Original Research	Open Access

Influence of Ionic Strength, pH and Cation Exchange Capacity for Different Types Clay Minerals from Libya; Regions Gharyan, Murzuq and Taourgha

Abdulhakim A. Jangher[*]
Department of Chemistry, Faculty of Science, Tripoli University, Tripoli, Libya

Fahima N. Almasoude
Department of Chemistry, Faculty of Science, Tripoli University, Tripoli, Libya

Mahmoud M. Aban
Department of Chemistry, Faculty of Science, Tripoli University, Tripoli, Libya

Dr. Mohamed Tahher Mahabbis
Department of Chemistry, Faculty of Science, Tripoli University, Tripoli, Libya

Saeed N. Wadi
Petroleum Training and Qualifying Institute, Tripoli, Libya

Abstract

Samples of clay were collected from three regions in Libya; Gharyan, Murzuq and Taourgha. Each sample has been taken regard to the place and depth. Because the natural clay is found in deep layers from the soil surface about 20 m. $CaCO_3$ and $CaSO_4$ are precipitated at shallower depths. Results recorded have shown high percent of calcite $CaCO_3$ and Illite in Taourgha clay. Whilst Kaolinite is found in Gharyan clay, however, Bentonite (Na-Montmorillonite), Nontronite, Cr-Volkonskoite wre found in Murzuq. Murzuq white clay sample contained the Na-bentonite. Investigations of conductivity, pH and total dissolved of solids (T.D.S) were cried out on the collected clay samples. In particular the effect of the ionic strength, chemical composition, as well as cation exchange capacity (CEC) were elaborated. pH values for all samples tend to the alkaline media. CEC values were leached by 500 ppm Ca^{+2} at pH = 8 for samples of Gharyan-Quasim (GQ), Gharyan-Abughalan (GA), Murzuq-Green (MG), Murzuq-White (MW),Taourgha-Mardom (TM) and Taourgha-Temeana (TT) were 6.25, 84.5, 79, 24, 27 mmoles/kg respectively. Otherwise, at pH = 2, values were in constant range for all samples 20.5 mmoles/kg. Leaching process was measured by 500 ppm K^+ using flame emission photometer. The CEC values at pH = 8 for samples Gharyan, Murzuq, and Taourgha were 5.89, 91.50, 19.73 mmoles/kg, respectively. Conductivity values of weight ratios at 1:1, 1:3, and 1:5 of the extracted solutions of Murzuq samples were 0.324, 0.302, 0.198 dSm^{-1}, respectively.

Keywords: Libyan clay minerals; Bentonite CEC; Kaolinite; Illite; Ionic strength; Conductivity.

1. Introduction

Conductivity is a numerical expression of ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, their total concentration, mobility, valence, and relative concentrations, and on the temperature of measurement. Solutions of most inorganic acids, bases, and salts are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all. The resistance of a conductor is inversely proportional to its cross-sectional area and directly proportional to its length [1]. The solubility of material determines how much of it will move and influences how fast and how far it will go in a particular environment. Materials are often classified as either soluble or insoluble in water, but these should be considered as relative terms rather than absolutes. Even the insoluble materials can usually be shown to have slight solubility. Solubility varies with temperature and pH. Solubility increase when salts are added to the solution like $CaSO_4$, it is mean a salt whose ions don't react with the other ions, and it say that the ionic strength of the solution increase because cation are attracted to the anion but anions are repelled. These interactions create a region of net positive charge a round any particular anion. It is call this region the ionic atmosphere which is attenuates decrease the attraction between ions. The greater ionic strength of a solution was the higher the charge in the ionic atmosphere. Each ion plus atmosphere cation less net charge and there is less attraction between any particular cation and anion [2, 3]. The important structural and chemical differences among the clay minerals are the basis for the individual mineral species names and the arrangement of the species in groups.

