Iraqi Journal of Agricultural Sciences –2026:57(7):2066-2075
P-ISSN: 0075- 0530 /E-ISSN: 2410-0862
DOI: https://doi.org/10.36103/r0yx6h29

The Mineral Composition of the Tigris River Sediments in Baghdad and Its Impact on the Adsorption and Desorption of Nickel.

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ABSTRACT

This study was conducted to investigate mineral composition of the Tigris River sediments in the province of Baghdad and its impact on the adsorption and release of nickel ten areas were selected for the study It extends from Al-Rashidiya in the north to Al-Mada'in in the south soil samples were taken from within the waterway and a mineral analysis of those sediments was conducted for three areas: the beginning, middle and end of the river in Baghdad Governorate, and the results showed the presence of Variation in the nature of the mineral composition, as the presence of the mineral of smectite, palygoriskite and mica minerals of both types of triple- and diocta (biotite and muscovite) was observed in the presence of real chlorite minerals and mica trioctahydra biotite in the clay models of those soils. and the results of the nickel adsorption and release experiment showed a decrease in the values of the binding energy and the maximum adsorption at the beginning of the study area, reaching 2.70 ml and 437.4 µg Ni^{+2} respectively in where they increased at the end of the study area to 5.55 mg^{-1} and 1162 µg Ni^{+2}.

Key Words: binding energy ,Carbonate, Clay, sand, silt.

Received: 16/11/2024, Accepted: 23/2/2025, Published: 31/7/2026

INTRODUCTION

Studies on sediment chemistry related to river basins have received great attention from researchers during the last decade in order to know and understand the nature of the materials transported through those rivers and their final estuaries represented by the oceans and sediment is formed in the river channels, which have been transported and deposited naturally and represent self-formation. These sediments are divided into bed material, and these consist of materials and particles of rough sizes that form The bottom layer and banks of these rivers and have importance in determining the morphology of the channels through which these waters flow and transport these sediments either in the form of a suspended or semi-suspended load, while the other part of these sediments are washing materials, which are soft particles transported over long distances just to be acquired those minutes begin to sedimentation (Al-Shahmani,2020). Using metallurgy is better than using the physical properties of those Sediments when tracking these sediments from their sources until they reach the estuary, and the study of the nature of the mineral composition of clay minerals for these sediments can give a very clear idea of the nature of the materials from which these materials originated, as the volumetric distribution of those particles can give a clear idea of the nature of the processes and factors that contributed to their distribution within the stream, as other factors affect the distribution and spread of these minerals, such as the speed of water flow. The severity of the torsions and the degree of slope on the nature of the formation of these minerals and their percentage within the same site, and many minerals can be affected by the nature and conditions of sedimentation, and carbons and iron oxides, as well as the spread and distribution of organic matter, are also affected by the nature of the movement of these sediments in the water way (Al- Khalil, 2020, Al-Shahmani, 2020, Issa, 2022). Most studies conducted by several researchers as a study of

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(Al-badran,. 2000). when studying the nature of clay minerals at selected sites of the Tigris River and the Shatt al-Arab indicate that the mineral clusters of clay are chlorite, apatite, montmorillonite, and kaolinite and remarkable amorphous silicate in addition to the presence of carbonate minerals of both active and inactive types (whose size is larger than the size of alluvial particles) in addition to the presence of crystalline and amorphous iron oxides The mineral composition affects the chemical and physical properties of the soils as well as affects the nature and behavior of the elements in those soils through the processes of sedimentation, adsorption and complexity (Al-Taee, and Al Maamouri. 2020). and to the importance of this topic, this study was conducted to identify the nature of the mineral composition of the Tigris River sediments within the province of Baghdad and its impact on the chemical behavior of nickel, which is one of the polluting elements as a result of what is thrown from factory waste and fossil fuel products, in addition to other industrial facilities built on the banks of the Tigris River such as electric power plants, in addition to the sewage that is dumped into the river in some areas of the study.

