

"Study on the Treatment of High Voltage Used Transformer Oil by Using Natural Material"

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Abstract: The insulating oils play an important role for long life of electrical equipment. Deterioration and aging process of insulating oils effect on electrical equipment lifetime. The insulating oils are expensive so it is better to regenerate it than replacement. The commercial kaolin clay that enriched with aluminum and silicon oxides and other traces of Na, K, Ca oxides was used to improve the quality parameters of the insulating oil such as color, appearance, acidity, breakdown voltage, water content, dissolved gas analysis, flash point and viscosity. Nevertheless the using of commercial kaolin with Oxalic acid and deionized water to make dechlorination of toxic Poly Chlorinated Biphenyls (PCBs) under certain conditions. PCBs are priority pollutants acting as endocrine disruptors, human carcinogens and environmental estrogens. PCBs used in many industrial applications due to their dielectric characteristics, chemical stability at high temperatures, insulating properties and low vapor pressure.

Keywords: Insulating oils, Commercial kaolin clay, Refining unit, Oxalic acid, Deionized water, PCBs.

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I. Introduction

Power transformer is the most important and expensive equipment used in transmission and distribution of electric energy. Even though the failure risk of a transformer is small, when any failure does occur, it inevitably leads to high repair costs, long downtime, and an increase in the safety-related risk. Moreover, transformer is too expensive to be replaced on a regular basis, so it must be properly maintained in order to maximize its life expectancy [EL-Sayed MM, et al. (2005)], Huimin H, Xiaotian X., (2012) and Gradnik T, et al. (2011). Oils which are essentially electrical insulators are used in electrical power transformers, mainly to transfer the heat and to increase the dielectric strength of the insulating paper [M.S. El-Gayar, et al. (2008)]. Nowadays transformer maintenance has become a strategy in the management of electrical transmission and distribution networks. A large number of power transformers are filled with mineral oils because of their advantages that constitute unique combinations of dielectric properties, cooling properties, and properties related to oxidation stability [Gradnik T, et al. (2011)].

In service, mineral oil degrades due to the conditions of use. In many applications, insulating oil is in contact with air and is therefore subject to oxidation. Elevated temperatures accelerate degradation. The presence of metals, organo-metallic compounds or both may act as a catalyst for oxidation. Changes in color, the formation of acidic compounds and, at an advanced stage of oxidation, precipitation of sludge, may occur. Dielectric and, in extreme cases, thermal properties may be impaired. In addition to oxidation products, many other undesirable contaminants, such as water, solid particles and oil-soluble polar compounds can accumulate in the oil during service and affect its electrical properties. The presence of such contaminants and any degradation product of oil are indicated by a change of one or more properties. Deterioration of other constructional materials, which may interfere with the proper functioning of the electrical equipment and shorten its working life, may also be indicated by changes in oil properties. Often the first sign of oil deterioration may be obtained by direct observation of the oil clarity and color through the sight glass of the conservator. From an environmental point of view, this simple and easy inspection can also be used to monitor leakage and spills of oil. Fuller's earth is an active material containing both internal and external polar activities, which allow the non-polar components of the oil to pass through without retention but which retains the polar contaminants or degradation compounds dissolved in the oil. Several different clays are available that have proven suitable for these purposes. The most widely used are of the sepiolite, bentonite, attapulgite or

montmorillonite type of which fuller's earth is the most commonly used. They are constituted of silicate anions $[\text{Si}_2\text{O}_5]_n$ condensed with octahedral layers of the type $\text{X}(\text{OH})_2$ where X may be magnesium, aluminum, etc. [A.I.Hafez et al (2017)]. Normally, fuller's earth is treated to increase its specific surface area and the concentration and polarity of its Lewis acids. Fuller's earth can be used alone or in combination with other chemicals like trisodium phosphate, activated charcoal and sodium silicate. The retention of contaminants by adsorbent active sites is, generally, improved by temperature, thus the process normally takes place at 60 °C to 80 °C. Experience has shown that it is usually necessary to pass the total volume of oil through the adsorbent not less than three times, and equipment of appropriate capacity should be chosen for this purpose. The final number of cycles will depend on the degree of initial contamination and the desired final level for properties [IEC 60422: (2013), Edition 4, page 10, 11, 24, 37].

Currently, activated bauxite and bentonite are used as low cost adsorbents for the recovery of aged oil in order to; maintain its properties to be to some extent like the new oil [A. A. Al-Zahrani and M.A. Daous, (2000), L. Nasrat, et al. (2011) and A.I. Hafez (2015)].

It is thus necessary to examine the effectiveness of other raw materials, especially from renewable sources, that possess adsorbent properties for removing impurities in the treatment of insulating oil without any impacts on the environment. Kaolin is a natural material has both rock and clay mineral term include quartz, smectites, feldspars and micas. Kaolin is widely utilized in the paper, paint, rubber, ceramic and plastic industries. Other applications in wine and vegetable clarifiers, oil absorbers, iron smelting [(Ekosse G., (2000), Ekosse G., (2001)] and Murray H. H., (1986)].

More than four decades have passed since the production and use of polychlorinated biphenyls (PCBs) were banned, but they remain a big problem for human and environmental health [Behafrooz B, et al.(2017)]. PCBs are chlorine-bearing derivatives of biphenyl with 1–10 chlorine atoms and have many industrial applications due to their dielectric characteristics, chemical stability at high temperatures, insulating properties and low vapour pressure [Shin SK, Kim TS,(2006)]. PCBs were mainly used in the production of Askarel, which was produced in the reaction between Arochlor, a trade name for a mixture of PCBs in the USA, and trichlorobenzene. They were used as the dielectric fluid in capacitors, transformer oils, hydraulic fluids, etc.[Shin SK, Kim TS,(2006)]and [Simion AM, et al. (2013)].

According to the Stockholm Convention on Persistent Organic Pollutants (POPs), PCBs were placed in the group of POP Materials due to their destructive effects on the human body, their persistence in the environment and their bioaccumulation in the food chain. Member States of this convention are bound to destroy gradually their PCB stockpiles by 2025 [Jelic A, et al.(2015)].

In the case of oil contaminated with PCBs, environmental impact is a critical factor to consider, as are local regulations. If it is suspected that oil has become contaminated with PCBs specific analyses should be undertaken and interpretation of the results should be used in risk assessment to take into account prevention and mitigation of potential damage to the environment and to avoid unreasonable risks for staff and the public [IEC 60422: (2013), Edition 4, page 25].

Many methods for the dechlorination of PCBs have been consequently developed. Few methods like incineration, photochemical dechlorination, catalytic dechlorination [Waid JS,(1986), Hitchman ML, et al. (1995)] and Ishikawa M and Fukuzumi S, (1990)], high temperature decomposition with or without oxygen gas [Hagenmaler H, et al. (1987)] and [U.S. Congress,(1991)]. Oxidative treatment using supercritical water [Weber R, et al. (2002)] and dehalogenation by hydroxide using KOH in DMI (1,3-dimethyl -2-imidazolidinone) with heating [LaPierre R , et al. (1978) and Tavoularis G and Keane M,(1999)] seemed to present some success for detoxification. However, these methods which involve high temperature or high pressure conditions have some disadvantages in recovering the vaporized PCBs, in driving up operating costs and in incurring the high risk of de novo synthesis of dioxins. On the other hand, a few methods using mild conditions, such as an alkali metal like metallic sodium in oil [Forni P, et al. (1997)].

In this investigation, the constructing and using a lab-scale refining unit containing commercial kaolin as sorbent for treatment of aged transformer oil (more than ten years in service) was studied. In addition to the variations of acidity, breakdown voltage, viscosity, specific gravity, water content and some undesirable gases of the treated oil are measured. Nevertheless using of commercial kaolin with Oxalic acid and demineralized water to make dechlorination of toxic Poly Chlorinated Biphenyls (PCBs) under certain conditions was studied.

