EFFECT OF CLAY MINERALS, CALCITE, AND ORGANIC MATTER ON ADSORPTION AND DESORPTION OF CADMIUM AND LEAD

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ABSTRACT

A Factorial experiment of CRD was conducted, to study and evaluate the effectiveness of Calcite, Bentonite, and Kaolinite minerals, as well as organic matter, on adsorption and desorption of Pb and Cd. Bentonite and kaolinite clay minerals were treated by adding of 20 % calcite and 5 % organic matter of the weight of the mineral, so that the final weight became 100 g per treatment. Treatments were incubated for 180 days after that, and treated with five concentrations of Pb and Cd, (0, 10, 20, 30, 40, and 50 µg ml^{-1}) as $PbCl_2$ and $CdSo_4$ respectively, The results showed the superiority of bentonite mineral over kaolinite in the maximum adsorption Xm and binding energy K by 137, 312.5, 20, and 193.5 % for Pb and Cd respectively. In the case of calcite mineral with both minerals, an increase in the binding energy and the greater adsorption were observed in the case of Cd and a decrease in the case of Pb with bentonite. In case of presence of organic matter with kaolinite, the maximum adsorption Xm for cadmium increased, as it was 204.08 µg g^{-1}, while in the case of bentonite with organic matter it was 111.1 µg g^{-1}. In the case of Pb, it reached 93.46 and 208.3 µg gm^{-1} for both minerals betonies and kaolinite, respectively. Regarding collective release, the results showed that the order of the treatment for the released Cd was as follows: $M_2 + O.M + C = M_2 + O.M > M_2 > M_2 + C > M_1 + C > M_1 > M_1 + O.M + C > M_1 + O.M$ In the case of released Pb, the order of treatment was as follows: M1 > M1 + C = M1 + O.M > M1 + O.M + C > M2 + O.M + C > M2 + C > M2 + O.M > M2.

Keyword: binding energy; maximum adsorption; langamire equation; mineral installation,

مجلة العلوم الزراعية العراقية- 2024:55(5):1657-1666 شريف وآخرون

تأثير معادن الطين والكالسايت والمادة العضوية في أمتزاز وتحرر الكادميوم والرصاص

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المستخلص

أجريت تجربة عاملية بأستخدم تصميم تام التعشية (CRD)، لدراسة وتقييم كفاءة معدن الكالسايت، معدن البينتونايت، معدن الكاوؤليانايت والمادة العضوية في امتزاز وتحرر الرصاص والكادميوم. تمت معاملة المعادن الطينية البنتونايت والكأوولنايت بأضافة 20% من الكالسايت و5% من المادة العضوية من وزن المعدن بحيث اصبح الوزن النهائي 100غم لكل معاملة. حضنت المعاملات لمدة 180 يوم. عوملت بخمسة تراكيز من عنصري الرصاص والكادميوم هي 0 ، 10 ، 20 ، 30 ، 40 ، 50 مايكروغرام . مل$^{-1}$ على شكل $PbCl_2$ و $CdSo_4$ على التتابع، طبقت معادلة لانكماير ذات السطح الواحد لوصف الامتزاز وأظهرت النتائج تفوق معدن البنتونايت على معدن الكأوولنايت في قيم الامتزاز الاعظم Xm وطاقة الربط K وبنسبة بلغت 137 ، 312.5 ، 20 ، 193.5 % لكل من الرصاص والكادميوم على التوالي، وفي حالة وجود معدن الكالسايت مع كلا المعدنين فقد لوحظ زيادة في قيم طاقة الربط والامتزاز الاعظم في حالة الكادميوم وانخفاض في حالة الرصاص مع البنتونايت، وفي حالة وجود المادة العضوية مع الكاوؤليانايت فقد زادت قيم الامتزاز الاعظم للكادميوم إذ كانت 204.08 مايكروغرام.غم$^{-1}$ اما في حالة البنتونايت مع المادة العضوية فقد كانت 111.1 مايكروغرام.غم$^{-1}$ أما في حالة الرصاص فقد بلغت 93.46 ، 208.3 مايكروغرام.غم$^{-1}$ ولكلا المعدنين البنتونايت والكأوولنايت على التوالي. اما بالنسبة للتحرر التجميعي فقد اظهرت النتائج ان ترتيب المعاملات بالنسبة للكادميوم المتحرر كان كالتالي: $< C + M_1 < C+ M_2 < M_2 < O.M+ M_2 = C + O.M + M_2$ $O.M + M_1 < C + O.M+ M_1 < M_1$ وفي حالة الرصاص المتحرر فكان ترتيب المعاملات كالتالي: $+ M_1 < O.M + M_1 = C + M_1 < M_1$ $M_2 < O.M + M_2 < C + M_2 < C + O.M + M_2 < C + O.M$.