MATERIALS AND METHODS

This study included the collection of ten samples of river sediments from inside the Tigris River in Baghdad Governorate in the Rashidiya area to Al-Mada'in and as shown in Figure. (1) And from the areas that were not flooded during the time period of 8-9 in 2022 and after the drying up of a large part of the river. Physical and chemical analyses of these deposits were carried out as reported in (Jackson, 1979, Page, *et al*.,1982, Richards, 1954) as shown in Table (1) the mineral analysis of these deposits was als conducted after the separation of clay in three sites: Rashidiya, Dora power station and Al-Madain to find out the nature of clay minerals using X-ray technology. The properties of carbonate minerals in the study area such as the total and active quantity and surface area of these metals as mentioned. and the adsorption experiment of the nickel element was conducted by treating 5 g of these deposits with five concentrations of nickel element (0, 5, 10, 15, 20) By applying the single-surface Langmuir equation and extracting the values of the binding energy and the greatest adsorption in the study models, the aggregate release of nickel was carried out and by taking the last concentration coefficients and the successive extraction of nickel by adding DTPA and a volume of 20 ml as mentioned in (Lindsay and Norvell. 1978) and the process was repeated five times

Point	X	Y	Point	X	Y
S1	33.427749°	44.345548°	S6	33.282854°	44.3373034°
S2	33.388042°	44.358233°	S7	33.262965°	44.3375580°
S3	33.342997°	44.375862°	S8	33.259822°	44.518228°
S4	33.332186°	44.396104°	S9	33.233572°	44.518748°
S5	33.316024°	44.412573°	S10	33.097293°	44.569453°

Figure 1. Show Sampling places from study areas

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Table 1. Some chemical and physical properties of the studied models

Code	Station	Ec ds.ms-1	pH	CEC	Soil Clay	Silt	Sand	Soil Texture
S1	Al-Rashidya	3.54	7.1	19.7	635	235.0	130	S.L
S2	Al-Kadhimiya	4.87	7.3	21.3	598	250	152	S.L
S3	Medical City	5.31	7.2	22.5	607	240	153	S.L
S4	Al-Ahrar Bridge	7.32	7.4	26.1	520	220	260	S.CL
S5	Abu Nawas	6.11	7.5	23.6	620	183	197	S.CL
S6	Jadriyah	5.32	7.2	23.7	688	148.4	163.6	S.L
S7	Al-dawra Station	11.78	8.0	27.3	270	340	390	C.L
S8	Zafaraniyah	10.35	7.6	28.7	431	257	312	C.L
S9	Diyala Bridge	11.01	8.1	25.7	330	290	380	C.L
S10	Al-Madain	7.85	7.4	25.7	500	246	254	S.CL

RESULTS AND AISCUSSION

Mineral Analysis: The results of the X-ray diffraction analysis of the Rashidiya S1 model showed the presence of diffraction 14.03 anxtrom within the treatment of saturation with magnesium and air dried, which led to the treatment of saturation with ethylene glycol to widen its basal distance to reach 15.78 anxtrom within the two potassium saturation treatments heated to two temperatures of 350-550° C, thus confirming the presence of Smectite minerals within the muds of these sediments (Al-Jaf,, 2006, Al-khalil,. 2020, Al-Shammari, 2020). The continued presence of 14.03 anxtrom diffraction in all coefficients, accompanied by its third diffraction at the base distance of 5.77 anxtrom, confirms the presence of true chlorite in the examined model (Al-Watifi,. 2012). Palygoriskite in Rashidiya soil clays was also diagnosed by the presence of diffraction 10.52 Anxtrom in all treatments while mica minerals were diagnosed through the presence of diffraction 10.40 anxtrom in all treatments, which was accompanied by its second diffraction at the base distance of 4.92 anxtrom and medium intensity, which confirms the presence of mica minerals of both triple and dioctahydra (biotite and muscovite). The results also showed the presence of kaolinite in the model of the mentioned soil, through the appearance of diffraction 7.13 anxtrom within the magnesium saturation and air dried coefficients, ethylene glycol saturation, potassium saturation and heated to a temperature of 350 ° C (Al-Rawi and Razzaq. 2020). In the middle of the study area near the South Baghdad station S7, the results showed the presence of geode 14.25 anxtrom within the treatment of saturation with magnesium and dry air, which led to the treatment of saturation with ethylene glycol to widen the basal distance of the aforementioned diffraction to reach 16.06 Anxtrom, and then to return that distance to shrink recording 10.40 anxtrom within the two potassium saturation treatments heated to temperatures of 350 and 550 ° C, and confirmed the presence of fish minerals within the soil muds mentioned. Also, the high intensity of diffraction 10.40 anxtrom at the expense of diffraction intensity 14.25 anxtrom within the treatment of saturation with potassium and heated to a temperature of 350 ° C confirms that the minerals of Smectite within the soil clays of central Baghdad are originally inherited from mica minerals and are characterized by their properties, which are their high ability to stabilize potassium, and the high charge of their outer layers Highly layer charge. The results also showed the presence of diffraction10.52 anxtrom within the treatment of saturation with magnesium and dry air, and its continued presence within all treatments, confirming the presence of the mineral Palygoriskite within the soil clays mentioned. The results of Figure (3) also showed that mica minerals could be diagnosed during the appearance of diffraction 10.40 anxtrom in all treatments, which was accompanied by its second diffraction and medium intensity at the basal distance of 4.92 anxtrom, which confirms the presence of mica minerals of both triple and dioctahydra types (Muscovite, biotaite) and these results were consistent with many studies conducted on Iraqi soils (Al-khalil, 2020, Al-Shahmani,.2020, Al- Al-Watifi, 2012) The