II. Experimental

2.1. Materials:

2.1.1. Aged Transformer Oil:

Aged Transformer oil was collected from high voltage transformer (220/66 K.V.) after more than twenty years operation with the properties listed in Table (1) as follow:

Table (1) Specification of Aged transformer oil

Exp.	Standard Method	Results	Specification limits ⁽¹⁾
Specific Gravity at 60/60°F	ASTM : D 1298	0.8761	Max. 0.895
Appearance	ASTM : D 1524	not clear and contain sediment	Clear and free from sediment
Color	ASTM : D 1500	6	-
Water Content (ppm)	ASTM : D 1533	29	Max. 20 ⁽²⁾
Total Acidity (mg KOH/g Oil)	ASTM : D 974	0.32	Max. 0.01
Breakdown Voltage (Kv /2.5 mm)	IEC : 156	31	Min. 50 ⁽²⁾ for (220/66 k.v.)
Kinematic Viscosity at 40°C (mm ² /s)	ASTM : D445	10.45	Max. 12
Flash Point closed (°C)	ASTM : D93	142	Min. 135
Copper Corrosion	ASTM : D130	Not corrosive	Not corrosive

(1) Acceptable limits for mineral insulating oils: According to IEC 60296:2012.

(2) Acceptable limits for mineral insulating oils: According to IEC 60422:2013.

2.1.2. Commercial Kaolin clay:

Commercial kaolin clay in fine form that enriched with aluminum and silicon oxides and other traces of Na, K, Ca oxides was used. The typical grinded form of Kaolin clay is shown in Fig. (1).

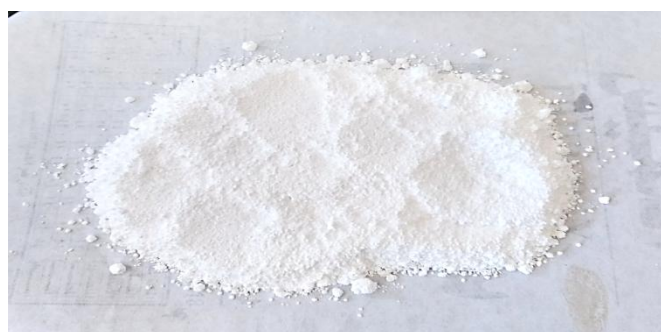


Figure (1): Typical grinded form of commercial kaolin clay.

2.1.3. Aged transformer oil containing PCBs:

Transformer oil was collected from high voltage transformer (66/11 K.V.) after more than fifteen years operation with the properties listed in Table (2) as following:

Table (2) Specification of Aged transformer oil containing (PCBs)

Exp.	Standard Method	Results	Specification limits ⁽¹⁾
PCBs content (ppm)	DEXIL PCB Test Method (Electrochemical Analysis)	730	50 ⁽³⁾
Specific Gravity at 60/60°F	ASTM : D 1298	0.8691	Max. 0.895
Visual examination	ASTM : D 1524	not clear and contain sediment	Clear and free from sediment
Color	ASTM : D 1500	2.5	-
Water Content (ppm)	ASTM : D 1533	21	Max. 20 ⁽²⁾
Total Acidity (mg KOH/g Oil)	ASTM : D 974	0.21	Max. 0.01
Breakdown Voltage (Kv /2.5 mm)	IEC : 156	48	Min. 30 ⁽²⁾ for (66/11 k.v.)
Kinematic Viscosity at 40°C (mm ² /s)	ASTM : D445	9.6	Max. 12
Flash Point closed (°C)	ASTM : D93	148	Min. 135
Copper Corrosion	ASTM : D130	Not corrosive	Not corrosive

(1) Acceptable limits for mineral insulating oils in-service: According to IEC 60296:2012.

(2) Acceptable limits for mineral insulating oils in-service: According to IEC 60422:2013.

(3) Acceptable limits for total PCB content must be <50 ppm according to Stockholm Convention on persistent and organic pollutants.

2.1.4. Oxalic acid:

Oxalic acid crystal was supplied by (Spectrum Chemical MFG. CORP.) with assay $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$. Oxalic acid was used for the regeneration of hydrogen species by supply more available H^+ without undesired side reaction which could greatly enhance PCB dechlorination [Neng-Min Zhu et.al, (2012)].

2.1.5. Deionized water:

Deionized water was used to dissolve oxalic acid to be more active and to form two liquid phases with oil.

2.2. Treatment process for reclamation of aged transformer oil:

2.2.1. Refining unit:

The refining unit for aged transformer oil consists of three main components:

- 1- Vacuum chamber and pump.
- 2- Acidity and impurities removal cartridge.
- 3- Fine and coarse filter.

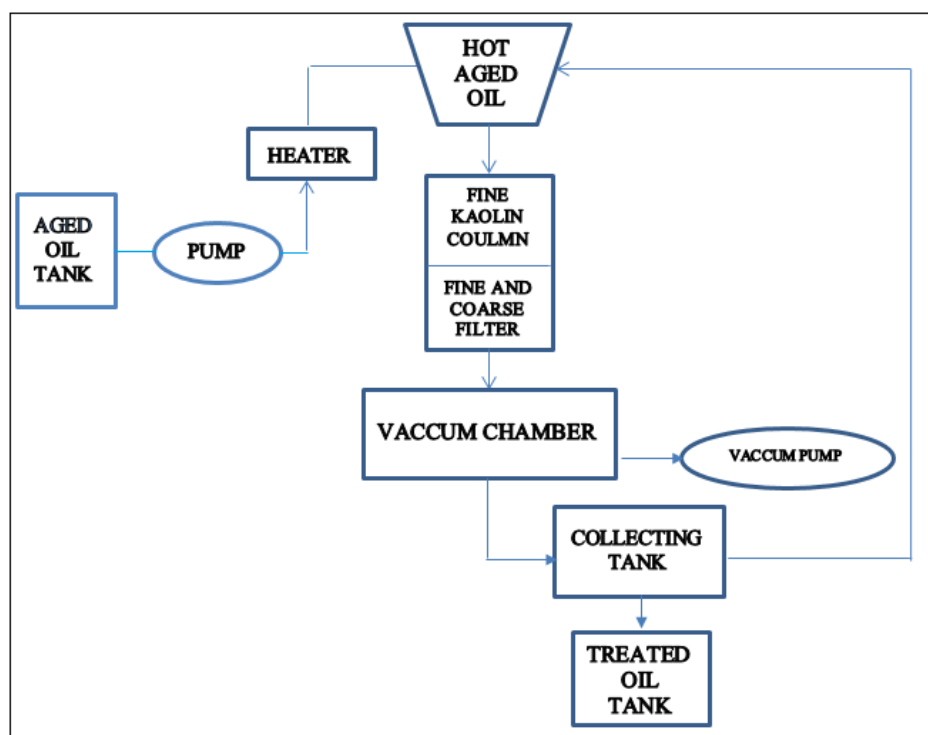


Figure (2): The schematic diagram of refining unit.

2.2.2. Treatment process:

The treatment process performed using one liter of the aged transformer oil with different doses of kaolin at different temperatures and time in the lab scale-refining unit. The amounts of kaolin were put in acid and impurities removal cartridge (fine kaolin column). The aged oil samples heated and passed through the cartridge for different time and temperature in stages of half an hour each. The oil then introduced to vacuum chamber to remove undesirable gases and water content after treatment. The treated oil finally collected in the treated oil tank. Samples of the treated oil were withdrawn and analyzed applying the standard methods of test.

2.3. Dechlorination of toxic Poly Chlorinated Biphenyls (PCBs) under certain conditions:

2.3.1. Apparatus:

- Heater with stirrer.
- Thermometer.
- Three conical flasks.
- Separating funnel.
- Centrifuge.
- Filter paper.
- Buchner funnel with conical flask attached to vacuum pump.

2.3.2. Procedure:

Deferent ml of 8% of dissolved oxalic acid in deionized water was added to hot oil sample at 60 °C with continuous stirring in 250 ml conical flask to form a mixture of oxalic acid in oil. The temperature of mixture then increased to 95 °C. After 15 min, 8% of kaolin clay (white powder) was added to the mixture very slowly with continuous stirring to prevent effervescence of the mixture outside the flask with continuous stirring at 95°C for (30 min.). The mixture will go to cool at room temperature. The mixture then transfer to separating funnel and shake well for 120 min in automatic shaker. The separating funnel will kept in fixed place to separate the water and mixture of exhausted kaolin and oxalic acid. The tape of separating funnel opened to remove the separated water and precipitated kaolin clay. The isolated oil then putted in centrifuge at 1000 RPM then heated to 60°C and filtered in Buchner with vacuum pump to remove any sediments, water and gasses from oil. The produced oil goes through PCBs analysis to measure its concentration. The previous steps can repeated several times until reach best removal of PCBs.

