# Determination and measuring some of the physical and chemical parameters in the clay of Lake Hamrin, Iraq

**Huda Dhia Jaffar**

Dept. of physics/ College of Education for Pure Science (Ibn Al- Haitham)/ University of Baghdad.

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## Abstract

The composition of the clay taken from the lake of Hamrin, Iraq was studied with the determination of the concentrations of the major oxides and the minor oxides in it. Kaolinite was the most dominant clay in the samples, while quartz was the most abundant non-clay mineral.

Some physico-chemical parameters in lake's water were determined such as oxygen, a chlorosity, nutrient salts, pH, total alkalinity, total nitrogen, total phosphorous and silicate.

The effect of increased wastewater and human activities affected the composition of water and lead to a decrease in the productivity of the lake which was reflected by the relatively low pH values (average 8.0) and alkalinity in water as a result of the pollution.

An increase in the levels of ammonia (average 5.5 IM), nitrite (average 1.6 IM) and nitrate (15IM average) were apparently due to the influence of large quantities of wastewater expelled into the lake and the utilization of ammonia by aquatic organisms with a slow assimilation.

Reactive phosphate showed lower concentration in samples collected in the mid of the lake comparing with samples collecting from the shores which indicate the influence of enriched wastewater with phosphate matters.

**Key words:** Hamrin lake, clay, oxides, x-ray diffraction, Nutrient salt, Total nitrogen, Total phosphorus

# Introduction

The Hamrin fold is the most prominent folds present in the Bulkana region and its modern sediments is characterized by the presence of high permeability sandstones which lead to increase the seeped water that was going inside the soil leading to a decrease in the amount of running water, but if non-permeable layers of rocks are present above these sandstones, this will increases the proportion of running water (tributaries and rivers) in the region. The fold decreases in height gradually until it reaches a sea level at Hamrin lake [1, 2].

The lake is a man-made lake which was established after the foundation of Hamrin dam and is located approximately 50 km north-east of the Baquba city, in Iraqi's Diyala province.

The lake has an appreciable thickness of sedimentary rock formation, and the dominant rock types include varieties of sandstone, sandy gravel rocks, mud-rock and alluvial rock. There are some gypsum crusts mixed with clay, sand, silt, and sand [3, 4].

Kaolin - hydrated aluminum silicate, $Al_2Si_2O_5(OH)_4$-, is an important industrial clay with properties such as: fine particle size, platy shape, inertness, non-toxicity, high brightness and whiteness which made it a more versatile mineral. It can be used in a wide variety of industries. Kaolin resources are found as sedimentary deposits, weathering or hydrothermal alteration product of rocks containing a high proportion of alumino-silicate minerals. Kaolin deposits are wide spread throughout Hamrin lake [5].

Members of the kaolin family include dickite, nacrite, allophone, and hallosite. The iron content in each type of kaolin clay determines its color. It is usually white to near white in color. Other colors such as purple, bleach brown, etc., are due to the impurities in the material [5, 6].

The scientists use the clay minerals as:

(i) Indicators of the environment during weathering, allothi- and authi-genesis in the sediments and in the study of source area of the detrital supply;

(ii) pH indicators of processes of changes in mineralogical, petrological, geological and geochemical investigations [7].

Lake Hamrin receives huge amounts of drainage water (domestic and agricultural) which contains unspecified quantities of urban, industrial and agricultural chemicals from the town nearby and beyond. Its amount of water varies through the years with the Lake reached its highest level in 1988 when the surface area was 358.3867 $km^2$. At present, the level is 21.23572 $km^2$ as a surface area [8. 9].

Iraq has suffered a severe drought in the past decades and lost a bulk water mass, with rainfall rates 40% below normal levels. In the same period, discharge of large springs and rivers decreased substantially due to project (GAP) in Turkey, which includes the construction of dams and irrigation schemes in the upstream Tigris catchment. Additionally, several dams and irrigation projects are under construction in the Iranian headwaters of the Tigris, which will reduce river flows in northern Iraq permanently [9].

Many chemicals from human activities would be present in the drainage water. Most of these chemicals would be at trace (less than ppb levels). Nevertheless nothing is known of the synergistic effects on non-targets of water containing trace levels of many chemicals. Many researchers have studied the hydrographic and chemical characteristics of the water and sediments of Lake Hamrin [10, 11], but the aim of the present work is to study the clay in the area of lake Hamrin in order to assess its quality and any variations in the hydrographic lineaments by determining some physico-chemical parameters such as oxygen, chlorosity, nutrient salts, pH, total alkalinity, total nitrogen, total phosphorous and silicate

## Materials and methods

### A. Clay collection

Samples (A, B, C and D) of clay were obtained from four different moisture places in winter from the Hamrin lake, Iraq.