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continued presence of diffraction 14.25 anxtrom in all transactions, which was accompanied by its second diffraction 7.25 anxtrom and its third diffraction 4.74 anxtrom confirms the presence of the real heat-resistant mineral chlorite in the clays of those soils, and these results came in agreement with (Al-Watifi,. 2012) during his study of the phenomenon of chloritization in some Iraqi soils. Just as the results of Figure (3) remained, the mineral kaolinite was diagnosed through the appearance of diffraction 7.25 anxtrom within the magnesium saturation and aerobically dry coefficients, sale of ethylene glycol, and radiation with potassium and heated to a temperature of 350 °C (Al-daini, and Naser. 2020). At the end of the study area at site S3, the results of Figure (4) showed the presence of diffraction 14.03 angstrom in all treatments, which was accompanied by its second diffraction at the base distance 7.13 anxtrom, and its third diffraction 4.77 anxtrom, confirming the presence of the real chlorite metal that is resistant to heat within the soil clays of Salman Pak (Al-Watifi, 2012). The results of Figure (4) also showed the presence of a diffraction of 40.10 Angstroms in all the coefficients. Which was accompanied by its second diffraction with weak intensity at the base distance of 4.92 anxtrom, confirming the presence of mica trioctahydra (biotaite) in the soil mud model (Al-Jaf, 2006, Al-Shammari, 2020). Kaolinite mineral in Salman Pak soil clays was diagnosed by the appearance of 7.13 angstrom diffraction in magnesium saturation and air-dry, ethylene glycol saturation, potassium saturation heated to 350 °C. Either the presence of 7.3 anxtrom diffraction within the potassium saturation treatment heated to a temperature of 550 °C is due to the second geode of the real mineral chlorite (Al-Rawi and Razzaq. 2020).

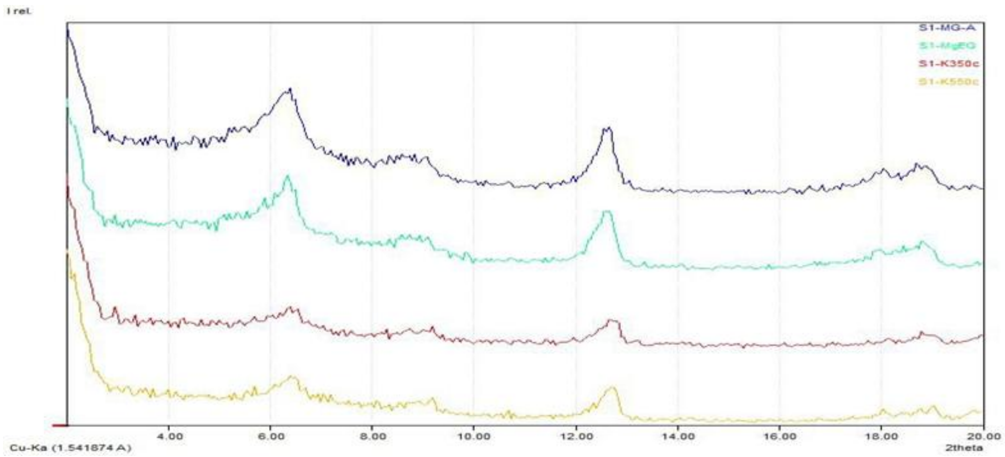

Figure 2. Show X-ray diffraction analysis of sediment model in Al-Rashidiya area at the beginning of the study area