الكلمات المفتاحية: طاقة الربط، الامتزاز الاعظم، معادلة لانكماير، تركيب معدني.

Received:13/8/2022, Accepted:18/12/2022

INTRODUCTION

Pollution is one of the most important problems for iraq with significant industrial activity, such as oil refineries, electric power stations, laboratories and industrial installations, as a natural result of the release of gas and fumigation from these enterprises with high concentrations of polluting elements such as Pb^{+2}, Cd^{+2}, Co^{+2}, Ni^{+2} and the soil is the final stop for these pollutants (2, 5, 23). The different soil components of clay minerals, carbonate minerals and organic matter contribute to reducing the impact of these elements through adsorption, deposition, oxidation and reductions, which leads to reducing the role of these elements in affecting one of the most important components of the ecosystem which is soil (3, 24). Most heavy metals except As, Sb, Sc as non-metallic and Mo, V as metallic elements are found in the soil solution as cations, so their chemical behavior (adsorption, deposition, fusion) depends on the negative charge density on the surface of the soil components (organic matter, carbonate minerals) where the negative charge is offset by a positive charge. The ion exchange process represents the release of a cation from the exchange surfaces of soil colloids into the solution and replacing another ion in its place. The cation exchange is regarded as reserves and is controlled by diffusion and preference. The exchange process is subject to the influence of important factors such as concentration, valency and ionic radius. The specific adsorption process of most pollutants elements tends to form covalent bonds with metal crystal ions and this depends mainly on the type of clay metal and the density of the negative charge found on the surface, this was also explained by the slow release of these polluting elements into the soil solution through the formation of complexities on the surfaces of these components and sometimes by the so-called contemporaneous fusion, which restricts the movement of these pollutants (26). Heavy metals such as Pb, Cd, Ni... etc. in the soil naturally as a result of the occurrence of pedogenic processes, erosion and weathering rocks containing certain percentages of those elements. The other source of the presence of these elements in the soil is storm dust and volcanoes, as well as the great role played by various industrial human activities through the combustion of fuel of various types and wastewater. The chemical behavior of these elements in the soil is also influenced by many factors, the most important of which are soil pH, organic matter, the quantity and quality of the prevailing clay mineral, containing oxides and cation exchange capacity (1, 16). The presence of heavy metals in the soil is similar to the presence of other elements in the soil and takes different forms they may be dissolved in the solution of equilibrium or adsorbed on the different surfaces of different soil components. The proportions of these components affect their effectiveness and activity and thus their relative movement in the soil and their availability for the plant (9). (10,14) found that the variation in the soil's ability to restrict or neutralize those polluting elements was due to the variation in the components of those soils of carbonate and organic minerals and that the type of clay mineral had a significant impact on the behavior of those elements in the soil. The polluting elements differ in the interaction with different soil components vary according to the type of element. In the case of organic matter, the arrangement of the elements is $Zn^{+2} < Cd^{+2} < Ca^{+2} < Pb^{+2}$. In the case of soil minerals, the arrangement is $Cd^{+2} < Zn^{+2} < Ni^{+2} < Pb^{+2}$ (15). To understand the chemical behavior and effect of clay minerals, carbonates and organic matter on adsorption and release of these polluting elements Pb and Cd into the soil, this study was conducted.

MATERIALS AND METHODS

Clay minerals (Bentonite and kaolinite) and calcite samples were collected from Iraqi Geological Survey Company, and diagnosed in the laboratories of the same company using X-ray diffraetometer (XRD) device type Phillips PW 1190. The chemical properties of mineral samples were estimated after their digestion by HF and HCL acids according to (25), (Table 1).

Table 1. Chemical properties of the minerals used in the study

Mineral properties	Bentonite	Calcite	Kaolinite	Unit
EC 1:1	3.72	4.31	1.33	dS m^{-1}
pH	5.21	8.68	6.03	-
Ca	8.80	158.00	6.30	g.Kg^{-1}
Mg	-	3.80	-	g.Kg^{-1}
Fe	2.70	0.40	2.00	g.Kg^{-1}
Cd	0.003	0.002	0.01	%
Pb	0.005	0.003	0.002	%

The collecting samples were air dried, crashed with wooden hammer, and passed through the sieve of 0.5 mm openings.The organic matter was also selected from one of the private factories affiliated to the General Authority for Agricultural Research which is grinded and passed through the sieve of 0.5 mm openings to obtain a homogeneous size, the characteristics are shown in Table (2). The study included the following treatments:

1- Kaolinite (M1)
2- Bentonite (M2)
3- Kaolinite (M1) + Organic matter (OM)
4- Bentonite (M2) + Organic matter (OM)
5- Kaolinite (M1) + Calcite (C)
6- Bentonite (M2) + Calcite (C)
7- Kaolinite (M1) + Organic matter (OM) + Calcite (C)
8- Bentonite (M2 + Organic matter (OM) + Calcite (C)