The major classifications of clay minerals are 1:1 layer and 2:1 layer. The simplest 1:1 layer is Kaolinite, comprises a single layer of silicate tetrahedral with an Al octahedral layer on top. The apical oxygen of the tetrahedral and one of the hydroxyl layers of the octahedral from common layer. The mesh size of Al octahedral sheet is smaller than that of tetrahedral sheet. The structure of kaolinite is a tetrahedral silica sheet alternating with an octahedral alumina sheet. These sheets are arranged so that the tips of the silica tetrahedrons and the adjacent

*Corresponding Author

layers of the octahedral sheet form a common layer [1]. In the layer common to the octahedral and tetrahedral groups, two-thirds of the oxygen atoms are shared by the silicon and aluminum, and then they become oxygen instead of hydroxide (OH). The charges within the structural unit are balanced. Analyses of many samples of kaolinite minerals have shown that there is very little substitution in the lattice. Kaolinite has a low shrink swell capacity, low exchange capacity (5-15 mmoles/kg). It was a soft and usually white mineral. It was colored pink, orange and red by iron oxide to give it a distinct rust hue. Lighter concentrations yield white, yellow or light orange, minerals of these groups is 1:1 layer silicates. Their basic unit of structure consists of tetrahedral and octahedral sheets in which the anions at the exposed surface of the octahedral sheet are hydroxyls.

The general structural formula may be expressed by $Y_{2-3}Z_2O_5(OH)_4$, where Y are cations in the octahedral sheet such as Al^{3+} and Fe^{3+} for di- octahedral species and Mg^{2+}, Fe^{2+}, Mn^{2+}, and Ni^{2+} for tri- octahedral species, and Z are cations in the tetrahedral sheet, largely Si and to a lesser extent, Al and Fe^{3+}. A typical di-octahedral species of this group is kaolinite, with an ideal structural formula of $Al_2Si_2O_5(OH)_4$. Kaolinite is electro-statically neutral and has triclinic symmetry. 2:1 clay, ideal formula $Si_8Al_4O_{20}(OH)_4$ mineral structure is exemplifying by bentonite. In the bentonite hydrogen bonding between the layers is not possible as the hydroxyls are within the center of the layer and the exteriors of adjacent layers comprise only apical oxygen. Thus, interlayer bonding is weak and bentonite can take up water between the layers. Isomorphous substitution also occurs and the additional cation needed for electro-neutrality sit between the layers. 2:1 layer silicate, an octahedral sheet is sandwiched between the apices of two tetrahedral sheets [4, 5]. These T-O-T layers are either held together by weak Van der Waals forces if they are neutral or may have cations between them for charge balance, if substitution in either sheet results in a residual layer charge; for examples, micas and Illite [6-8].

This comprises an almost flat sheet of silicon linked by bridging oxygen atoms, with singly bonded oxygen (termed apical oxygen) all pointing in the same direction almost normal to the plane of the sheet. In the second; kind of the structural unit, termed the octahedral sheet, silicon is replaced by Al^{+3}, Mg^{+2}, or Fe^{+3} and the oxygen O^{-2} or hydroxyls OH^- occupy an octahedral structure. Water molecules and cation occupy the space between the 2:1 layers [9-11].

It is well known that the ionic charge and the porous structure of cla minerals give the ability to adsorb the toxins [12]. Numerous researches have been conducted on natural bentonite to examine its potential for the removal of heavy metal ions. It is found that natural bentonite could be used effectively for the removal of zinc ions from aqueous solutions [13, 14]. This study concern the investigation on conductivity, pH and total dissolved of solids (T.D.S) of Libyan clay minerals collected from regions of Gharyan, Murzuq and Taourgha. In particular the effect of the ionic strength, chemical composition, as well as cation exchange capacity (CEC) were elaborated.

2. Materials and Methods

Samples of clay were collected from three regions in Libya; Gharyan, Murzuq and Taourgha two samples of each regions. All samples were digested by concentration HNO3 with (65%) manufactured by Carlo ERBA Lab, Italy.