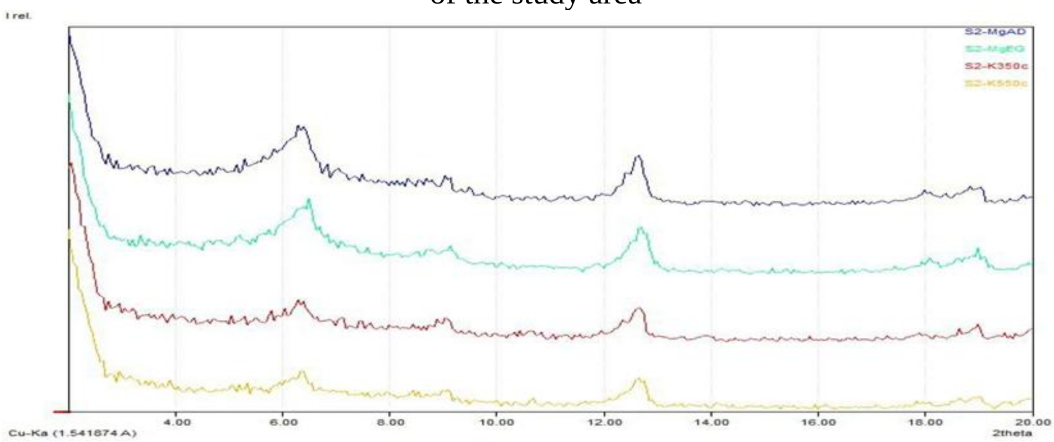

Figure 3. Show X-ray diffraction analysis of sediment model at South Baghdad station in the center of the study area

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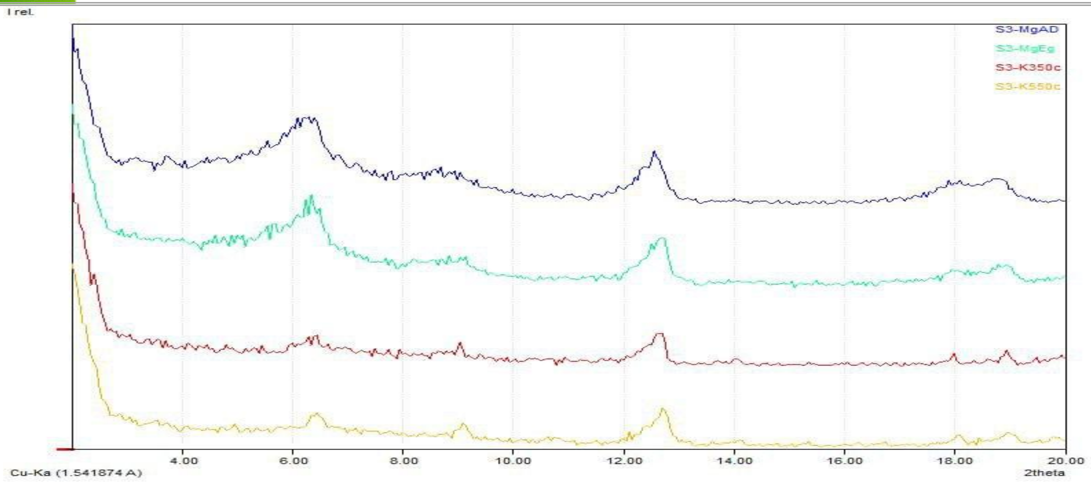

Figure 4. Show X-ray diffraction analysis of sediment model in Salman Pak area at the end of the study