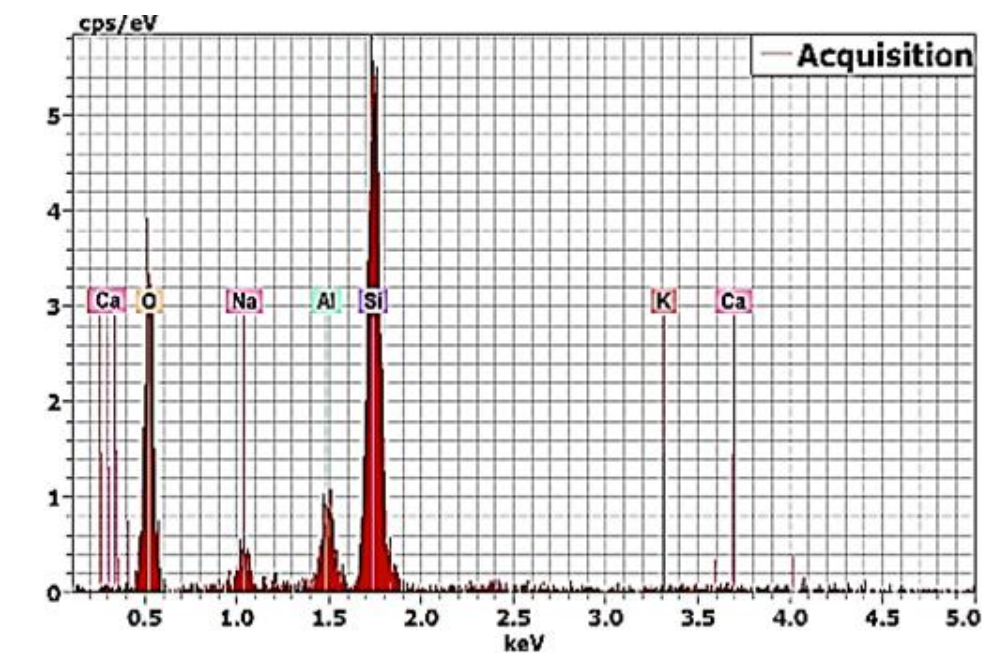
III. Results and Discussion

Experimental work revealed that kaolin has approximately the same constituents of bentonite and bauxite that are the most substances used in reclaiming the transformer oils [P. M. Balma, et al.(1999)]. Therefore, the kaolin was chosen to use as reclaiming substance. The electrical, chemical and physical properties of insulating oil considerably improved by its filtering, degassing and dehydration. During its operation, transformer-insulating oil is absorbing moisture over its free surface in the expansion vessel and it becomes polluted by absorbing dirty particles, fibers, soot, undesired gases and aging products. Therefore, oil upgrading has to eliminate these contaminants. The abovementioned contaminants can be removed by filtering, degassing and dehydration of insulating oil to the extent depending on moisture content and reducing the acidity by an acid adsorbent agent.

3.1. Structure and chemical composition of kaolin:

3.1.1. Energy Dispersive X-ray analysis:

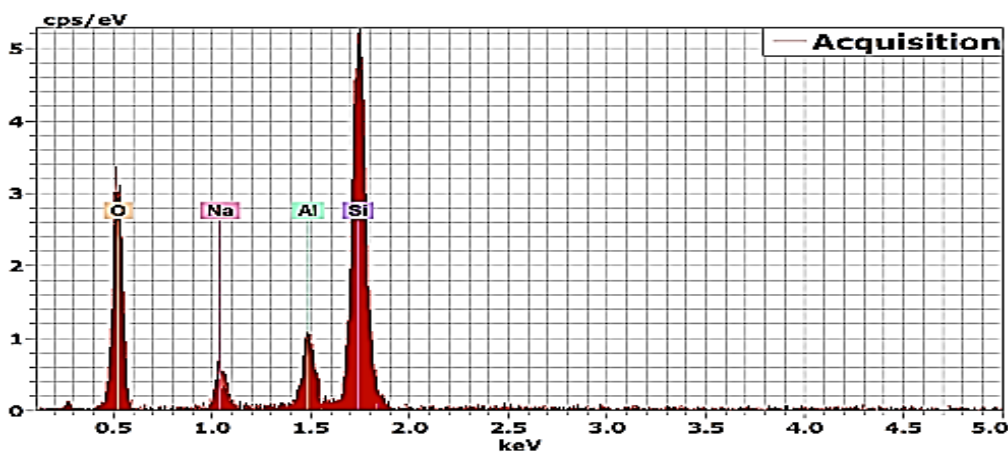
Commercial kaolin clay was analysed using; Energy Dispersive X-ray spectrometer (EDX) ISIS Link Instrument P/C. Oxford Co, which is attached to a SEM. Figure (3),(4) show two spectrum of kaolin sample. One of them was thermally treated at 650 °C and the other without treatment. It is evident that thermally treated kaolin sample was enriched by some inorganic elements whose amounts are represented by the peaks. The presence of (Al) and (Si) ions as shown in the figures confirm that the thermally treated sample enriched by these two elements. There are traces of (Na, K, Ca) present also in the thermally treated kaolin clay. Therefore, thermally treated one is used in this work.



Spectrum: Acquisition

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
O	8	K-series	41.51	56.12	68.73	9.8
Na	11	K-series	2.83	3.83	3.26	0.4
Al	13	K-series	4.25	5.74	4.17	0.4
Si	14	K-series	25.06	33.88	23.63	1.3
K	19	K-series	0.15	0.20	0.10	0.1
Ca	20	K-series	0.17	0.23	0.11	0.1
Total:			73.97	100.00	100.00	

Figure (3): EDX chart of thermally treated kaolin sample



Spectrum: Acquisition

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
O	8	K-series	41.53	55.65	68.13	7.6
Na	11	K-series	3.61	4.84	4.13	0.4
Al	13	K-series	4.90	6.56	4.76	0.4
Si	14	K-series	24.59	32.95	22.98	1.2
Total:			74.63	100.00	100.00	

Figure (4): EDX chart of kaolin sample

3.1.2. Thermo gravimetric analysis (TGA):

Thermo gravimetric analysis of kaolin sample was performed using (Thermo gravimetric determinator Leco: Mac-500, ST. Joseph, Michigan-USA). This apparatus provides a continuous measurement of sample weight at a range of temperatures between ambient and 900 °C. The samples were heated in an alumina cell to 900 °C at heating rate of 10°C/min with nitrogen as the circulating gas.

The diagram obtained (Fig. 5) shows four characteristic stages of decomposition. The first stage starts at 55 °C and ends at 90°C with weight loss of 5.3 %. This could be recognized as due to the moisture content of kaolin sample. The second stage which related to the main decomposition of the sample occurs in one step of decomposition starts at 90°C and ends at 220°C with weight loss of 11% representing the hydrated hydroxide $[\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}]$ and others. The third stage of decomposition is related to the carbonization process, which occurs up to 600 °C with a weight loss of 32%. The fourth stage is related to calcination stage, which started at 600 °C and ended at 900°C with weight loss of 37%.

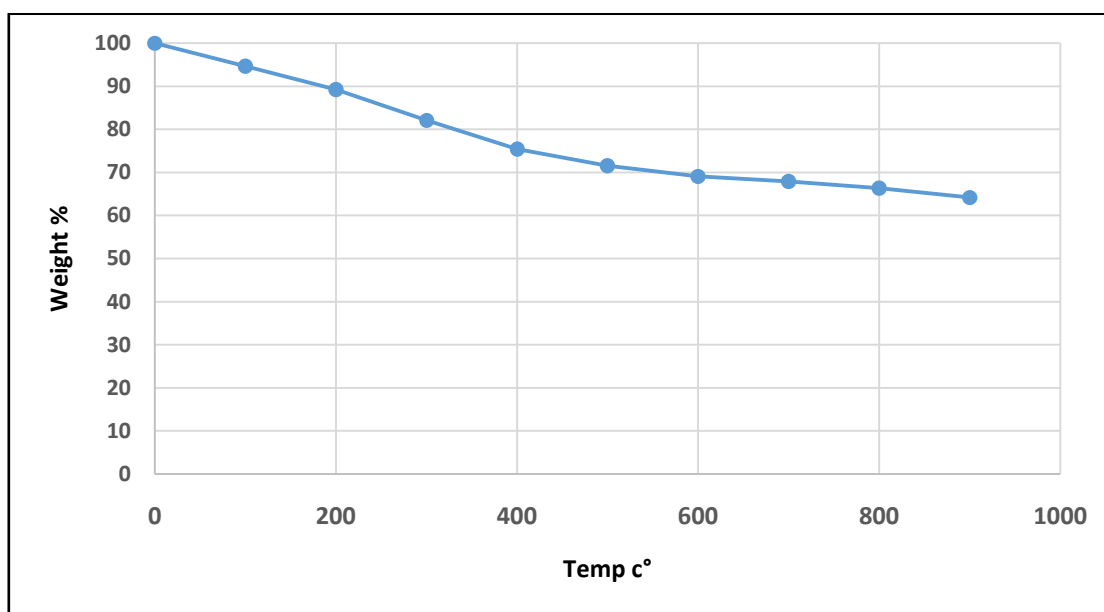


Figure (5): TGA of kaolin.