The instruments were used, XRD from Bruker company (AXS), (Model D-5005 TIGER, Germany), Flame Emission Photometer (PFP7, JENWAY, Germany), Mixer Rotating, (Edmund Buhler, 400 rpm, Mot./min,(Germany), and pH meter.

Preparation of Samples:

Clay samples were prepared by extraction with distilled water by saturated paste a 1:1, 1:3, and 1:5 weight ratio of clay to water. A series of extraction media will be used in a particular sequence to liberate metals associated with different clay component. Three selected weight 10 g of clay sample (320 meshes) were put in conical flasks 10, 30 and 50 ml of distilled water were added, and closed with the cap. The samples were shacked well in mixer rotating at 300 rpm for 2h, after that filtrated by using filtration funnel and filter paper (41 mm) .Finally, were obtained saturated solutions which content different components by ratio 1:1, 1:3, and 1:5. Then the extracted samples were used to measure, conductivity, T.D.S, and were titrated with 0.01 M EDTA to determine the concentration of Ca^{+2} and Mg^{+2}. Concentrations of Na^+ and K^+ were determined by flame emission photometry. The samples were diluted with distilled water by 25 fold to measure exchangeable K^+, when using flame emission photometry.

3. Results and Discussion

T.D.S was estimated by multiplying conductivity factor 640 for conductivity between (0.1-5.0 dS/m) for lower saline soils and a factor 800 for conductivity > 5.0 dS/m for hyper-saline samples. To obtain the total concentration of soluble cation (T.S.C), conductivity dS/cm is usually multiplied by a factor of 0.1 for mol/L and a factor of 10 for mmol/L, [15, 16] , see Table 1.

Table-1. Conductivity and T.D.S values

Conductivity (µS.cm⁻¹)				T.D.S ppm		
Weight Ratio of Clay to Water				Weight Ratio of Clay to Water		
Clay Sample	1:1	1:3	1:5	1:1	1:3	1:5
GQ	1267	983	556	810	630	356
GA	1615	1198	635	1034	766	405
MW	324	302	198	205	195	125
MG	2130	766	302	1360	490	195
TW	1463	1329	387	935	850	245
TT	6950	5820	3450	5560	4650	2210
TM	2260	1770	928	1445	1130	595

Ionic strength (I) is measurement of total concentrations of ions in solution which emphasizes contribution of species with charges greater than one to solution non-ideality.

$$I = 0.5 \sum m z^2 \qquad (1)$$

Where; (m) is the concentration of a given ion in mol/L and (z) is the charge on that ion. When more water is adding to clay sample (dilution ratio), the electrical conductivity decreased, while the ionic strength of the solution increased because the conductivity is inversely proportional to its area and directly proportional to its length [4, 5]. The critical coagulation concentration of salts, which area of clay suspensions coagulate, depends strongly on the valence of cation present in solution and coagulation can be promoted by increasing the ionic strength of the solution. This may be termed double layer compression. It has been calculated by equation (2), at 25 ºC below [15]:

$$I = 0.0127\ EC \qquad (2)$$

Where; EC is the electrical conductivity of the extract of a saturated paste of clay.

Table-2. Values of Ionic Strength for Extracted Solutions

| Clay Sample	1:1 ratio, mol/L	1:3 ratio, mol/L	1:5 ratio, mol/L
GQ	1.610×10^{-2}	1.250×10^{-2}	7.061×10^{-3}
GA	2.050×10^{-2}	1.522×10^{-2}	8.065×10^{-3}
MW	4.115×10^{-3}	3.835×10^{-3}	2.515×10^{-3}
MG	2.710×10^{-2}	9.728×10^{-3}	3.840×10^{-3}
TW	1.860×10^{-2}	1.690×10^{-2}	4.915×10^{-3}
TT	8.830×10^{-2}	7.410×10^{-2}	4.380×10^{-2}
TM	2.890×10^{-2}	2.250×10^{-2}	1.790×10^{-2}