Table 2. Properties of Organic matter used in the study

Properties	Value unit
Organic matter	85 %
Humic Acid	12 – 13 %
Fulvic Acid	5 – 6 %
pH 1:5	5 – 6
EC 1:5	2 – 5 dS m^{-1}
C/N	41.10
Moisture Content	20 – 25 %
Total Nitrogen	1.2 – 2.0 %
Phosphorus P	0.2 – 0.4 %
Potassium K	0.4 – 0.6 %
Sulfur S	0.2 – 0.3 %
Calcium Ca	0.2 – 0.3 %
Magnesium Mg	0.1 – 0.15 %
Iron Fe	0.06 – 0.10 %

After conducting the grinding and sieving the pH of clay minerals, it was found necessary to standardize the pH of the clay minerals and this is achieved by washing minerals with a $CaCl_2$ solution (M1) and adjusting their pH using CaO at pH 7. The samples are then washed with distilled water three times and then washed with ethyl alcohol 95 %, until dissolved salts are removed, and this is confirmed by the follow-up of the chloride ion. As for Calcite it is washed once with distilled water and three times with ethyl alcohol 95%. After that, 100 g of each clay mineral has been dried and mix with 20% of calcite. Then mix with 5 % organic matter, then incubated for (120 days) four months at 28 ± 2 C^0 taking into account the addition of distilled water to maintain the condition of chemical equilibrium.

Isothermic adsorption

After incubation period, the adsorption experiment was conducted on the samples using the Langmuir equation to describe the adsorbents (c/x =1/kxm + c/xm). as each sample was treated with five concentrations of Pb and Cd (0, 10, 20, 30, 40 and 50 µg ml^{-1}), which were prepared using $PbCl_2$, $CdSO_4$, and the values of maximum adsorption Xm and binding energy k were extracted for each treatment.

Release Experience

To find out the ability of each of Cd and Pb to release, a study of the release of these elements was conducted by taking 10 g of each treatment and adding these elements to each treatments at a concentration 50 µg ml^{-1}, the materials are placed in plastic tubes of 50 ml with shaking for 24 hours, after that the sediments was separated from the solution and estimated the remaining Pb and Cd in the sediment and extracted using DTPA (21 , 22) for five consecutive times to determine the ability of these materials to restricting the movement of such pollutants. As for the solution estimates the concentration of the elements to determine the amount of elements adsorbed by the sediments.

RESULTS AND DISCUSSION

The results of Table (3, 4) and Figs. (1 - 16) shows, that there were a discrepancy in the behavior of the elements with those components, which are mainly included in the components of each soil of the world. Bentonite mineral has been observed exceed kaolinite mineral in the greatest adsorption (Xm) and the binding energy (K) in holding of Cd and Pb elements by (137 %, and 312.5%) for the Xm and (20% and 193.5%) for the K value. This is due to the high exchange capacity and surface area of bentonite mineral, which leads to provide more negative sites on the mineral surfaces. This is confirmed by (8). When calcite was present with both minerals, it was shown that the maximum adsorption values Xm were higher for Cd and lower for Pb with an increase of (5.3%) It was also observed that the average binding energy values for Cd were superior compared to Pb with an increase (40.4%). This may be attributed to the role of calcite in the process of Cd adsorption compared to Pb. This is due to the close radii of Ca and Cd. Since the radius of Cd and Ca are (0.97A^0 and 0.99 A^0) respectively. Therefore, the possibility of replacing Cd ion with Ca^{+2} at the sites of carbonate surfaces, this is confirmed by (17, 27). In the case of presence bentonite mineral with calcite, the results showed that there were differences in the chemical behavior of the two elements, as the values of binding energy and maximum adsorption were increased for Cd and decreased for Pb, and this confirms the result obtained in the treatment of kaolinite with calcite. When the organic matter was present with both minerals, it observed that there were a significant difference in the maximum adsorption values, of Cd which record (87.79 µg g^{-1}) in the kaolinite treatment with the organic matter, while its value decreased (204.08 µg g^{-1}) treatment of bentonite with organic matter. While lead recorded low values (83.33 and 93.46 µg g^{-1}) for bot treatments respectively. The high values appeared in the presence of organic matter, was attributed to the high cation exchange capacity of organic matter (300 Cmol charge kg^{-1}), which provides suitable sites for the adsorption of these ions on their surfaces, this was confirmed by (13, 19, 23).