Chemical properties of carbonate minerals : Table (2) shows some chemical properties of carbonate minerals in river sediments, as the results showed a noticeable variation in the total and active quantity of these minerals, as it increased at the beginning of the study area, as it was 211.21 and 110.3 $g.kg^{-1}$ respectively, where an increase in its quantity was observed at the end of the study area, reaching 238.3 and 158.30 $g.kg^{-1}$ respectively. The increase in the total and active quantity at the end of the study area may be attributed to the nature of the sedimentation conditions that contributed to the occurrence of chemical deposition of these minerals, and this was also contributed by the nature of the waterway and the movement of water, as most of the carbonate minerals are not inherited and were formed by pedogenic processes such as dissolution, sedimentation, transport and removal, especially with regard to the soft part represented by active lime (Al-Taee, and Al Maamouri. 2020).

Table 2. Show Properties of Carbonate Minerals in Study Area Sediments

Code	Station	Total carbonate minerals $g.kg^{-1}$	Active carbonate minerals $g.kg^{-1}$	Surface area of carbonate minerals
S1	Al-Rashidya	211.21	110.3	98.71
S2	Al-Kadhimiya	207.5	105.7	103.53
S3	Medical City	217.3	108.7	107.25
S4	Al-Ahrar Bridge	226.2	144.3	113.26
S5	Abu Nawas	218.5	139.7	115.81
S6	Jadriyah	222.5	130.8	107.52
S7	Al-dawra Station	238.3	158.3	113.38
S8	Zafaraniyah	233.3	148.5	117.53
S9	Diyala Bridge	235.5	155.3	110.51
S10	Al-Madain	235.5	145.6	120.35

As for the surface area of these minerals, it was noted that the surface area of these minerals increased with the increase of the soft part of them due to the small size of the particles, as well as the role of water in the process of dissolving and dismantling large particles into smaller minutes, as it reached at the beginning of the study area S1 Al-Rashidiya 98.71 $m2.g^{-1}$, while it was larger at the end of the study area 120.35 $m^2.g^{-1}$ This is consistent with the findings of (Al-Shahmani,.2020) who indicated that the surface area values of carbonate minerals increased with the increase in the soft part

Adsorption and release of nickel in river sediments of the study area: showed the results obtained from the application of the Langmuir equation in describing the adsorption and release state of the Ni^{+2} element of the river sediment soils of the study area and after it was treated with five concentrations of it are 0, 5, 10, 15 and 20 $mg.l^{-1}$. The results obtained showed that this equation could be used to describe the

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adsorption and release state of heavy elements in the light of the points drawn within the straight-line equation and the values of the release coefficient. The results shown in Table (3) and figures (5-14) showed that the values of the binding energy varied from one area to another, as it was the lowest value in the Rashidiya area and amounted to 2.70 ml. mg^{-1} Ni^{+2} while the highest value was in Al-Madaen area and amounted to 5.55 ml. μg^{-1} Ni^{+2} The variation in binding energy values may be attributed to the nature of the components of these deposits of clay minerals and total and active carbons Some studies conducted by researchers indicate the effect of the type of metal on the process of adsorption, sedimentation and liberation of elements from the soil, and this is confirmed by (Ibrahim, and Naser, 2020, Naser et al., 2020). The results also showed that the values of the binding energy have increased with the increase in the sediment content of total and active carbon minerals, and this indicates the nature of these metals in their ability to adsorb nickel and the possibility of nickel being exposed to fixation within the crystal structure of carbonate or replacing calcium ion in parts of the crystal structure of the metal or the possibility of these metals being affected by sedimentation conditions and the formation of crystal structures containing porous cavities with an internal surface area that contributed to the process of adsorption of the largest amount of it and this What he confirmed(Ahmed,et al.,2020).