Figure-1. Ionic strength vs. conductivity of natural aqueous solutions for Clay extract of samples 1:1 weight ratios
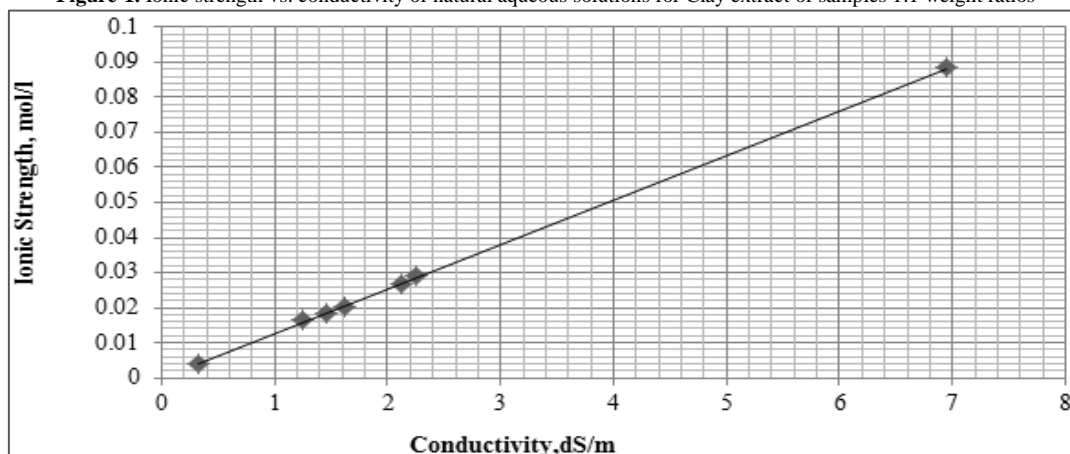
Increasing of concentration ions in solution causes enhanced surface concentrations of counter ions, thereby decreasing the surface charge, since, higher ionic strength of the surface potential increased concentration of ions in solution, thereby decreasing the surface charge and decreases in a shorter distance, than that similar net charge in dilute solution. The combined effect diminished the electrostatic repulsion between particles. The colloidal system is therefore destabilized and aggregation occurs (see in Figures 1 - 3). The strength of the contacts between the oppositely charged surfaces is much higher than the strength of the contacts formed due only to Van der Waal's,

London attraction in base condition. In high ionic strength solution where monovalent Na⁺ tends to dominate Na⁺ will reside on exchange sites. Displacement with a lower salinity Ca²⁺ clay solution will produce a new equilibrium with more Ca²⁺ on the clays. The distribution is then governed by the selectivity coefficient determined for this system. Unlike solubility constants (K) for pure minerals, selectivity coefficients are specific to the clay types, and so will differ for each system. Each cation has its own selectivity or tendency for sorption onto a charged surface. This characteristic relates to the surface charge of the cation, and the stability of its hydration sheath, which reduces its electrostatic interaction. Divalent cations have a greater tendency for exchange than monovalent ions. Cations with smaller hydrated radii are also more readily adsorbed, [17].