Table 3. Cd adsorption

	Treatments	Xm	K
1	**Kaolinite (M1)**	**60.24**	**23.80**
2	**Bentonite (M2)**	**142.86**	**26.48**
3	**Kaolinite (M1) +Organic matter (O)**	**87.79**	**24.30**
4	**Bentonite (M2) +Organic matter (O)**	**204.08**	**27.50**
5	**Kaolinite (M1) +Calcite (C)**	**166.76**	**23.14**
6	**Bentonite (M2) +Calcite (C)**	**192.30**	**27.60**
7	**Kaolinite (M1) +Organic matter (O) + Calcite (C)**	**111.11**	**20.67**
8	**Bentonite mineral (M2 + Organic matter (O) +Calcite (C)**	**75.19**	**22.44**

Table 4. Pb adsorption

	Treatments	Xm	K
1	**Kaolinite (M1)**	**50.50**	**27.70**
2	**Bentonite (M2)**	**208.33**	**21.80**
3	**Kaolinite (M1) +Organic matter (O)**	**83.33**	**26.18**
4	**Bentonite (M2) +Organic matter (O)**	**93.46**	**26.12**
5	**Kaolinite (M1) +Calcite (C)**	**156.25**	**25.46**
6	**Bentonite (M2) +Calcite (C)**	**270.27**	**23.25**
7	**Kaolinite (M1) +Organic matter (O) + Calcite (C)**	**333.33**	**22.46**
8	**Bentonite mineral (M2 + Organic matter (O) +Calcite (C)**	**58.14**	**25.45**

Concerning to the values of binding energy values, results in Figs (1 - 16) shows, there were a significant difference in the binding energy values for both elements when they presence with the organic matter. It was observed that the values of the binding energy decreased with presence bentonite compared to the presence of kaolinite mineral for both elements, as the rate of decrease with the presence of Cd was (49%), while it was presence of Pb, increased with (20.4%), the reason for this is attributed to the properties of the element itself, as well as to the nature of the interaction between organic and mineral colloids, which is reflected on the behavior of the element itself. This was confirmed by (19) that the chemical behavior of any element depends on the nature of the interactions between the components that system and according to the conditions of the medium in which the element is found. The radius of the ions also has a significant impact on determining the correlation of those two elements, any component of the medium, whether it is the ionic radius.

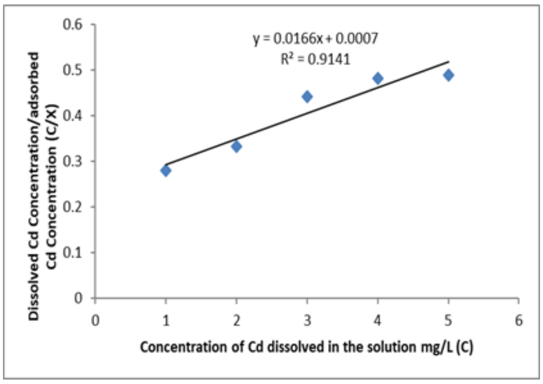

Figure 1. The relationship between Cd adsorption in the equilibrium solution and Kaolinite (M1)

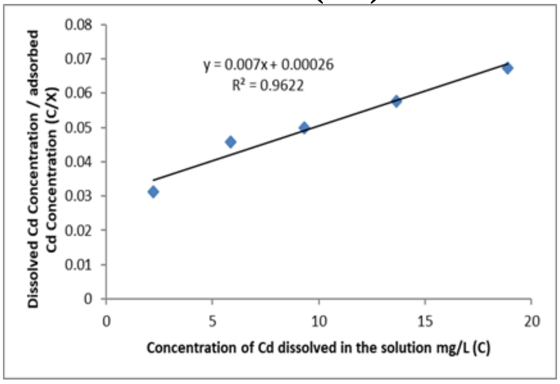

Figure 2. The relationship between Cd adsorption in the equilibrium solution and Bentonite (M2)

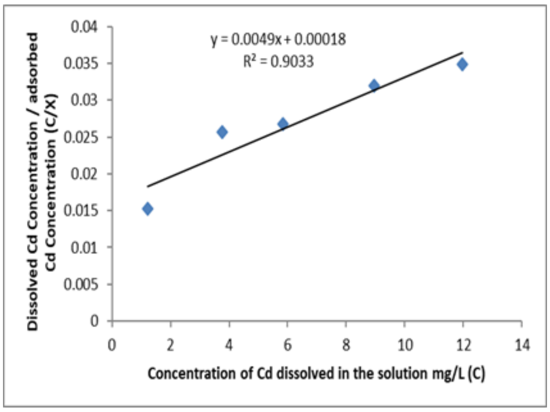

Figure 3. The relationship between Cd adsorption in the equilibrium solution and Kaolinite (M1) + Calcite (C)