Table 3. Shows the binding energy and the values of the maximum adsorption of nickel in the sediments of the study areas

Code	Station	Binding energy values K(ml μg^{-1})	Maximum adsorption values ($\mu g.g^{-1}$)	Equation
S1	Al-Rashidya	2.7	434.7	Y=0.0023X+0.00085
S2	Al-Kadhimiya	3.00	526.3	Y=0.0019X+0.00067
S3	Medical City	2.54	665.0	Y=0.0016X+0.00063
S4	Al-Ahrar Bridge	3.24	833.3	Y=0.0012X+0.00037
S5	Abu Nawas	3.69	714.2	Y=0.0014X+0.0038
S6	Jadriyah	3.24	833.3	Y=0.0012X+0.00037
S7	Al-dawra Station	5.55	1000	Y=0.0015X+0.00058
S8	Zafaraniyah	4.34	1000	Y=0.0010X+0.00023
S9	Diyala Bridge	4.87	1162.7	Y=0.00086X+0.00018
S10	Al-Madain	4.4	1000	Y=0.001X+0.00018

As for the values of the greatest adsorption, which expresses the number of sites where the element nickel was associated with those deposits, the results showed a variation in the rate of the values of the greatest adsorption, as the lowest value was 434.7 µg Ni^{+2} g^{-1} soil in the Rashidiya area and the highest value in the Diyala Bridge area, as it amounted to 1162.7 µg Ni^{+2} g^{-1} soil. Values with increasing amount of clay due to the high surface area possessed by this separator and as shown in Table (1) This corresponds to the findings of many researchers that heavy elements increase their adsorption with increasing soil content from the clay separator .

Figures showing the relationship between the concentration of nickel in the equilibrium solution C and its concentration C/X in the soil

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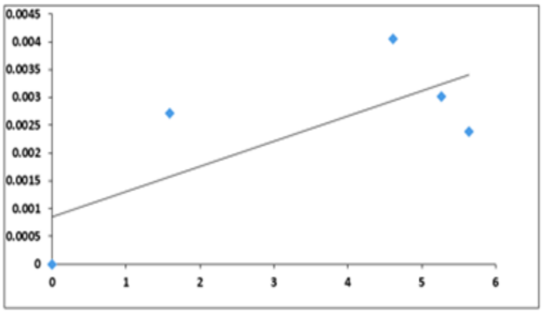