Figure-2. Ionic strength vs. Conductivity of natural aqueous solutions for Clay extracts of samples 1:3 weight ratio
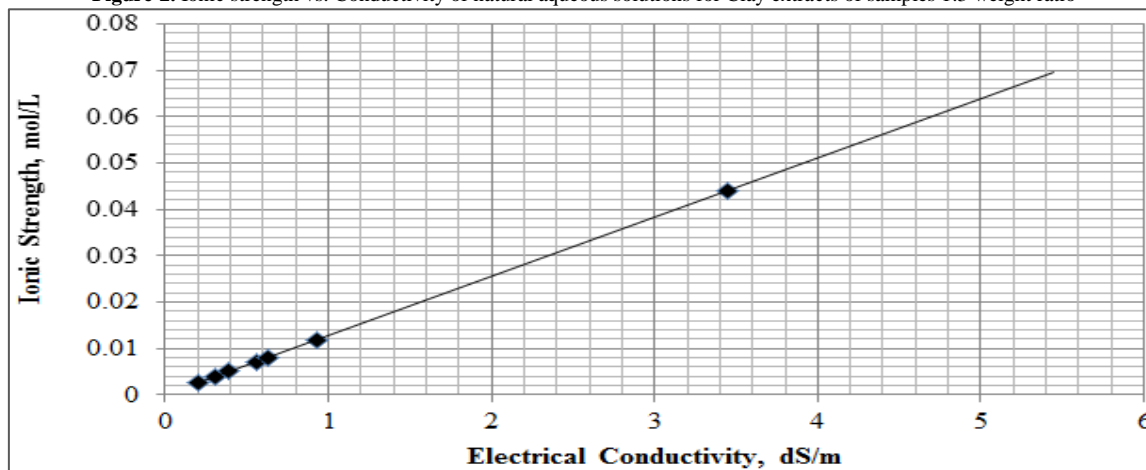
The order of selectivity for adsorption of the major monovalent and divalent cations are increased solubility $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$, and increased sorption $Cs^+ > Rb^+ > K^+ \approx NH_4^+ > Na^+ > Li^+$ While the selectivity coefficient can be determined for any cation exchange reaction, it less of a constant than an empirical value incorporating the heterogeneities of the surface in question and the bulk ion geochemistry of the solution and ionic strength. Thus, the exchange of Na^+ and Ca^{2+} for example between solution and a clay surface will be affected also by other cations in solution, and by the ionic strength of the solution. Calcium absorption decreased with increase in ionic strength, and behaved differently in single- and multi element systems. The study showed that Ca availability might vary when it is present alone, or mixed with other metals, cations and anions, which is generally expected in the contaminated clay environments. Since typical contaminated sites often contain multitude of cations and anions, the physico-chemical properties of clay solution, such as pH, electrical conductivity and ionic strength must be taken into account in predicting Ca availability and devising different remediation strategies for a given contaminated site, [18, 19]. Some exchange capacity for both cation and anions occurs on the edges of silicate clay crystals, whereas the basic cation was principally Ca^{+2}, Mg^{+2}, K^+ and Na^+. Kaolinite should therefore have nearly as much anion exchange capacity (AEC) as cation exchange capacity (CEC). Variations in pH cause deviations from equality in the

Figure-3. Ionic strength vs. conductivity of natural aqueous solutions for Clay extracts of samples 1:5 weight ratios
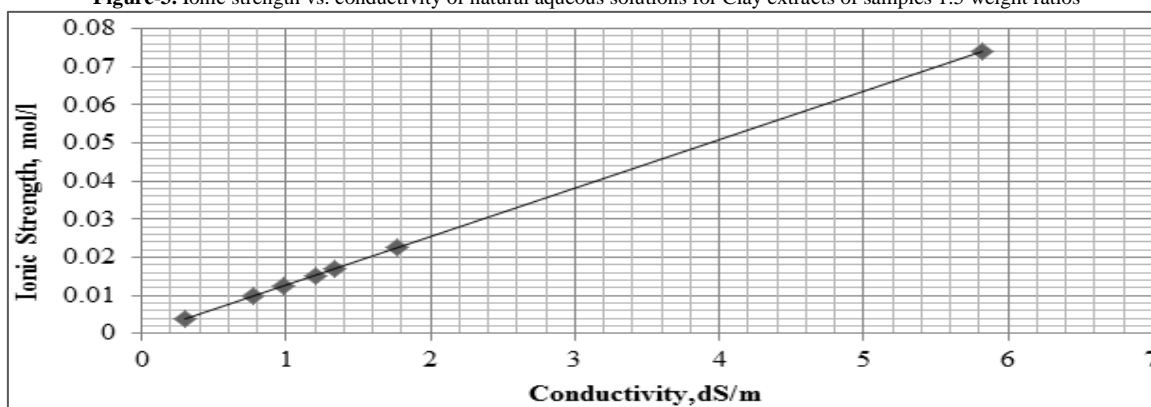
numbers of positive and negative edge charges. AEC increases at low pH=2, and CEC increases at high pH=8. The likelihood of ionizing significant amounts of OH^- depends on the abundance of clay minerals containing OH^- and on pH. Relatively untreated clays have a high proportional of 2:1 layer silicate minerals such as Illite and bentonite. Finally, the free Fe_2O_3 and Al_2O_3 that accumulate in the clay fraction may cause the AEC to go beyond the decreasing CEC. At pH = 8, practically all the H^+ in the percolating water is absorbed by the soil irrespective of the salt concentration supplied. At pH =2, the influence of neutral salts increases as the pH falls, resulting in reduce soil acidification and a corresponding increase of the leached acidification.