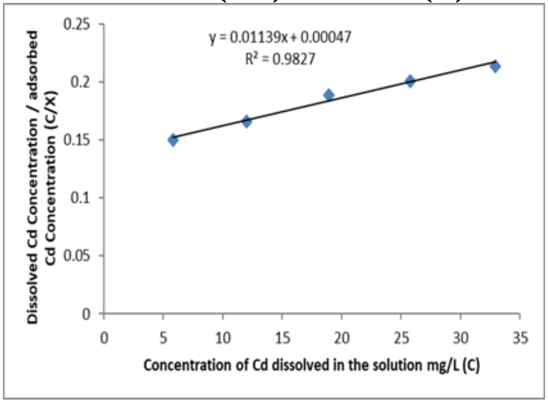

Figure 4. The relationship between Cd adsorption in the equilibrium solution and Bentonite (M2) + Organic matter (O.M)

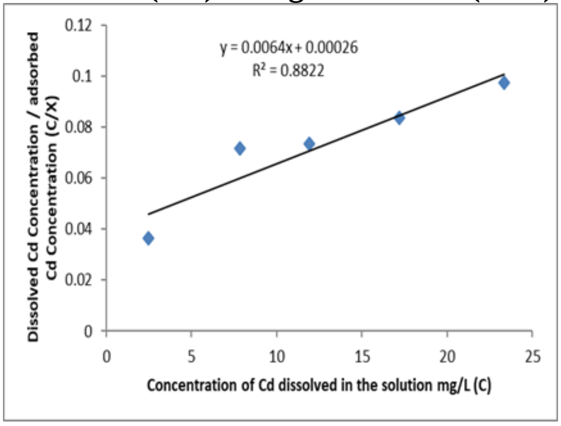

Figure 5. The relationship between Cd adsorption in the equilibrium solution, bentonite (M2) + Calcite (C)

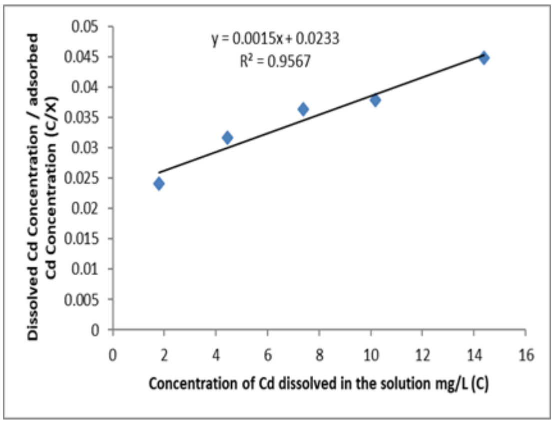

Figure 6. The relationship between Cd adsorption in the equilibrium solution, Bentonite (M2) + Organic matter (O.M) + Calcite (C)

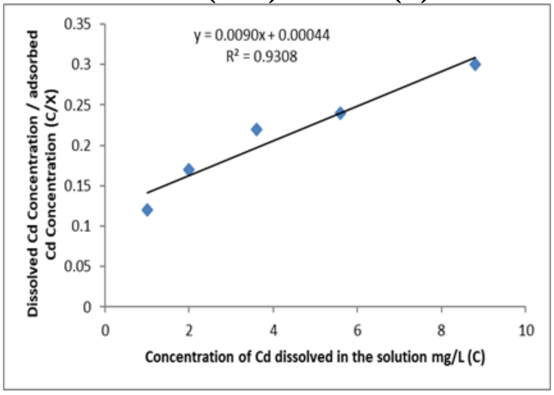

Figure 7. The relationship between Cd adsorption in the equilibrium solution and Kaolinite (M1) + Organic matter (O.M)

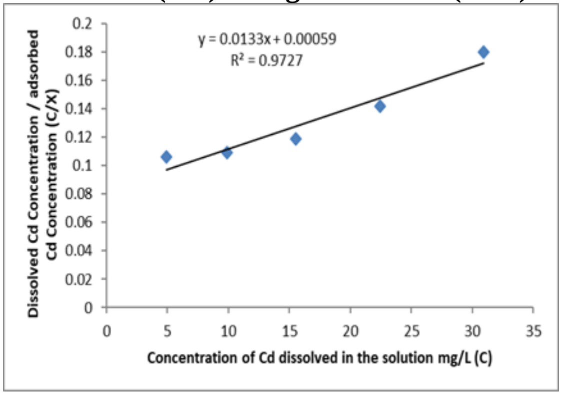

Figure 8. The relationship between Cd adsorption in the equilibrium solution and Kaolinite (M1) + Organic matter (O.M) + Calcite (C)

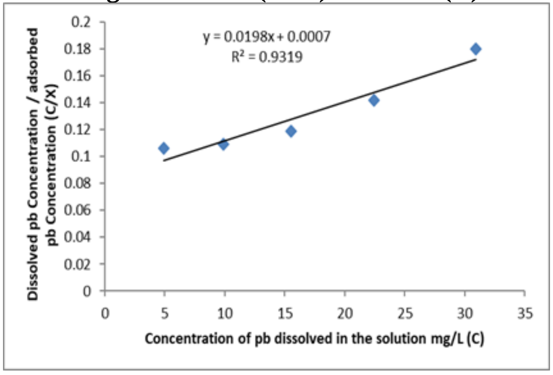

Figure 9. The relationship between Pb adsorption in the equilibrium solution and Kaolinite (M1)