Figure (5) Al-Rashidiya soil

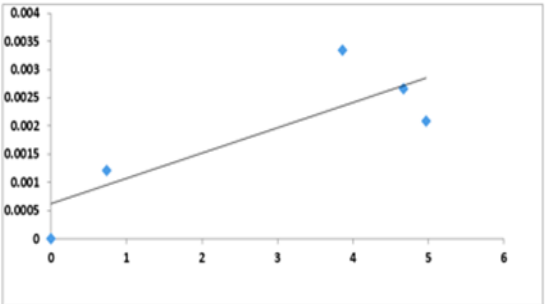

Figure (6) Al-Kadhimiya soil

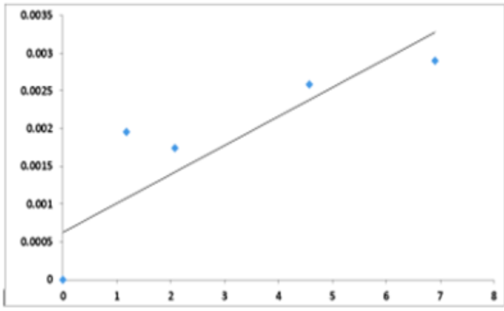

Figure (7) Soil of the City of Medicine

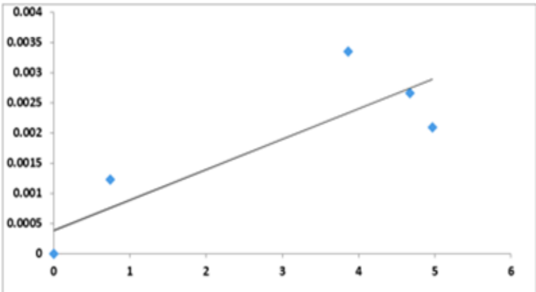

Figure (8) Al-Ahrar Bridge soil

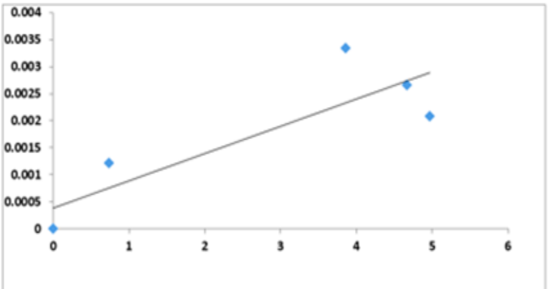

Figure (9) Abu Nuwas soil

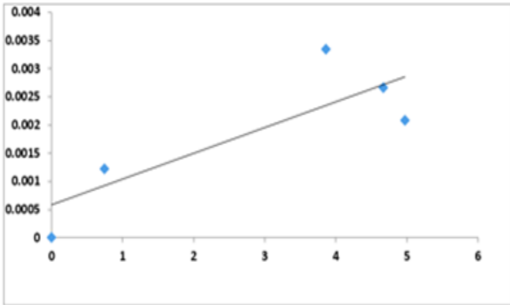

Figure (10) Al-Jadriya soil

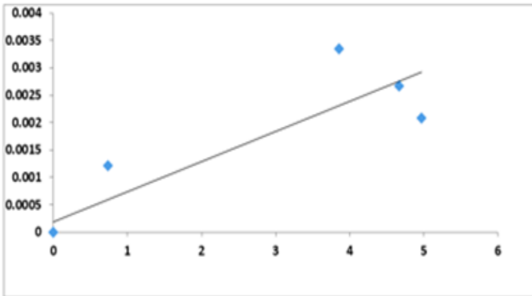

Figure (11) aldawra area

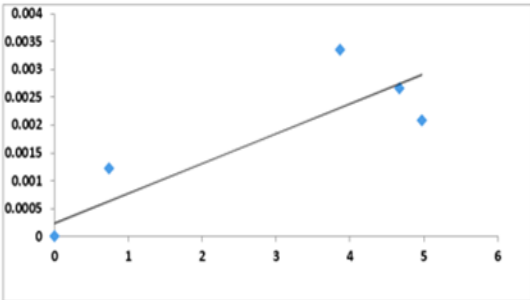

Figure (12) Zafaraniyah Soil

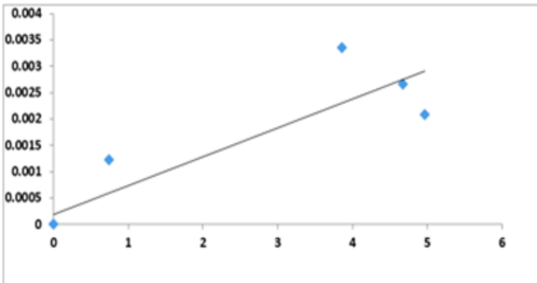

Figure (13) Diyala Bridge soil

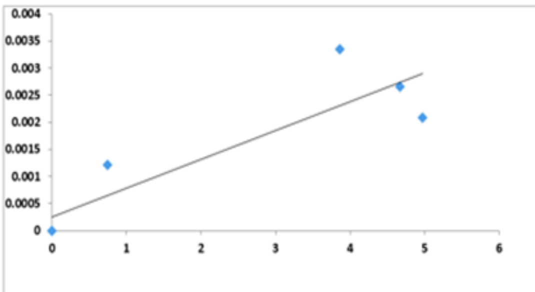

Figure (14) Madain soil

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P-ISSN: 0075- 0530 /E-ISSN: 2410-0862
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Table 4. Show concentrations of Aggregately Liberated Nickel

Code	Station	Nickel concentrations					Total
		L1	L2	L3	L4	L5	
S1	**Al-Rashidya**	6.20	4.11	2.15	0.94	0.00	13.40
S2	**Al-Kadhimiya**	5.33	3.88	1.58	0.60	0.00	11.31
S3	**Medical City**	4.32	3.18	1.53	1.15	0.60	10.78
S4	**Al-Ahrar Bridge**	3.55	2.56	1.82	1.00	0.00	8.93
S5	**Abu Nawas**	3.23	2.14	1.76	0.00	0.00	7.13
S6	**Jadriyah**	2.88	1.98	1.02	0.64	0.00	6.52
S7	**Al-dawra Station**	2.53	1.78	0.72	0.00	0.00	5.03
S8	**Zafaraniyah**	2.11	1.53	0.23	0.00	0.00	3.81
S9	**Diyala Bridge**	1.47	0.32	0.00	0.00	0.00	1.79
S10	**Al-Madain**	1.57	0.80	0.00	0.00	0.00	2.37