3.2. Enhancement of aged transformer oil properties by using kaolin clay treatment.

3.2.1. Effect of kaolin treatment on acid number of oil:

The degradation of oil produces some organic acids such as carboxylic acids that will either dissolve in the oil or volatilize into the headspace of transformer. Dissolved acids may cause damage to the paper and copper windings, while volatile acids corrode the top of the unit. As a result, all of the necessary conditions exist properly in a power transformer for the degradation of the oil.

The acid number of aged and reclaimed oil was measured using ASTM D 974. The effect of kaolin on the removal of acidity is represented by Figures (6-9). These Figures indicate that the acidity decreases by increasing the amount of adsorbent material (kaolin) at different temperatures and stages of refining (stage time is ½ hour). The maximum decrease of acidity was at kaolin dose of 20% for 4 stages at 60°C, it reached 0.02mg KOH /g of oil.

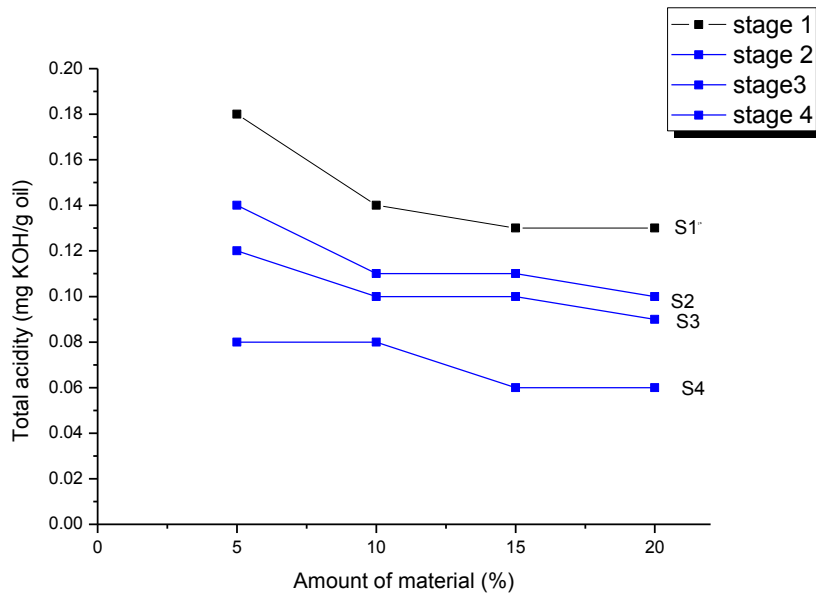


Figure (6): Variation of acid number with kaolin dose (at 30°C)

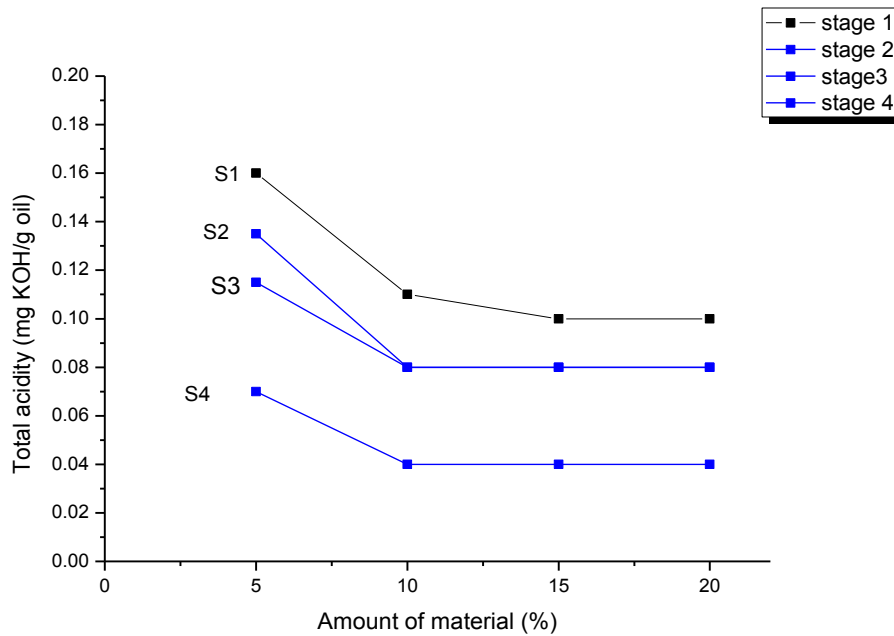


Figure (7): Variation of acid number with kaolin dose (at 40°C)

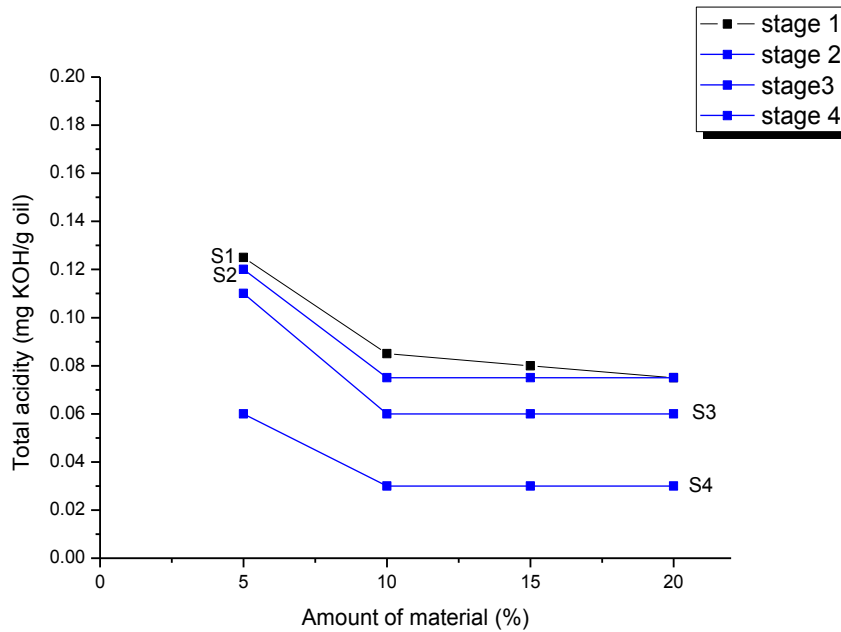


Figure (8): Variation of acid number with kaolin dose (at 50°C)

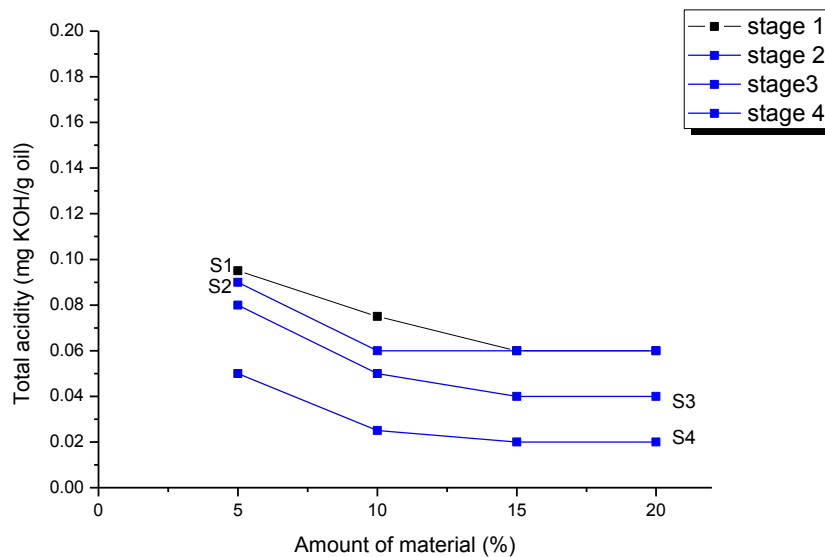


Figure (9): Variation of acid number with kaolin dose (at 60°C)

3.2.2. Effect of kaolin treatment on the color of oil:

The color of an oil sample related to the deterioration of the sample. Fresh virgin mineral oil from the refinery essentially colorless. However, as the sample ages over time or subjected to severe conditions such as local hot spots or arcing, the sample will become darker in color. The clarity of a fresh virgin sample of oil should be sparkling with no indication of cloudiness, kaolin, or particulate matter. The clarity of an oil sample determined by observation of the sample when illuminated by a narrow focused beam of light .