The effects of neutral salts on soil acidification are markedly influenced by the bonding energy H^+ to the clay exchange sites. In the majority of situations, the adsorption of anions applied as neutral salts is very small, so that exchange acidity is usually greater than exchange alkalinity. If the soil becomes very acidic then Al associated with clay minerals may become soluble in the form Al^{+3} or aluminum hydroxyl cation. These ions may then become adsorbed even in preference to hydrogen ions, present in clay solution, by the permanent (pH-independent) negative charge in clay mineral surfaces. The adsorbed Al is in equilibrium with Al^{+3} ions in the solution. The solution Al^{+3} ions can contribute to clay acidity through their tendency to hydrolyze.

Table-3. Values of K_d and CEC at pH=8 (Leaching by 500 ppm $CaCl_2$)

Clay Sample	Type of clay	K_d (L/kg)	CEC mmoles/kg	Standard values*
GQ	Kaolinite	0.694	6.25	2–15
GA	Kaolinite	0.694	6.25	2–15
MG	Nontronite	8.740	80.0	-------
MW	Bentonite	9.375	84.50	80 –150
TT	Illite	2.624	27.0	20 – 40
TM	Ankerite	2.99	≈24.0	--------

(*) The Standard Values for Wyoming (USA) [15].

Table-4. Values of K_d and CEC at pH = 2 (Leaching by 500 ppm $CaCl_2$)

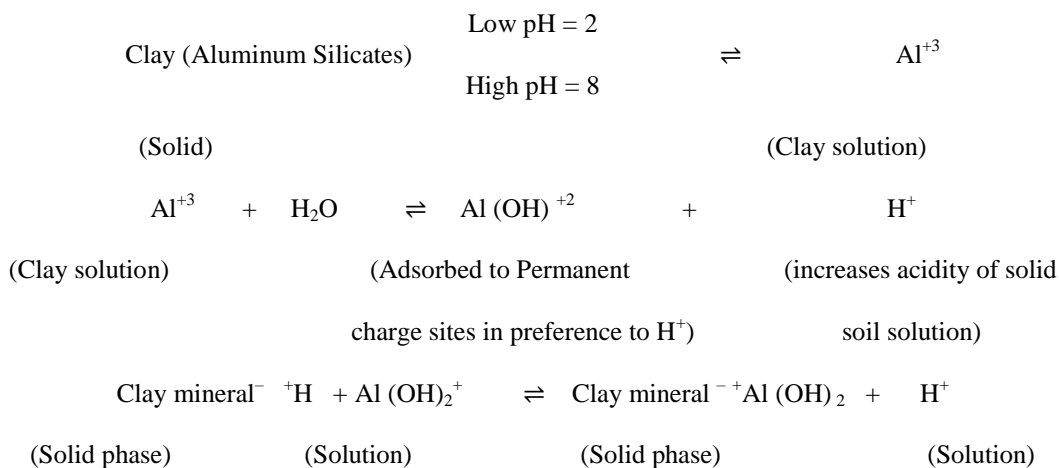| Clay Sample	Type of clay	K_d (L/kg)	CEC mmoles/kg	Standard values
GQ	Kaolinite	2.273	20.5	2–15
GA	Kaolinite	2.273	20.5	2–15
MG	Nontronite	2.990	27.0	-------
MW	Bentonite	2.273	20.5	80 –150
TT	Illite	2.273	20.5	20 – 40
TM	Ankerite	2.273	20.5	--------