As for the release of the nickel element from these deposits, which evaluated its study in the last concentration of 20 mg.l^{-1} and after the washing process of the models and according to what was mentioned in (Lindsay and Norvell. 1978). and repeating the process for five times until reaching non-liberation, the results shown in Table (4) showed that the amount of nickel released collectively was the highest in the Rashdiya area, as it amounted to 13.4 mg.kg^{-}1 soil, and the lowest in the Diyala bridge area, as it amounted to 1.79 mg.kg^{-1}. The results also showed that the amount of liberated nickel was high in the first wash L1 in all those soils and then gradually decreased with the increase in the number of washing times, but differently from one soil to another, and this came in conformity with what was obtained from the adsorption experiment, as the adsorbed quantity increased with the increase in the amount of clay and carbonate minerals and the decrease in the amount of free from it with their increase in the equilibrium medium, and this came in conformity with what he found (Al-daini, and Naser. 2020, Al-Rawi, and Razzaq, 2020) who found that increasing the amount released from heavy elements in the soil is associated with an increase in the content of those soils of organic or mineral matter such as clay minerals and carbonates.

ACKNOWLEDGEMENT

The authors would like to express their sincere appreciation to all individuals and institutions that supported this study and contributed to the completion of the research work**.**

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

AUTHOR/S DECLARATION

We confi This study investigated the mineral composition of Tigris River sediments in Baghdad Province and its influence on nickel adsorption and release. The results revealed noticeable variations in mineralogical composition along the river, with the presence of several clay and mica minerals in the studied sediments. These mineralogical differences significantly affected the sediments' capacity to retain and release nickel, with adsorption efficiency generally increasing toward the southern part of the study area. rm that all Figures and Tables in the manuscript are original. Any Figures or images adopted from other sources were used with the necessary permissions for re-publication. All authors have approved the final version of the manuscript.

Ethical Clearance and Animal Welfare: Not applicable.

Funds: This research received no external funding.

AUTHOR’S CONTRIBUTION STATEMENT

All authors contributed to the study conception, data collection, laboratory analysis, interpretation of results, manuscript writing, and final approval of the submitted versio

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Iraqi Journal of Agricultural Sciences –2026:57(7):2066-2075
P-ISSN: 0075- 0530 /E-ISSN: 2410-0862
DOI:

التركيب المعدني لترسبات نهر دجلة في بغداد وأثرها في امتزاز وتحرر النيكل

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المستخلص

أجريت هذه الدراسة لمعرفة التركيب المعدني لترسبات نهر دجلة في محافظة بغداد وأثرها في امتزاز وتحرر النيكل تم اختيار عشر مناطق للدراسة تمتد من الراشدية شمالا الى المدائن جنوبا اخذت عينات الترب من داخل المجرى المائي وتم اجراء التحليل المعدني لتلك الترسبات لثلاث مناطق هي بداية ووسط ونهاية النهر في محافظة بغداد واظهرت النتائج وجود تباين في طبيعة التركيب المعدني اذ لوحظ وجود معدن السمكتايت والباليكروسكايت ومعادن المايكا بنوعيها ثلاثية و ثنائية الاوكتا (البايوتايت والمسكوفايت) في حيث لوحظ وجود معادن الكلورايت الحقيقي والمايكا ثلاثية الاوكتاهيدرا البايوتايت في نماذج اطيان تلك الترب. كما لوحظ تباين في كمية معادن الكاربونات الكلية والنشطة وأظهرت نتائج تجربة الامتزاز والتحرر للنيكل انخفاض قيم طاقة الربط والامتزاز الأعظم في بداية منطقة الدراسة اذ بلغت 2.70 مل. مايكروغرام$^{-1}$ و437.4 مايكروغرام Ni^{+2} على التوالي في حيث ازدادت في نهاية منطقة الدراسة اذ كانت 5.55 مل مايكروغرام$^{-1}$ و1162 مايكرو غرام Ni^{+2}.غم$^{-1}$ تربة.

كلمات مفتاحية: طاقة الربط، الكاربونات، الطين، الرمل، الغرين.