7.14	0.75
5	Hashmiah	0-34	7.40	7.63	2.03	1.70	4.13	0.032	1.05	2.66	0.63	Nill	21.36	270	9.78	1.69
6		34-62	10.74	7.69	3.22	2.82	5.86	0.039	1.43	4.03	0.87	Nill	23.00	278	6.29	2.38
7		62-115	1.832	7.61	0.59	0.39	0.88	0.022	0.22	0.69	0.14	Nill	22.18	246	6.00	1.08
8	Diwaniyah	0-35	5.19	7.38	1.55	1.20	2.83	0.034	0.65	1.89	0.42	Nill	33.65	294	12.73	0.76
9		35-69	8.18	7.46	2.41	2.14	4.66	0.045	1.10	3.30	0.16	Nill	34.12	132	8.25	0.85
10		69-130	6.62	7.42	2.32	1.46	3.63	0.032	0.97	2.41	0.52	Nill	31.65	240	7.12	0.46
11	Rumitha	0-49	3.69	7.55	1.22	0.87	2.38	0.026	0.53	1.54	0.32	Nill	36.28	278	14.12	0.28
12		49-72	3.32	7.51	0.91	0.85	1.78	0.02	0.38	1.22	0.28	Nill	37.40	246	11.45	0.56
13		72-100	4.14	7.63	1.26	0.94	2.40	0.024	0.54	1.56	0.33	Nill	33.74	228	8.26	0.24

Table (6) Some of the chemical characteristics of the soils that is adjacent to the Al-Daghara River.

	Location	Depth	ECds. m^{-1}	PH	Soluble ions Cmolc.kg^{-1}								CECds. m^{-1}	Carbonates metals	O.M	Gyps
					Ca^{+2}	Mg^{+2}	Na^{+2}	K^{+1}	SO_4^{-2}	Cl^{-1}	HCO_3^{-1}	CO_3^{-1}		Gm.kg^{-1}		
1	Al-Daghara	0-24	2.10	7.56	0.69	0.48	1.04	0.027	0.26	0.80	0.15	Nil	38.69	235	14.65	1.23
2		24-54	4.14	7.51	1.30	0.99	2.46	0.025	0.55	1.57	0.34	Nil	35.17	289	9.82	1.40
3		54-85	3.68	7.60	0.99	0.91	2.03	0.31	0.44	1.32	0.32	Nil	36.26	294	8.59	0.82
4		85-110	3.20	7.58	0.89	0.80	1.7	0.032	0.37	2.07	0.53	Nil	32.18	250	7.29	0.60
5	Affak	0-21	6.48	7.81	2.18	1.36	3.62	0.028	0.93	2.32	0.51	Nil	22.30	285	10.33	0.42
6		21-47	6.66	8.03	2.25	1.4	3.74	0.036	0.95	2.34	0.55	Nil	29.06	261	9.29	0.31
7		47-76	5.56	7.88	1.71	1.31	3.22	0.026	0.70	2.07	0.52	Nil	27.85	279	8.10	0.38
8		76-110	4.12	7.83	1.23	0.91	2.38	0.025	0.53	1.57	0.35	Nil	30.18	257	6.23	0.26

III. Results and Discussion

Total soil copper of the main Euphrates River adjacent soils:

Table (7) shows total copper concentrations of the soils soil that are adjacent to the main Euphrates River. There is a reduction in its concentration as going deep in soil body. The highest value of aggregate copper is at the first level of depth on Al-Samawa location (35.91) mg.kg^{-1}. The least value is at the second depth level on Kufa. On the other hand, the third depth level of Kufa County has a greater value than the second level, which is an exception along with the third level of Gamas County, which has also a greater value of total copper than the upper depth level, which is close to the ground water, table (3). The results in table (7) is consisted with what (13) (14) found, but not with the research of Jadoa who study copper situations in some of the Iraqi soils. According to his research, values of total copper is between (16.80- 57.85) mg.kg^{-1}, and he state that soil contents of total copper are varied from one location to another. He attributes that variation to the differences in mineral composition of the original soil and to the factors the compose it (15) (2). refer to that copper content of original soil and factors that compose soil are the main factors in determining total copper and its distribution in the soil body. Results presented that aggregate copper values are the highest at surface layer. This agrees with (16) (17). They state that copper is strongly attached to the organic matter compounding mineral organic components since there are especial locations to tightly linked copper to carboxylic group. Existence of high quantity of carbonate minerals and rising power of hydrogen limit unleashing copper and then block losing it from the soil. Samawa's soils soil has greater total copper content than other locations of the Euphrates River. This refers to that an increase in total copper content as going south with the river slop. This could due to the increases in adding pollutants to the river (Sewage and drain waste), which increase their accumulations with the river slop. There are significant differences among locations of the main Euphrates River counties and within location depth according to level of confidence (0.05).