The color of a sample determined by direct comparison with a set of color standards using "Colorimeter as colorimeter degree according to ASTM D1500/03". The color of an oil sample used mainly as a guide to the degree of refinement of the oil when it is new. If the sample is from a transformer that has been in service then the color can be followed over a period of time to indicate the possible condition of the oil. It should be pointed out that the color of the oil by itself should never be used to indicate the dielectric quality of the oil [L. Nasrat, et al.(2011)]. However it can be used to determine whether more definitive tests should be done to determine specific characteristics of the sample that are more related to the performance of the oil .The clarity of the sample can also give possible suggestions for further tests. Cloudiness of the sample

can indicate the presence of water, which in turn will decrease the dielectric strength of the sample. Figures (10-13) represent the variation of oil color with amount of adsorbent material (kaolin) at different temperatures through the four stages of treatment. There is a significant improvement in the color of the treated oil resulting from increasing the amount of adsorbent material (kaolin), at the working temperatures. The color of oil was changed from 6 degree of aged oil to 1 degree after 4 stages as can be seen from the Figures.

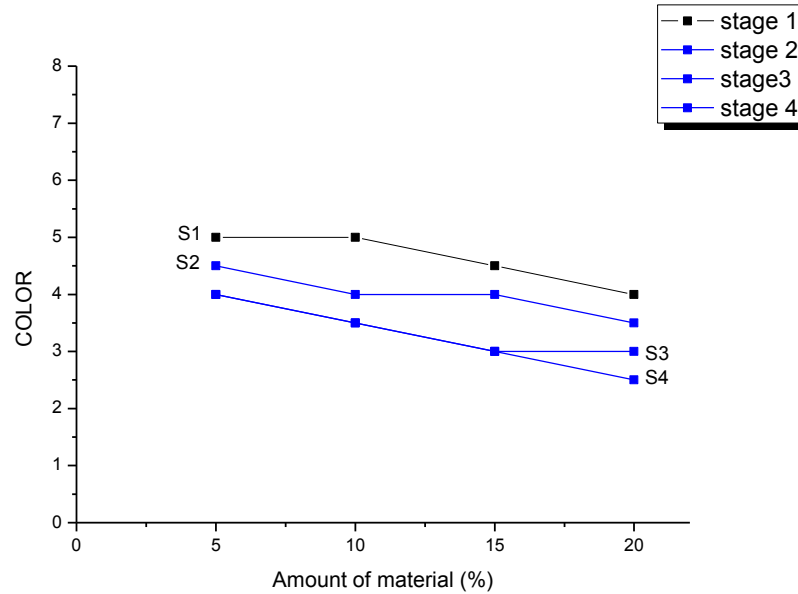


Figure (10): Variation of color with kaolin dose (at 30°C)

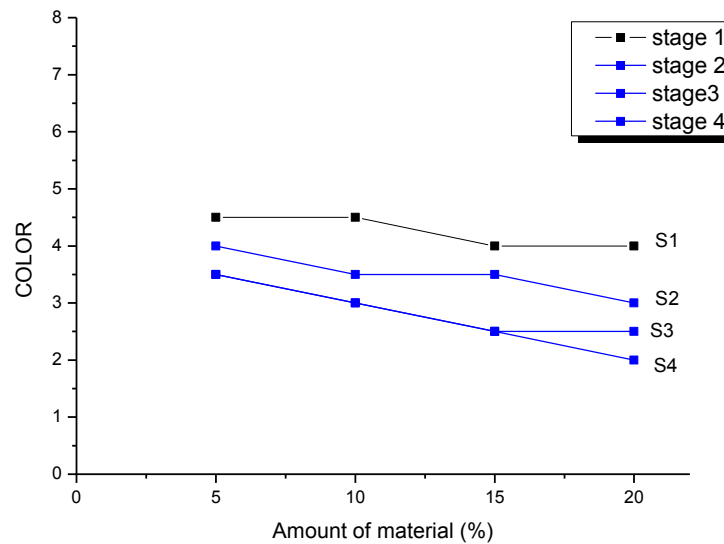


Figure (11): Variation of color with kaolin dose (at 40°C)

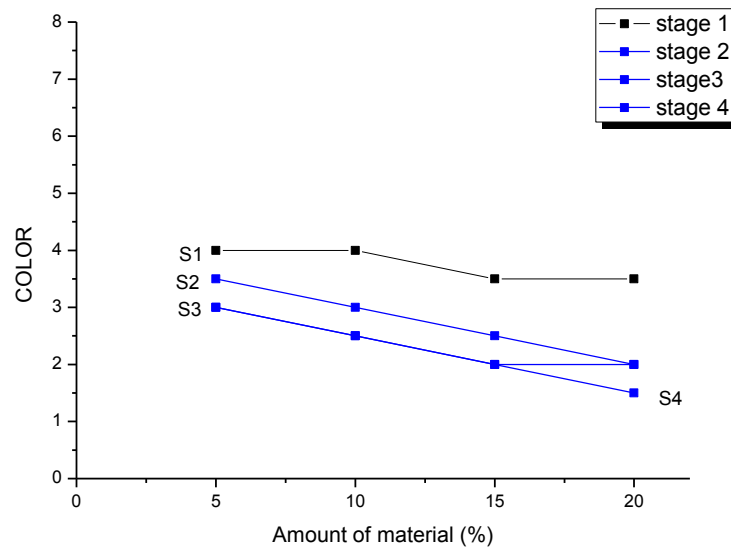


Figure (12): Variation of color with kaolin dose (at 50°C)

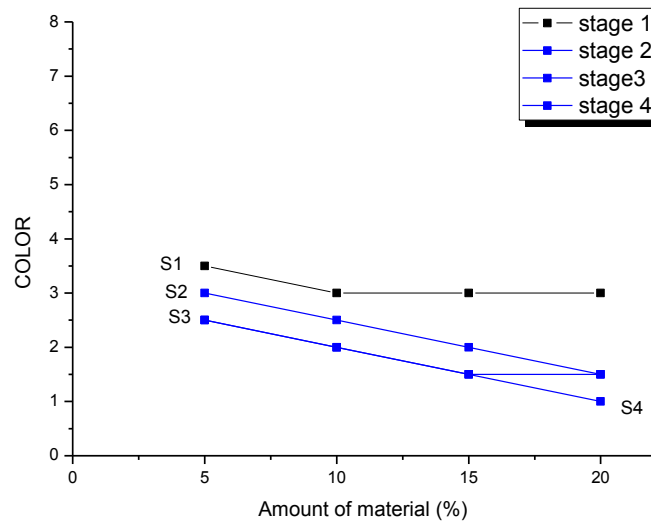


Figure (13): Variation of color with kaolin dose (at 60°C)

Also figure (14) shows the color oil samples photographs of untreated and treated oil at different reclaiming stages at 60°C

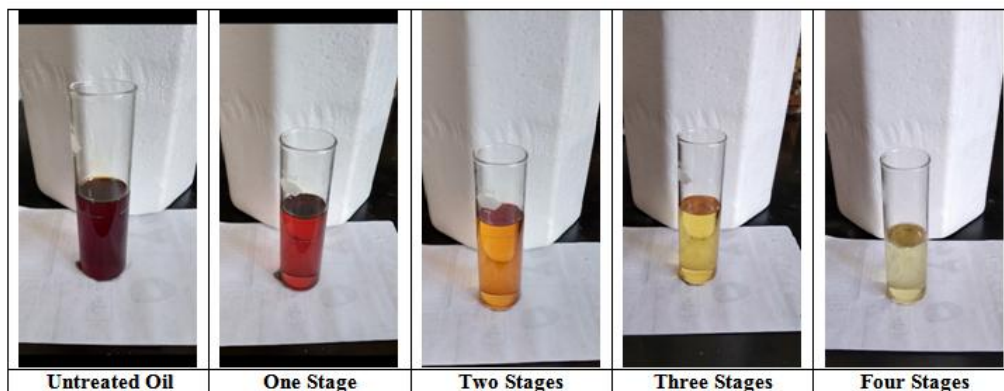


Figure (14): Color of treated and untreated transformer oil at 60°C

3.2.3.Effect of kaolin treatment on the breakdown voltage:

Low breakdown voltage of oil indicates deterioration and/or contamination of oil by some undesirable matter such as water, carbon or other conducting particles, including metal ions caused by acids attacking transformer body and products of oxidation. If the breakdown voltage value is less than the standard acceptable limit, the oil may cause failure of the transformer. Replacement or purification of the oil is required immediately. The breakdown voltage of aged and reclaimed oil measured by (Megger OTS100AF)device according to IEC60156. Figures (15-18) show the variation of breakdown voltage of oil by increasing the amount of adsorbent material. The value changed from 31K.v. for aged oil to 74 Kv for reclaimed oil by such material at temperature 60 °C after the four stages treatment.