Table-5. Values of K_d and CEC at pH = 8 (Leaching by 500 ppm KCl)

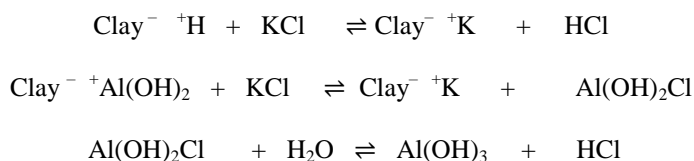| Clay Sample	Type of clay	K_d (L/kg)	CEC mmoles/kg	Standard values*
GQ	Kaolinite	0.877	≈ 6.0	2–15
GA	Kaolinite	0.877	≈ 6.0	2–15
MG	Nontronite	13.64	91.5	--------
MW	Bentonite	13.64	91.5	80 –150
TT	Illite	2.94	≈ 20	20 – 40
TM	Ankerite	2.94	≈ 20	--------

(*) The Standard Values for Wyoming (USA) [15].

3.1. Mechanism of Chemical Reaction for CEC

This is illustrated in the equations below, when leaching by 500 ppm Ca^{+2} and 500 ppm K^+ at pH=8 and pH=2:

$$\text{Clay (Aluminum Silicates)} \quad \overset{\text{Low pH = 2}}{\underset{\text{High pH = 8}}{\rightleftharpoons}} \quad Al^{+3}$$

(Solid)   (Clay solution)

$$Al^{+3} + H_2O \rightleftharpoons Al(OH)^{+2} + H^+$$

(Clay solution)   (Adsorbed to Permanent   (increases acidity of solid

charge sites in preference to H^+)   soil solution)

$$\text{Clay mineral}^- {}^+H + Al(OH)_2{}^+ \rightleftharpoons \text{Clay mineral}^- {}^+Al(OH)_2 + H^+$$

(Solid phase)   (Solution)   (Solid phase)   (Solution)

The cation of the salt may replace (H^+ or Al^{+3}) ions associated with clay exchange sites and cause a pH drop in the clay solution:

$$\text{Clay}^- {}^+H + KCl \rightleftharpoons \text{Clay}^- {}^+K + HCl$$

$$\text{Clay}^- {}^+Al(OH)_2 + KCl \rightleftharpoons \text{Clay}^- {}^+K + Al(OH)_2Cl$$

$$Al(OH)_2Cl + H_2O \rightleftharpoons Al(OH)_3 + HCl$$

These equations above are called exchange acidity, and its magnitude on many factors including bonding energy of salt cation, pH, and salt content of the clay and amount of neutral salt added to clay. Exchange acidity increases with cation valence and falls with the extent to which ions may be hydrated. Thus, under particularly acidic clay conditions, complex equilibrium processes can occur between (H^+, Al^{+3}) and aluminum hydroxyl compounds on exchange sites and in clay solution.

4. Conclusion

Most clay minerals have a net charge on their surface. They are affected by many factors including; conductivity, ionic strength and cation exchange capacity. Surface charges of the clay minerals allow to adsorb ions to their surface.

Samples of clay were collected from Libya, regions Gharyan, Murzuq and Taourgha. pH values for all samples tend to the alkaline media. CEC values were leached by 500 ppm Ca^{+2} at pH = 8 for samples of Gharyan-Quasim (GQ), Gharyan-Abughalan (GA), Murzuq-Green (MG), Murzuq-White (MW),Taourgha-Mardom (TM) and Taourgha-Temeana (TT) were 6.25, 84.5, 79, 24, 27 mmoles/kg respectively. Otherwise, at pH = 2, values were in constant range for all samples 20.5 mmoles/kg. Leaching process was measured by 500 ppm K^+ using flame emission photometer. The CEC values at pH = 8 for samples Gharyan, Murzuq, and Taourgha were 5.89, 91.50, 19.73 mmoles/kg, respectively. Conductivity values of weight ratios at 1:1, 1:3, and 1:5 of the extracted solutions of Murzuq samples were 0.324, 0.302, 0.198 dSm^{-1}, respectively.