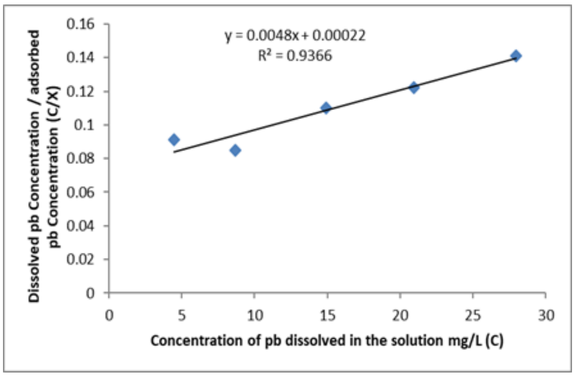

Figure 10. Relationship between Pb adsorption in equilibrium solution and Bentonite (M2)

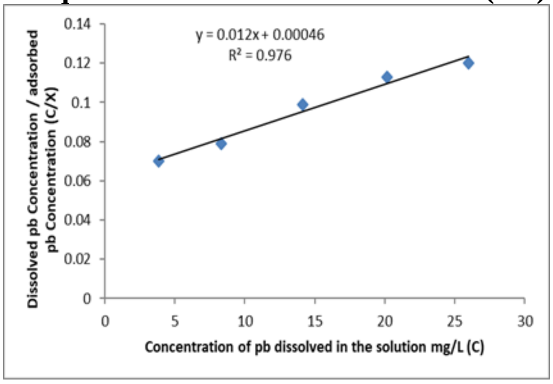

Figure 11. The relationship between Pb adsorption in the equilibrium solution and Kaolinite (M1) + Calcite (C)

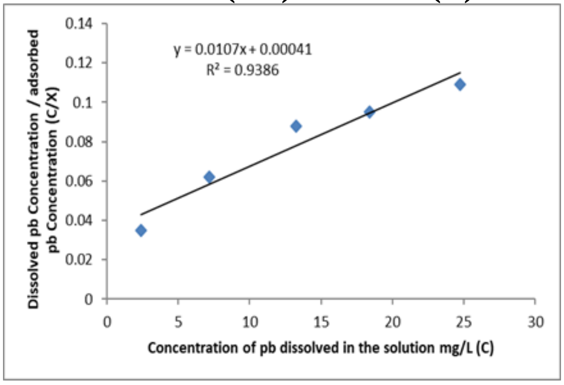

Figure 12. The relationship between Pb adsorption in the equilibrium solution and Bentonite (M2) + Organic matter (O.M)

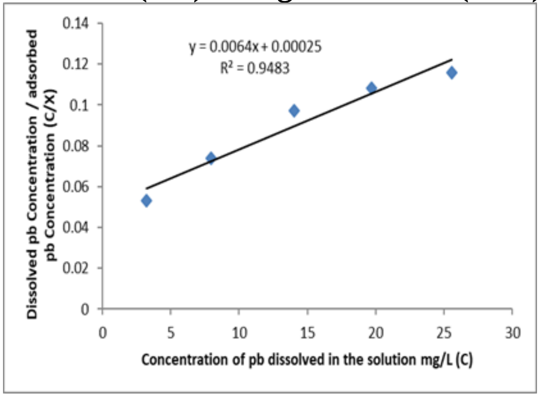

Figure 13. The relationship between Pb adsorption in the equilibrium solution, Bentonite (M2) + Calcite (C)

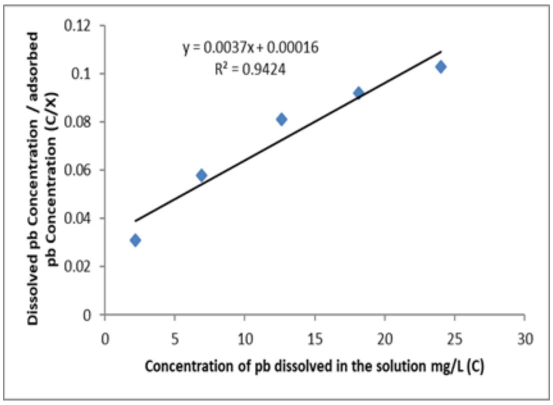

Figure 14. The relationship between Pb adsorption in the equilibrium solution, Bentonite (M2) + Organic matter (O.M) + Calcite (C)