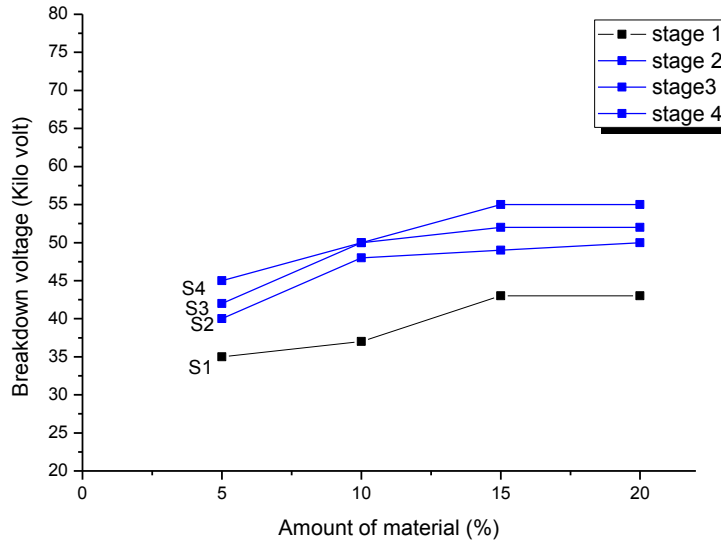


Figure (15): Variation of breakdown voltage with kaolin dose (at 30°C)

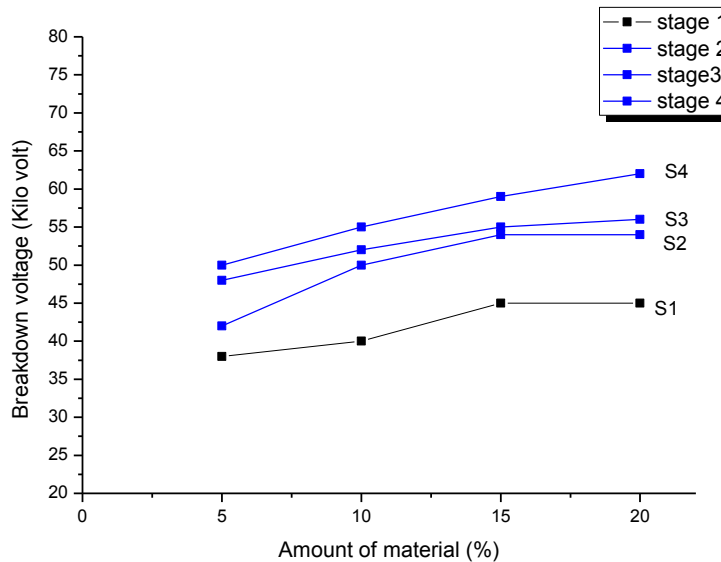


Figure (16): Variation of breakdown voltage with kaolin dose (at 40°C)

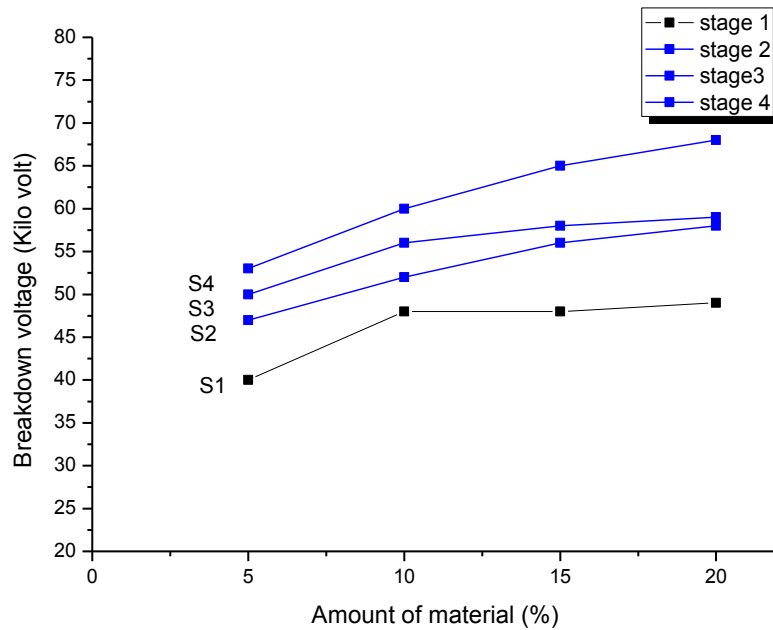


Figure (17): Variation of breakdown voltage with kaolin dose (at 50°C)

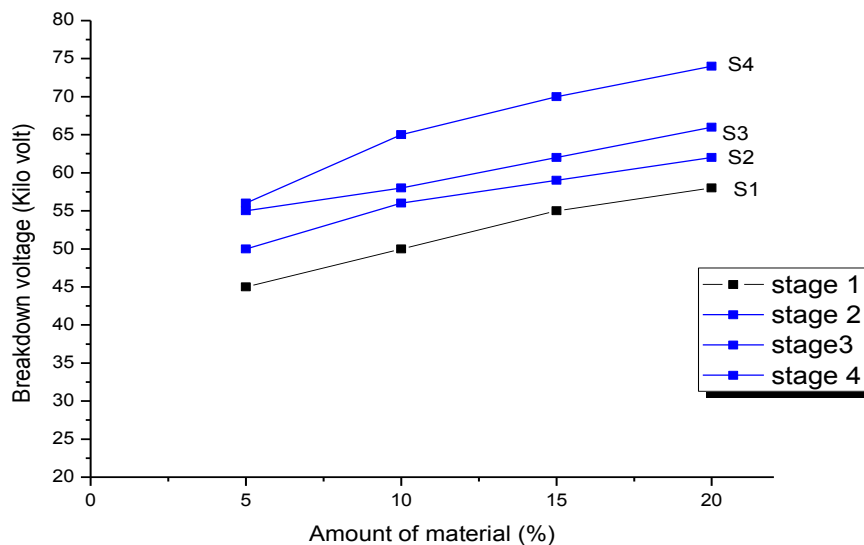


Figure (18): Variation of breakdown voltage with kaolin dose (at 60°C)

3.2.4. Effect of kaolin treatment on water content of oil:

The water content in the liquid and solid insulation thus has a significant impact on the actual operating conditions and the lifetime of the transformer. There are two main sources of water increase in transformer insulation:

- Ingress of moisture from the atmosphere.
- Degradation of insulation.

Water is transferred in oil filled electrical equipment by the insulating liquid. Water is present in oil in a dissolved form and may also be present as a hydrate adsorbed by polar ageing products (bonded water). Particles, such as cellulose fibers may bind some water (IEC 60422: 2013, Edition 4, page 12). Flash point of aged and treated oil was measured by [Karl fisher - MKE500-serial no. Lcb32a22- KEM (Japan)]. Table (3) shows the decreasing of water content of oil during the four stages of treatment at 60 °C for 20% adsorbent material (kaolin).