References

[1]   Adamis, Z. and Fodor, J., 2005. "Bentonite and Kaolin selected clay minerals", US. environmental protection agency, Washington, DC, and regional office for the Americas of the WHO, Geneva." pp. 50-69.

[2]   Al-Ani, T. and Sarapaa, O., 2008. *Clay and Clay Mineralogy", Geological survey in Finland*. Helsinki University, pp. 84-90.

[3]   Al-Kateeb, A. and ph, D., 2001. *Soils pollution, Alexandria*. USA: Egypt, University of W. Virginia. p. 186.

[4]   Atkins, P. and de Paula, J., 2001. *Physical chemistry*. 7th ed. Oxford: Oxford University Press. pp. 508-595.

[5]   Atkins, P. and Beran, J., 1992. *General Chemistry*. 2nd ed. New York: Scientific American Books, W.H. Freeman.

[6]   Wright, J., 2003. *Environmental chemistry*. UK: Printed in Rutledge by Taylor & Francis Group. pp. 163-188.

[7]   Navarotsky, A., 1994. *Physics and chemistry of earth materials*. USA: Cambridge University, printed. pp. 50-70.

[8]   Dietrich, R. and Skinner, B., 1990. *Gems, Granites, Gravels, "Knowing and using rocks and minerals*. UK: University Press Cambridge. pp. 32-44.

[9]   Harrison, R. and de Mora, S., 1996. *Introductory chemistry for the environmental sciences*. 2nd ed. Cambridge: Printed in the UK at the University Press. pp. 133-160.

[10]   Atkins, P. and Shriver, D., 1999. *Inorganic chemistry*. 3rd ed. Oxford, p. 367.

[11]   Lutgens, F. and Tarbuck, E., 2006. *Essential of geology", by Pearson education Inc*. 9th ed. New Jersey, USA: Pearson Prentice Hall. p. 117.

[12]   Mellah, A. and Chegrouche, S., 1997. "The removal of zinc from aqueous solutions by natural bentonite." *Water Research,* vol. 31, pp. 621-629.

[13]   Arias, M., Perez-Novo, C., Osorio, F., Lopez, E., and Soto, B., 2005. *J Colloid Interface Science,* vol. 288, pp. 21-29.

[14]   Bennour, H. A. M., 2012. "Influence of pH and ionic strength on the adsorption of Copper and Zinc in Bentonite Clay." *Chem Sci Trans,* vol. 1, pp. 371-381.

[15]   Sparks, D., 2003. *Environmental soil chemistry", China translation and printing services Ltd*. 2nd ed., pp. 43-291.

[16]   Domenico, P. and Schwartz, W., 1990. *Physical and chemical hydrogeology*. New York:John Wiley, p. 824.

[17]   Christian, G., 2004. *Analytical chemistry*. 6th ed. USA: John Wily and Sons Inc. p. 211.

[18]   Charlet, L. G. J. P., Szenknect, S., Barthes, V., and Krimissa, M., 2007. "Sorption isotherms: A review of physical bases, modelling and measurement." *Applied Geochemistry,* vol. 22, pp. 249-275.

[19]   Echeverria, J., Inurain, J., Churio, E., and Garrido, J., 2005. "Colloids and surfaces physicochemical engineering aspects, Simultaneous effect of pH, Temperature, Ionic strength, and initial concentration on the retention of Ni on Illite." *Garrido, Elsevier Science,,* vol. 218, pp. 175 -218.