### B. Water collection

Samples of water were obtained 50 cm below the surface from four sites, two in the mid of the lake and two about 50 meter distance from the shores. Water and air temperatures were measured immediately in the field by using mercury thermometer (0-100°C). The pH is measured also using a portable pH meter.

### C. Physical analysis

### 1. Particle size distribution

The clay samples were crashed, sieved and divided into 100g lots. Each lot was washed with 100ml 5% $NaPO_3$ (as a deflocculant) and mixed thoroughly with 250 ml of distilled water, and then left to stand for 40 min and was completed to 1000 ml. The dimensions of a particle were measured using laser diffraction spectroscopy (Mastersizer 3000E, Malvern Instruments, England)

### 2. Determination of particle density

The particle density was measured according to the method of Cresswell and Hamilton [12]. Each sample was weighted (and its diameter was measured) and then heated for 20h at 110°C. Each sample was weighed after it was cooled down.

### 3. Determination of porosity

The surface porosity ($\phi$) of a sample was calculated from the particle density according 10 the method of Horgan [13].

### X-ray diffractometry (XRD) analysis

The composition of the clay was determined using diffractometer (XRD) (Empyrean, PANalytical, Netherlands).

### Determination of soil moisture

Estimated soil moisture was measured using 10 ml soil moisture sensor (VH440, Sigma) after calibration.

### Determination of organic carbon content

The soil carbon content was measured according to colorimetric method using methyl orange as an indicator as indicated by Strickland and Parson [14, 15].

10g of clay were crashed and sieved and then mixed with 100ml 1N $K_2Cr_2O_7$. Concentrated $H_2SO_4$ (200ml) was added to the mixture with careful shaking before the mixture left to stand for 1h at room temperature.

10 ml of sodium dichromate (0.5N) mixed with 4M $H_2SO_4$ was added to 1g of clay (after it was crashed and sieved). The mixture was shacked for 20min and then left to stand for 1h and the upper level of the mixture was removed carefully and its absorption was read at 660nm using vis-uv spectrophotometer (Shimadzu, Japan). The calibration curve was drawn using (0-1g glucose)

### . Ammonia, nitrite, nitrate and silicate compositions determination

Ammonia, nitrite and nitrate were determined as indicated by Jaber et al [16].

Silicate was determined by a modified method as indicated by Sletten and Bach using stannous chloride [17, 18].

Vis-uv spectrophotometer is used for the measurements of the parameters.

### 1. Total nitrogen and phosphorous content

Total nitrogen content as well as total phosphorous content (in clay and water) were determined by Bray and Kurtz method [19].

The sample (1g) was crashed and sieved before mixing with ammonium fluoride (15ml) and HCl (25ml). After shaking, distilled water was added to 500ml, and after another shaking, the mixture was centrifuged and the supernatant (4ml) was added to 6ml L-ascorbic acid in distilled water and 4ml ammonium molybdate solution.

The mixture stands for 5min, and absorbance at 852nm was read by vis-uv spectrophotometer as before. A standard phosphorus solution (0-50mg/l) was prepared.

### 2. Determination of calcium and magnesium in water

The determination of calcium and magnesium (total hardness) were done titrimetrically against EDTA standardized solution according to Szabo [20].

### 3. Determination of total alkalinity and chlorosity

Total alkalinity was determined as indicated by Brinkman [21], while Chlorosity was determined using Mohr's titration method as indicated by Sheen and Kahler [22].

## Results and Discussion

### 1. Chemical composition of the clays

The concentrations of the major oxides are ranging from `48.4 to 51.2% for $SiO_2$, from 25.2 to 28.1% for $Al_2O_3$ and from 13.5 to 14.1% for $Fe_2O_3$, while the concentrations of minor oxides were relatively low (Table 1).

Minor oxides are ranging between 1.9-2.5% for $K_2O$ and less than 0.8 for all other clay samples, while the percentage for MgO, $P_2O_3$, $TiO_3$ and ZnO were negligent (Table 2).

The percentage of minerals in the clay of Hamrin lake is shown in (Table 3).

Quartz was considered to be the most non-clay according to X-ray diffraction, and closely corresponding with $SiO_2$ values, while the most dominant clay was kaolin in the samples.

Kaolin samples have an average particle density of $1.35g.cm^{-3}$ and an average porosity of 0.44% (Table 4).

Kaolin is found as sedimentary deposits containing high concentrations of alumino-silicate minerals. The muscovite and bentonnite were observed in very few samples.