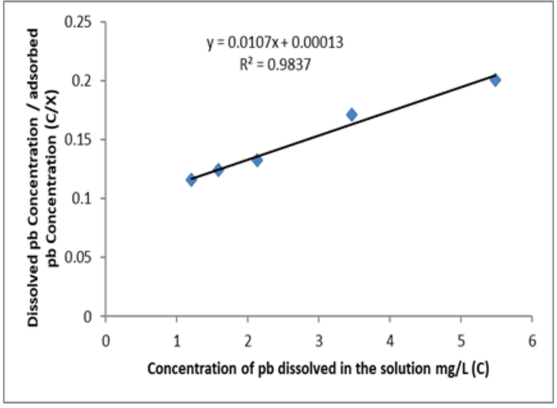

Figure 15. The relationship between Pb adsorption in the equilibrium solution and Kaolinite (M1) + Organic matter (O.M)

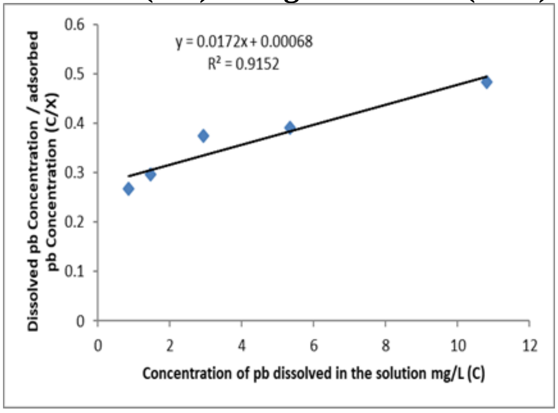

Figure 16. The relationship between Pb adsorption in the equilibrium solution and Kaolinite (M1) + Organic matter (O.M) + Calcite (C)

In case of presence all studied components together (organic matter, clay mineral and calcite), it were observed that there is a significant difference in the behavior of these two elements. In the case of Cd, it observed that the values of the greatest adsorption were increased (155.7%) in the treatment of presence bentonite with calcite and organic matter compared to the presence of kaolinite with these components. While the binding energy values were decreased (52.2%) in the case of presence of bentonite mineral with organic matter and calcite, compared to kaolinite mineral with those components. As for the element Pb, the results were in the same trend, as the maximum adsorption values increased in the case of presence of bentonite mineral with organic matter and calcite, compared to the treatment of kaolinite with these components, with an increase (360%). As for the binding energy, the decrease was (5%), and this attributed to the high cation exchange capacity of bentonite which provides lots adsorption sites on its surfaces compared to kaolinite. In addition to the layer of interactions between the organic matter and the clay mineral, there is also the affinity between the element and each component of the medium represented by the organic matter, clay minerals and calcite, this agrees with (1, 6, 20). As for the effect of clay minerals, calcite and organic matter and their interactions on the amount of Pb and Cd released. Figure (17) and Table (5, 6) shows the effect of kaolinite, bentonite, calcite and organic matter on the amount of Cd and Pb released during five stages of extraction. The results showed an increase in the amount of Pb released compared to the amount of Cd released in the presence of kaolinite, with an increase rate of (16.33%). While bentonite excelled in the release of Cd compared to the release of Pb at a rate (21.46%). In contrast to the bentonite mineral, which retained the largest amount of Pb at rate of 19.2 µg.gm^{-1} minerals, while the amount of Cd retained was about (13.25 µg g^{-1}) mineral, this is consistent with what (4) indicated about the susceptibility of minerals that have a high charge prefer to adsorbed more lead compared to minerals that have a lower charge. In the case of the presence of calcite with both minerals (kaolinite and bentonite), an increase in the amount of released lead were observed when kaolinite was present with calcite, compared to the treatment in which calcite was present with bentonite, at a rate of (13.13%). While the treatment of bentonite with calcite, the amount of Cd released increased compared to the treatment of kaolinite with calcite (4.77%). This is due to the similar size of the radii of Ca and Cd (0.99 – 0.97 A^0) respectively, in addition to the role of kaolinite, in retain the largest amount of Cd compared to Pb, which leads to decrease in the amount released from it with an increase in the number of extraction times, this was confirmed by (7) It is clear that the decrease in the amount of liberated Cd is due to the increase in carbonate minerals, including calcite, in the soil and its ability to restrict the movement of this ion as a result of its incorporation into the crystalline system of the mineral.