Table (7) Total copper values of the soils that are adjacent to the main Euphrates River

	Location	Depth cm	Total copper mg.kg^{-1}
1	Twarije	0-32	21.210
2		32-62	16.172
3		62-86	10.403
4		86-120	8.621
5	Kufa	0-31	14.396
6		31-60	5.710
7		60-120	6.312
8	Gamas	0-49	12.960
9		49-90	7.236
10		90-115	7.831
11	Al-Samawa	0-33	35.915
12		33-58	28.203
13		58-99	15.627
14		99-120	11.416
LSD values: Location=0.0004*, Depth=0.0002* Location depth interaction=0.0007*			

Total soil copper of the Hilla's River adjacent soils:

Table (8) presents total copper concentrations of the soils soil that are adjacent to the Hilla River. Results showa reduction in its concentration as going deep in soil except for Diwania's pedons where the second depth levels have the greatest copper content as compared with other levels of depth of the same location. The highest total copper value is at the first depth level at Missaib county (30.68) mg.kg^{-1}. The lowest value is at the third depth level on Hashmiah county (7.35) mg.kg^{-1}. Soil content of total copper is varying from one location to another, which due to the differences in mineral composition of the original soil. Copper is strongly attached to soil separators. Thus, its movement into the soil is not easy, and then its level srise up close to the surface and drops as going down (18) (5). Aggregate copper values are the highest close to the surface and get declinedas going deep except for Diwana's pedons, which the second level has the highest copper content as compared with the upper level.in the soil leads to copper lacking since it by sedimentation it forming $CuCO_3$(19) (20). Missaib County has more total copper content than other counties, and this because it's high content of clay and organic matter, table (5). There are significant differences not just among locations of the Hilla River soils, but also within depth levels of each location using confidence level of (0.05).

Table (8) total copper values of the soils that are adjacent to the Hilla River.

	Location	Depth cm	Total copper mg.kg^{-1}
1	Missaib	0-39	30.68
2		39-64	22.267
3		64-98	20.416
4		98-125	14.290
5	Hashmiah	0-34	19.83
6		34-62	11.21
7		62-115	7.35
8	Diwania	0-35	19.715
9		35-69	21.366
10		69-130	14.398
11	Rumitha	0-49	23.630
12		49-72	20.528
13		72-100	12.419
LSD values: Location = 0.0004*, Depth = 0.0001* Location depth interaction =0.0005*			

Total soil copper of the Daghara's River adjacent soils:

Total copper concentration is presented in table (9). Results clearly show that copper concentration decreases with depth. The highest copper content value was recorded at the surface level of depth at Al-daghara county (41.13) mg.kg^{-1}. The least value was found at the fourth depth level on Afak County (10.41) mg.kg^{-1}. On Al-daghara location, the fourth level had higher copper content than the upper one because it is ground water limits table (9). This refers to the level of contamination that ground water causes. This situation led this depth level to has more copper content. Table (9) shows significant differences among and within locations using 5% confidence level. These variations are due to the changing in the original soil and to the effect of other factors in the soil (21) (22). For all of the studied locations, the highest value of gross copper is excited in the surface layer, table (9). This may due to the strongly attachment of copper with organic matters and carbons minerals (5) (23). Therefore, soils of the upper level have more copper concentration as compared with deeper levels for all of the studied soils. Values of total copper in all counties clearly suggest that total copper concentration is the highest at the surface layer and gets reduced as going deeper, tables (7,8,9). There is an increase in total copper concentration as the river slops down toward the south where it is stream flows to. The highest copper

concentration value is recorded on Rumitha County, which is located southern of the Euphrates River. The reverse was found at both of Daghara and Hilla Rivers because the contamination of the added waste to the river. This may also due to the lacking of water quantity supplied, which the contamination with this element comparing to the Euphrates River.

Table (9) Total copper values of the soils that are adjacent to the Al-Daghara River.

	Location	Depth cm	Total copper $mg.kg^{-1}$
1	Al-Daghara	0-24	41.139
2		24-54	33.530
3		54-85	20.467
4		85-110	22.810
5	Affak	0-21	26.910
6		21-47	21.731
7		47-76	13.521
8		76-110	10.416
LSD values: Location = 0.0004*, Depth = 0.0001* Location depth interaction =0.0005*			

References

[1]. Tisdle, S. L., W. L. Nelson, J. D. Beaton, and J. L. Havlin. (1997). Soil fertility and Fertilizers. Prentice. Prentice-Hall of Indea. New Delhi.

[2]. Wei XR, Hao MD, Shao MA. 2007. Copper Fretitizers effects on copper Distribution Vertical Transport in Soil. Gerderma. 138, 213-220.