These results showed some similarities to those found in other lakes in northern Iraq [3, 11].

### pH of water

The pH values in water fluctuated between 7.70 and 8.5. The obtained low pH values (comparing with pH values obtained by previous researchers in past decades) are showing how the productivity of Hamrin lake is decreased with an increase in pollution due to wastewater expelled into the lake.

Ahmad [3] and Ghasan [8] found that the pH varied between 9.04 and 8.26 and 8.9 to 8.5 respectively in 1999 and 2008. The present researcher estimated the difference between the previous data and the present data contemplate an increase in the polluted water in the lake during the previous four decades.

There was no doubt that pH values were influencing factors that control other physiochemical parameters.

### Nitrogenous compounds (Nutrient salts)

### Ammonia

An increase in the levels of ammonia was apparently due to the utilization of ammonia by aquatic organisms as well as to the reducing of nitrate concentrations via a de-nitrification process. The concentration of ammonia in water of the lake varied between 3.2 and 7.9 IM.

The lower content of dissolved oxygen inhibits the rate of chemical oxidation of ammonia and that may cause the high concentrations of ammonia. The decay of most organic compounds under anaerobic conditions stopped when reached the ammonia stage [21].

The lowest ammonia content was probably due to the utilization of ammonia by aquatic microorganisms, while the increase in ammonia may be due to the formation of ammonia through nitrate via de-nitrification process [23, 24].

## Nitrite

Nitrite was ranged between 1.4 and 1.9 IM. The high concentration of nitrite was probably due to the influence of large quantities of wastewater expelled into the lake. Actually, a main source of nitrite in the lake was probably the continuous increasing in the decomposition of organic matters.

The decreased values of nitrite can be explained due to the reduction process from nitrite to ammonia under anaerobic conditions. This will explain why an increase in ammonia was accompanied by lower nitrite values [10, 26].

## Nitrate

The concentration of nitrate content in the lake is between 11.1 and 22.4 IM. The speedy decomposition of organic matters and an increase in amounts of wastewater may explain the high concentration values of nitrate, while a slow assimilation (due to the presence of high concentrations of inorganic matters) might explain the low concentrations of nitrate sometimes in the lake

## Total nitrogen

The fluctuations of total nitrogen are probably due to the various agricultural inflows.

Total nitrogen (TN) was fluctuated between 25.4 and 28.9 IM. These values may be due to the slower rate of assimilation by the aquatic organisms than that of inorganic species [24].

## Silicate compounds

Reactive silicate content was varied between 27.3 and 39.5 IM. The slow rate of rejuvenation of silicate from the deposits may lead to minimize the silicate concentration values, while the high level of silicate concentrations values might be directly correlative to wastewater expelled into the lake.

It was found that the content of dissolved oxygen was influencing the higher concentrations of silicate (Table 5). It seemed that in poorly oxygenated area, the decay of siliceous compounds increases under the influence of fresh-water microorganisms [25, 26].

## Calcium, magnesium and phosphate compounds

It was found that calcium was fluctuated between 56.59 and 75.11 mg/l, while magnesium differed between 79.22 and 98.35 mg/l.

Phosphate compounds were always at high concentrations which were probably due to the influence of enriched wastewater with phosphate matters. Reactive phosphate was ranging between 7.2 and 10.2 IM (Table 5).

The reproduction and growth of aquatic microorganisms were controlled by phosphate since these microorganisms used organic and inorganic phosphate [7, 24].

From personal point of view, the wastewater enriched with phosphate compounds will increase the concentration of reactive phosphate.

If a sample was collected from mid of the lake, it would show decreased value of reactive phosphate due to its uptake by aquatic organisms.

## 2. Total alkalinity

Total alkalinity varies between 4.0. meq/l and 8.78 meq/l g (Table 5). The higher values of total alkalinity might be influenced by the higher $CO_2$ content generated as a result of the growth and degradation of aquatic microorganisms as suggested by references [10, 11]. They suggested that the effect of discharged wastewater into the lake and the variation of biological oxygen demand (BOD) and pH must be taken into account.

Generally, there was an increase in the total alkalinity during the present time comparing with the previous data [5, 9, 10, 11].

### 3. A chlorosity

The distribution pattern of cholorsity varied between 768 mg/l to 1262 mg/l (Table 5). The chlorosity of Hamrin lake presented a successive decreasing trend in comparison with the previous decades (9). This is might be due to an increase in wastewater entering Hamrin lake. The shrinkage of Hamrin lake area may play a role in this as well as an increase in the aquatic plants, which overlay most shores of Hamrin lake.