Table (3): Variation of water content during the four stages of treatment

Exp.	AgedOil	One stage	two stages	three stages	four stages
Water content(ppm)	29	19	12	8	7

3.2.5.Effect of kaolin treatment on oil viscosity:

The viscosity of dielectric coolants within the range of normal operating temperatures is important because it can impact both the cooling and performance of some internal components. The oil closed to the windings in the field transformer flows up at higher temperature while the oil at lower temperature flows to bottom from the wall. The heat is scattered from windings in this way. So, transformer oil with lower viscosity has better cooling effect. The increase of viscosity, which has negative effect on load and efficiency, is adverse to the safe operation of the unit. Therefore, it is essential to control the viscosity of transformer oil in service. The viscosity of aged and treated oil was measured by [viscometer Koehler”K2337].Table (4) shows the variation of kinematic viscosity of oil during the four stages of treatment at 60 °C for 20% adsorbent material (kaolin).

Table (4): Variation of oil viscosity during the four stages of treatment.

Exp.	AgedOil	One stage	Two stages	Three stages	Four stages
Kinematic Viscosity (mm²/s)	10.45	10	9.9	9.8	9.8

3.2.6. Effect of kaolin treatment on flash point (closed):

Breakdown of the oil caused by electrical discharges or prolonged exposure to very high temperatures may produce sufficient quantities of low molecular weight hydrocarbons to cause a lowering of the flash point of the oil. A low flash point is an indication of the presence of volatile combustible products in the oil. This may result from contamination by a solvent but, in some cases, the cause has been observed to be extensive sparking discharges [IEC 60422: (2013), Edition 4, page 19].Flash point of aged and treated oil was measured by[Pensky marten - APM-7-serial no. 20311-Tanaka (Japan)].Table (5) shows the increasing of flash point of oil during the four stages of treatment at 60 °C for 20% adsorbent material (kaolin).

Table (5): Variation of oil flash point during the four stages of treatment.

Exp.	AgedOil	One stage	two stages	three stages	four stages
Flash Point(°C)	142	144	146	148	148

3.2.7.Effect of kaolin treatment on dissolved gas analysis (DGA):

The dissolved gases in the oil play an important role in the transformer operation because of the probability of explosion. There is a limit for every gas in the transformer oil according to its load. The gases in the aged and treated oil were analyzed by Gas Chromatograph "DANI Auto sampler GC1000"according to ASTM D3612 and the results are listed in Table (6). It is obvious that the amount of gases in the reclaimed oil is within the standard limits of operation.

Table (6): Analysis of gas in the aged and treated oil

Gas	Ppm					Alert limits
	Aged oil	One stage	two stages	three stages	four stages	
Hydrogen (H ₂)	57	30	11	9	5	100 – 700
Oxygen (O ₂)	20147	34185	9763	11404	7235	-
Nitrogen (N ₂)	107894	135537	14876	39284	67552	-
Carbon monoxide (CO)	73	52	22	57	18	350 – 570
Carbon dioxide (CO ₂)	3285	1133	1701	1077	1008	2500 – 4000
Methane (CH ₄)	2786	101	73	3	0.0	120 – 400
Ethane (C ₂ H ₆)	1468	740	365	4	0.0	65 – 100
Ethylene (C ₂ H ₄)	6976	2763	3381	2	0.0	50 – 100
Acetylene (C ₂ H ₂)	167	44	37	5	0.0	1 – 9
Total Dissolved Combustible Gas (TDCG) =	11527	3730	3889	80	23	720 – 1920

3.2.8. Effect of kaolin treatment on the Elemental analysis of reclaimed oil:

The elemental analysis (C, H, N and S) determined by (LecoTruspect (CHN) Analyzer, Leco Corporation 3000 LAKE View AVE.ST. Joseph,MI-USA). The results are listed in Table (7).

Table (7): The elemental analysis of aged and reclaimed transformer oil.

Element % \ Sample	Aged Oil	One stage	two stages	three stages	four stages
C	85.55	85.01	85.00	84.80	84.81
H	12.97	13.01	13.31	12.93	13.00
N	0.20	0.19	0.18	0.18	0.17
S	0.30	0.13	0.08	0.04	Nil

The data represented by Table (7) reveal that the carbon element in oil slightly reduced by the reclamation stages. The reduction in carbon element by the treatment may be attributed to the elimination of carbon impurities present in the aged oil due to ageing conditions. The results indicate also that there is a significant reduction in sulfur content at the third and fourth stages of treatment.

3.3. Dechlorination of toxic Poly Chlorinated Biphenyls (PCBs) by using kaolin clay under certain conditions:

PCBs act as endocrine disruptors, human carcinogens and environmental estrogens and have been reported as most toxic organic pollutants [Olea N and Pazos P, (1998)] and [Bumpus JA, et al. (1985)] and [Hutzinger O, et al. (1974)].

The PCBs was determined by using **L 2000DX Analyzer**. It is one of screening methods for determining the presence of PCBs in transformer oil but it is better than other screening methods because it quantifies the result and shows it in ppm. The device uses the technique of addition of sodium metal. The sodium metal makes dechlorination to PCBs. Then add aqueous extraction solution which (adjust PH, destroy excess sodium after reaction and separate chloride ions in clear aqueous layer which is decanted in analysis vial) then we use ion specific electrode to determine concentration of free chloride ions in ppm then convert it into PCBs concentration in ppm as a trade name Aroclor 1242 (contains 42% of chlorine with a predominance of congeners bearing three and four chlorine atoms. Device measurement range is (2-2000 ppm) for oil samples.

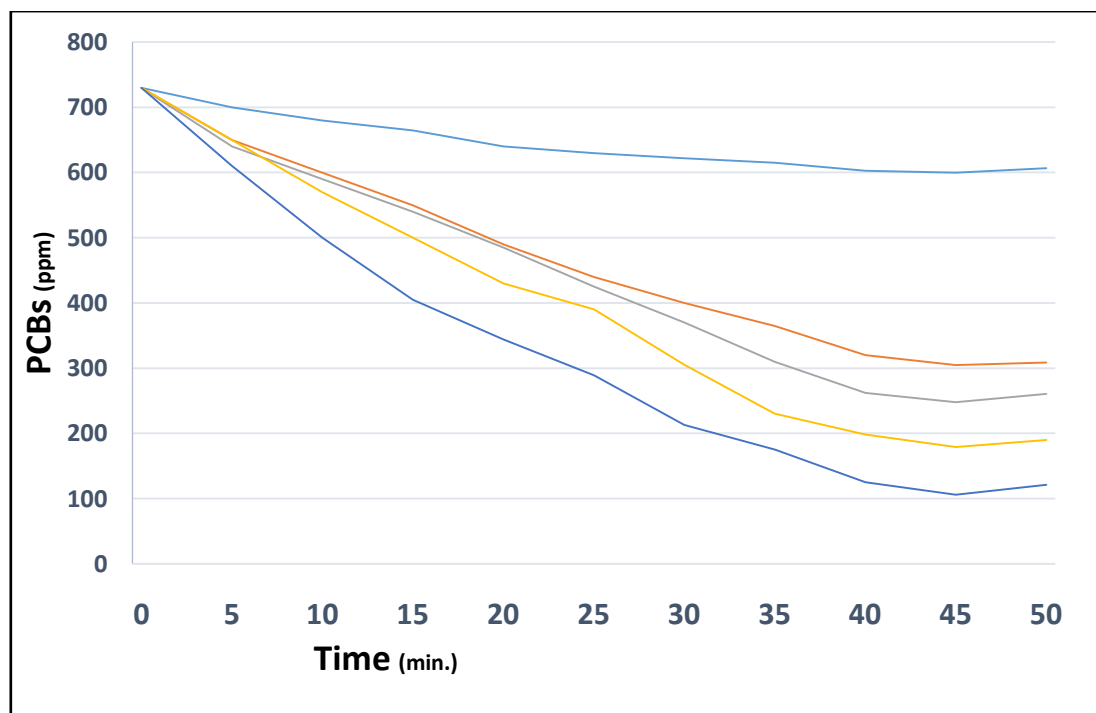


Figure (19): Variation of PCB content with kaolin and oxalic acid dose at different times.

Figure (19) shows the variation of PCBs removal (percentage) with kaolin and oxalic acid dose at different times. The results showed that the best percent of removal reached to 85.48% with addition of 32% oxalic acid and 32% commercial kaolin for 45 min. through 10 stages.