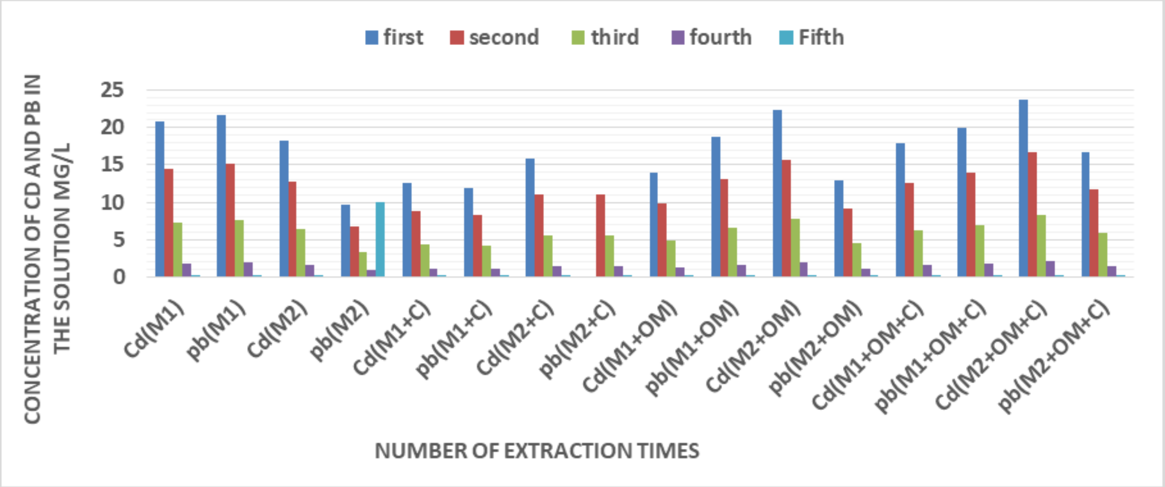

Figure 17. Effect of kaolinite, bentonite, calcite and organic matter on the amount of Cd and Pb released during five stages of extraction

Table 5. Effect of kaolinite, bentonite, calcite and organic matter on the amount of Cd released during five stages of extraction

extraction	Cd(M1)	Cd(M2)	Cd(M1+C	Cd(M2+C)	Cd(M1+OM)	Cd(M2+OM)	Cd(M1+OM+C	Cd(M2+OM+C
first	20.78	18.32	12.60	15.81	14.01	22.35	17.87	23.75
second	14.54	12.82	8.82	11.06	9.81	15.64	12.51	16.63
third	7.27	6.41	4.41	5.53	4.90	7.82	6.25	8.31
fourth	1.82	1.60	1.10	1.38	1.23	1.96	1.56	2.08
Fifth	0.22	0.19	0.13	0.17	0.15	0.23	0.19	0.25

Table 6. Effect of kaolinite, bentonite, calcite and organic matter on the amount of Pb released during five stages of extraction

extraction	pb(M1)	pb(M2)	pb(M1+C)	pb(M2+C)	pb(M1+OM)	pb(M2+OM)	pb(M1+OM+C)	pb(M2+OM+C)
first	21.75	9.75	11.83	15.7o	18.70	13.01	19.91	16.76
second	15.23	6.83	8.28	10.99	13.09	9.11	13.94	11.73
third	7.61	3.41	4.14	5.49	6.55	4.55	6.97	5.87
fourth	1.90	0.85	1.04	1.37	1.64	1.14	1.74	1.47
Fifth	0.23	10.0	0.12	0.16	0.19	0.14	0.21	0.18

In the case of presence of organic matter with the bentonite and kaolinite and their effect on the amount of Pb and Cd released, the results showed that the interaction between the organic and colloids in soil had a significant effect on the amount released from both elements, as the amount of Cd released increased (33.04 %) in the case of presence of bentonite minerals with the organic matter compared to the presence of Kaolinite mineral with organic matter, while the amount of released lead increased (16.29 %) in presence of kaolinite mineral with the organic matter compared to the presence of bentonite mineral with it. Organic and mineral colloids and the amount of negative charge in each of kaolinite, bentonite and organic matter, as the total concentration of Cd and Pb released in the presence of bentonite mineral with organic matter was (27.5 and 22.46 µg g^{-1}). As for the presence of kaolinite, with organic matter the total concentrations of Cd and released Pb were (20.67 and 26.12 µg g^{-1}), this was confirmed by (6). When organic matter is present alongside both minerals, kaolinite and bentonite, in the treatment, the results indicate that the released amount of Pb exceeded that of Cd, the total concentrations released reached (25.45 and 22.44 µg g^{-1}) respectively, with an increase for Pb compared to Cd reaching 13.41%, this variation in released amounts when these materials are present together attributed to the interaction between organic and metallic colloids, as well as the affinity between these components and the same element (11, 12) . It could also be influenced by the inherent properties of each element, such as atomic and ionic radius, and the number and capacity of outer electrons in the outer orbit when associating with other components through both physical and chemical adsorption processes. The complexity and association state of the element with these materials also play a role, this was confirmed by (18) about the effect of the overlap between mineral and organic colloids on the behavior of the elements in the interaction environment. It was observed that the maximum adsorption was higher in the case of bentonite mineral with calcite and organic matter, compared to kaolinite mineral with organic matter and calcite, reaching (155%). Meanwhile, the binding energy (K) decreased to (52.2%) in the presence of bentonite with calcite and organic matter, in contrast to the presence of kaolinite with organic matter and calcite in the case of Cd. The results for Pb followed a similar trend.

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