There are great differences between previous data collected during previous studies and the data presented in this paper which emulate a rise in the wastewater expelled leading to a rise in polluted water in Hamrin lake during the previous four decades

## Conclusions

Hamrin lake is fed by wastewater expelled from adjacent areas (domestic and agricultural). The present study throws light on the following:

1. There are great differences between previous data collected during previous studies and the data presented in this paper which emulate a rise in the wastewater expelled leading to a rise in polluted water in Hamrin lake during the previous four decades.
2. An increase in the levels of ammonia is apparently due to the utilization of ammonia by aquatic organisms as well as to the reducing of nitrate concentrations via a de-nitrification process.
3. The fluctuations of total nitrogen are probably due to the various agricultural inflows.
4. Phosphate compounds were always at high concentrations which are probably due to the influence of enriched wastewater with phosphate matters.
5. N/P ratio is so low indicating that nitrogen contributes poorly to the growth of aquatic microorganisms. Nitrogen can be considered a limited factor.

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**Table (1): Major oxides (%) in samples of clay from Hamrin lake**

| | Percentage (%) | | | | |
|---|---|---|---|---|---|
| | **$SiO_2$** | **$Al_2O_3$** | **$Fe_2O_3$** | | **Total** |
| **A** | 51.2 | 26.7 | 13.5 | | 91.4 |
| **B** | 49.3 | 25.2 | 13.6 | | 88.1 |
| **C** | 48.9 | 27.1 | 14.1 | | 90.1 |
| **D** | 48.4 | 28.1 | 13.9 | | 90.4 |

**Table (2):Minor oxides (%) in samples of clay from Hamrin lake**

| | Percentage (%) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **CaO** | **$Cr_2O_3$** | **CuO** | **$K_2O$** | **MgO** | **MnO** | **$Na_2O$** | **$P_2O_3$** | **$TiO_2$** | **ZnO** | | **Total** |
| **A** | 0.1 | 0.1 | 0.33 | 2.5 | *n.d | 0.1 | 0.1 | n.d | n.d | n.d | | 3.23 |
| **B** | 0.1 | 0.1 | 0.35 | 2.0 | n.d | 0.1 | 0.1 | n.d | n.d | n.d | | 2.75 |
| **C** | 0.2 | 0.2 | 0.32 | 2.5 | n.d | 0.2 | 0.2 | n.d | n.d | n.d | | 3.62 |
| **D** | 0.2 | 0.2 | 0.31 | 1.9 | n.d | 0.2 | 0.2 | n.d | n.d | n.d | | 3.01 |

*n.d = not detected

**Table(3): The percentage of minerals in the clay of lake Hamrin**

| Minerals | Symbol | Average percent (%) |
|---|---|---|
| Aluminum | Al | 25 |
| Calcium | Ca | 1 |
| Copper | Cu | 2 |
| Iron | Fe | 13 |
| Phosphorous | P | 1 |
| Potassium | K | 3 |
| Silicon | Si | 50 |
| Sodium | Na | 1 |
| Titanium | Ti | 1 |
| Zinc | Z | 1 |

**Table(4): The particle density and porosity of Kaolin samples**

| Samples | Particle density ($g.cm^{-3}$) | Porosity (%) |
|---|---|---|
| 1 | 1.42 | 0.56 |
| 2 | 1.28 | 0.47 |
| 3 | 1.30 | 0.58 |
| 4 | 1.25 | 0.42 |
| 5 | 1.45 | 0.33 |
| 6 | 1.45 | 0.30 |
| 7 | 1.34 | 0.44 |
| 8 | 1.33 | 0.46 |

**Table(5): Physicochemical variables in Hamrin lake during the studyPeriod**

| | A* | B* | C* | D* |
|---|---|---|---|---|
| Degree | | | | |
| pH of water | 7.7 | 7.5 | 8.5 | 8.4 |
| ammonia | 3.2 | 4.2 | 7.9 | 6.3 |
| Nitrite | 1.4 | 1.5 | 1.9 | 1.7 |
| Nitrate | 11.1` | 13.1 | 22.4 | 20.2 |
| phosphorous | 6.7 | 7.8 | 10.1 | 9.9 |
| Silicate | 27.3 | 29.4 | 39.5 | 37.0 |
| Total alkalinity | 4.0 | 4.3 | 8.7 | 8.8 |
| Total nitrogen | 25.4 | 26.3 | 36.9 | 34.2 |
| Chlorosity | 768 | 779 | 1262 | 1251 |
| BOD | 0.11 | 0.14 | 2.13 | 1.91 |

*A and B are samples collected from the mid of the lake, while C and D are samples collected from the shores of the lake.