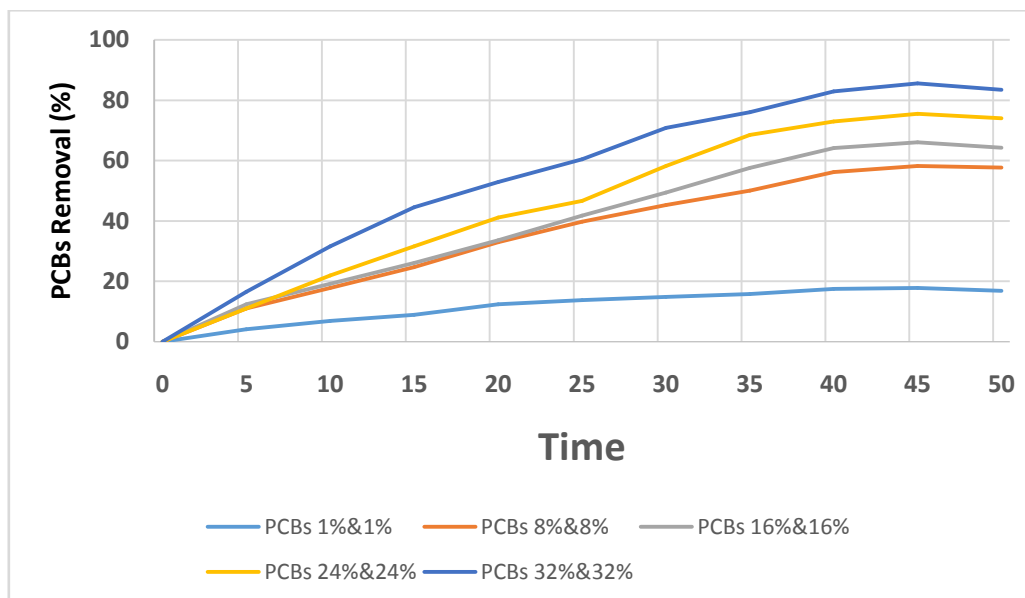


Figure (20): Variation of PCBs removal percentage with kaolin and oxalic acid dose.

Figure (20) shows decreasing of PCBs content with increasing kaolin and oxalic acid dose for 45 min. at 95°C. The lowest value of PCBs reached to 106 ppm in 10 stages. Farther stages of treatment reduce the amount of PCBs to less than 50 ppm.

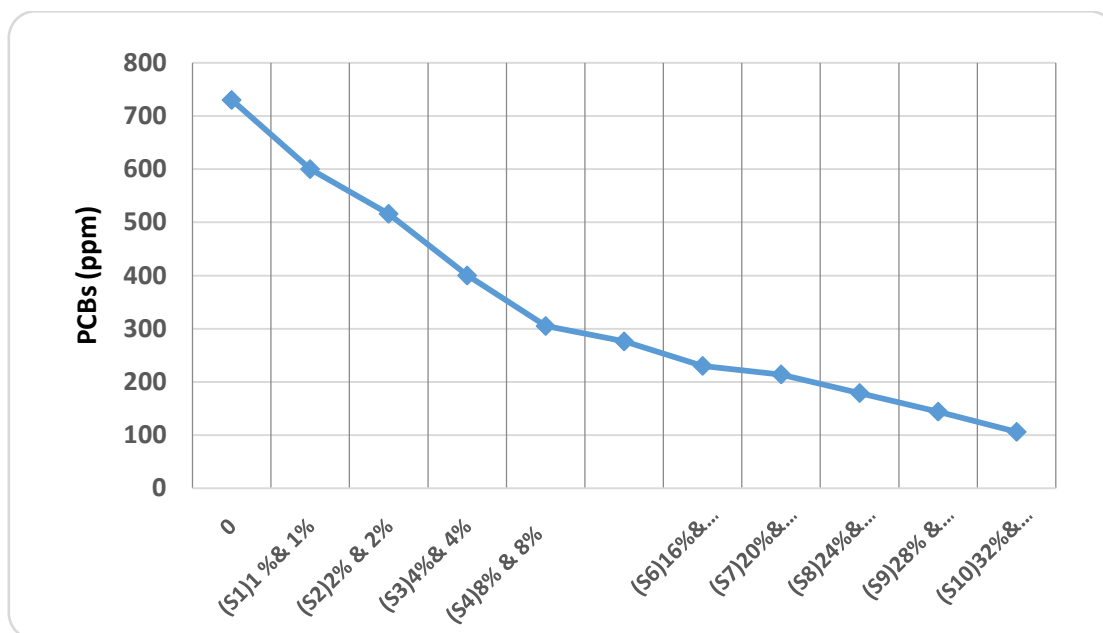


Figure (21): Variation of PCBs content with kaolin and oxalic acid dose (at 95°C and for 45 min.)

Figure (21) shows Variation of PCBs content with kaolin and oxalic acid dose at different times and every result represents a separated experiment. The temperature was rise to 95°C in order to increase reaction activation so the temperatures of reaction increase the dechlorination of PCBs increase. The experimental results showed that when the temperature below 95 °C, the results of dechlorination does not good, also the temperature does not exceed 95 °C because the use of water in the experiment will boiled at 100 °C leading to incomplete reaction. The lowest value of PCBs that achieved was 106 ppm with addition of 32% oxalic acid & 32% commercial kaolin for 45 min. through 10 stages. Farther more stage leads to reduce PCBs to value less than 50ppm.

Table (8): Specification of the oil after treatment with kaolin clay and oxalic acid at the optimum conditions.

Exp.	Standard Method	Results	Specification limits ⁽¹⁾
PCBs content (ppm)	DEXIL PCB Test Method (Electrochemical Analysis)	106	50 ⁽³⁾
Specific Gravity at 60/60°F	ASTM : D 1298	0.8691	Max. 0.895
Visual examination	ASTM : D 1524	not clear and contain sediment	Clear and free from sediment
Color	ASTM : D 1500	2	-
Water Content (ppm)	ASTM : D 1533	9	Max. 20 ⁽²⁾
Total Acidity (mg KOH/g Oil)	ASTM : D 974	0.18	Max. 0.01
Breakdown Voltage (k.v. /2.5 mm)	IEC : 156	66	Min. 30 ⁽²⁾ for (66/11 k.v.)
Kinematic Viscosity at 40°C (mm ² /s)	ASTM : D445	9.6	Max. 12
Flash Point closed (°C)	ASTM : D93	146	Min. 135
Copper Corrosion	ASTM : D130	Not corrosive	Not corrosive

(1) Acceptable limits for mineral insulating oils in-service: According to IEC 60296:2012.

(2) Acceptable limits for mineral insulating oils in-service: According to IEC 60422:2013.

(3) Acceptable limits for total PCB content must be <50 ppm according to Stockholm Convention on persistent and organic pollutants.

Table (8) show that, with respect to PCBs the lowest value of PCBs was reached to 106 ppm in 10 stages. Farther stages of treatment reduce the amount of PCBs to less than 50 ppm. With respect to other tests of the oil such as (specific gravity, visual examination, color, water content, total acidity, breakdown voltage, kinematic viscosity, flash point and copper corrosion) improved after treatment stages and achieved specification limits.

IV. Environmental impacts of used transformer oil and thereclaiming material:

Used transformer oil is considered as a hazardous waste environmentally, because of its chemical reaction, toxicity, flammability, or ability of explosion. Aged transformer oil contains some toxic chemicals resulting from additives which used to improve oil properties such as heavy metals, organic materials (e.g. phenolic compound). Special synthetic transformer oils are very toxic and carcinogenic. Thus, it can mixed with water and penetrate in the soil and underground water.

The reusing of transformer oil by reclamation using kaolin can solve the above mentioned problems of aged oil disposal. In addition to PCBs act as endocrine disruptors, human carcinogens and environmental estrogens and have been reported as most toxic organic pollutants [Olea N and Pazos P, (1998)] and [Bumpus JA, et al.(1985)] and [Hutzinger O, et al.(1974)].

Dechlorination of PCBs of transformer oil can solve the mentioned problems and save the human health and the surrounded environment.

V. Conclusion

High improvement of breakdown voltage occurs after using kaolin reclaimed transformer oil and changed from 31 to 74 kV. Also some improvements have been achieved such as color changed from 6 to 1 and total acidity changed from 0.32 to 0.02mg/g of oil. Economically the actual cost for treated oil is negligible with respect to oil price. Kaolin is available with lower costs.

Using of kaolin and oxalic acid in presence of water under certain conditions make dechlorination of PCBs and does not effect on oil specifications. Economically we can reuse transformer oil after dechlorination of PCBs and this is better than oil disposal.

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