[3]. Stangev, L. F., failingf, S., Kurbanov, Y., Matev, Z. Tanev. (1990). Agricultural Chemistry. Treanslated byNadim Micha Ishaq and Ibrahim Mohammed Ali. Baghdad University. College of Agriculture. (In Arabic).

[4]. Hassan, N. A., and Hassan, Y. A. (1990). Soil Fertility and Fertitizers. Ministry of Higher Education and Scientific research. Baghdad University. College of Agriculture. (In Arabic).

[5]. Al-Naimi, Saadullah., Najm. Abdullah. (1999). Fertilization and Soil Fertility. Ministry of Higher Education and Scientific research. University of Mosul. (In Arabic).[6]. Black, C. A. (1965). Methods of Soil Analysis. Part2 Chemical and Microbiological Properties. AM. Soc. Agron. Inc Madison. Wisconsin, USA

[6]. Page, A. L., R. H. Miller and D. R. Keeney (ed). 1982. Methods of Soil Analysis Part 2, 2nd (ed) Agron., 9, Publisher, Madison Wisconsin, USA.[8]. Chpman, H. D. (1965). Cation Exchange Capacity. In: C. A. black. (ED), Methods of Soil Analysis. Part2. Agron., Madison, Wis.

[7]. Richards, L. A. (1954). Diagnosis and Improvement of Saline and Alkaline Soil. USDA. Hand Book 60. USDA., Washington, DC.

[8]. Hesse, P. R. (1971). A Test Book of Soil Chemical Analysis. Chemical Publishing Co. Inc. New Yourk.

[9]. Jackson, M. L. (1958). Soil Chemical Analysis. Prentic Hall, Inc. Englewood, Cliffs, N. J.

[10]. SAS. (2012). Statistical Analysis Sysistem, User's Guide. Statistical. Version 9.1th ed. SAS. Inst. Inc. Cary. N. C. USA.

[11]. Mohammed, I. J. (1988). Chimical Behaiver of Zinc, Copper and Other Selected Nutrient Elements in some Iraqi Acids Soils. Ph.D. Thesis. State University of Chent, Belguim.

[12]. Ponizovsky, A. A., H. E Allen and A. J. Ackerman. (2007). Copper Activity in Soil Solutions in Calcareous Soils. Enciron. Pollut. 145: 1-6.

[13]. ISO, 17402. (2008). Soil Quality – Requirements and Guidance for the Selectionand Appliction of Methods for the assesment of Bioavailability of Contaminations in soil and soil materials. International Oranization for Standerization, Geneve Switzerland, 35p.

[14]. Smirnova, E. V., and G. V. Motuzova. (1985). Evaluation of the state Cu, Zn, and Mn in soils of the Sikhte-Alin Biosphare Preserve for Backround Monitoring. Vest. Moskovskogo University. Pochhvovedenia. 40 (4): 49- 56. Translated by Allerton Press, Inc.

[15]. Aguilar, R. (2011). Spatial Distribution pf Copper, Organic matter and PH in Agricultural Soils Affected by Mining Activities. Journal of Soil Sceince and Plant Nutrition, 11 (3), 125-145.

[16]. Maftoon, M., N. Kariman and F. Moshiri, (2002). Sorption Characteristics of copper (II) in Selected Calcareous Soils of Iranin Relation to Soil Properties Common. Soil Sci. Plant Analysis 33:2279-2289.

[17]. Kabata-Pendias, A. (2011). Trace Elements in Soil and Plants. CRC. Press, Taylor and francis Group.

[18]. Serrano, N., Alberich, A. Diaz-Cruz, J. M., Arino., Esteban, M. (2013). Coating Methos, Modifiers and Applications of Bismuth Sacreen-printed Electrodes. Trends in Analytical Chemistry 46: 15-29.

[19]. Nemati, K., Abu Bakar, N . K., Sobhanzadeh, E. and Abas, M. R. (2009). A Modificationof the BCR Sequential Extraction Procedure to Investigate the Potential Mobility of Copper and Zinc in Shrimp Aquaculture Sludage. Microchemical Journal, 92, 165-169.

[20]. Kot, F. S. (2009). Boron Sources, Speciation and its Potential Impact on Health. Reviews in Environmental Science andBiochnology: 3-28.

[21]. Fuentes, A., Liorens, M., Saez, J., Soler, A., Aguilar, M. I., Ortuno, J. F., AND Messegurer, V. F. (2004). Simple and Sequential Extractions of Heavy Metals from Different Sewage Sludges. Chemosphere, 54, 1039-1047. Hhtp//dx.doi.org/10.1016/j.chemosphere.2003.10.029.