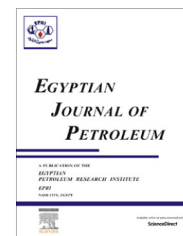




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FULL LENGTH ARTICLE

# Evaluation of kaolin clay as natural material for transformer oil treatment to reduce the impact of ageing on copper strip

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## KEYWORDS

Transformer oils;  
Kaolin clay;  
Sulfur content;  
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**Abstract** Copper sulfide formation is one of the possible corrosion mechanisms involving the corrosive sulfur of copper. EDX scans of copper strip before and after immersing in aged transformer oils containing sulfur without copper passivator at 100 °C for 3 h indicated that copper sulfide was formed on the copper strip surface. The reclaimed oil by using kaolin clay reduced the sulfur content of all tested aged oils reducing the corrosion on copper strips in all samples investigated. In every case studied, the oil after reclamation by kaolin clay showed no sign at all of corrosive sulfur on the surface of copper strips. Nevertheless the atomic absorption analysis of copper ions in oil samples showed that the dissolution of copper was increased with increasing the sulfur content in the oil at different times of immersed copper strip in the oil.

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## 1. Introduction

Crude oil as it comes out of the well contains besides hydrocarbons, significant amounts of other undesirable substances such as sulfur compounds, inorganic salts, and some trace metals [1,2]. In recent years, a significant number of transformers and reactors have failed as a consequence of the formation of copper sulfide in the windings, and much work has been made to understand this phenomenon, and to find mitigation techniques [3]. Copper sulfide is formed from the reaction

between copper and various corrosive or potentially corrosive sulfur compounds in the insulating oil, such as mercaptans and disulfides (e.g. dibenzyl disulfide, DBDS). Sulfur antioxidants are also one of the sources of corrosive sulfur in transformer oils [4]. CuS is usually generated over a wide temperature range from 80 °C to 150 °C [5,6]. Once CuS deposits on the surfaces of copper wires and diffuses into the oil-paper insulation, it greatly reduces the insulation strength between coils and leads to insulation failures in power transformers [7,8]. Copper corrosive sulfur is thus closely related to the safe operation of power transformers.

Oil refining, chemical and clay treatment represent the best technology for removing unwanted compounds from base oil stocks. The corrosive sulfur in transformer oil has been the

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cause of transformer failures due to copper corrosion. Oil treatments or reclamation have been only partially effective to reduce the copper corrosion in transformers [9]. Many trials have been done and proved to change oils with corrosive sulfur into non-corrosive status. There are many technologies currently available for the production of severely refined, corrosive sulfur free base fluids used in the formulation of high quality transformer fluids. The clay reclamation in refining units is one of them [9]. It has been shown that oil can pass through some adsorbents such as clay to eliminate free corrosive sulfur without the use of passivation additives (e.g. copper passivators). In addition, it will lead to increased oxidation stability, heat transfer and biodegradability characteristics compared with non-reclaimed mineral oils.

In the present investigation, we try to estimate the kaolin clay sorbent agent to eliminate the free corrosive sulfur from some transformer oils and study the effect of this technique on reducing copper strip corrosion.

## 2. Experimental

### 2.1. Refining unit

The refining unit consists of three parts; vacuum dehydrator, electric heater and acidity and impurities removal cartridge containing kaolin clay.

All essential parts of the unit (vacuum dehydrator and pump, transfer pump, heater and cartridge) are illustrated by Fig. 1.

### 2.2. Materials

#### 2.2.1. Aged transformer oil

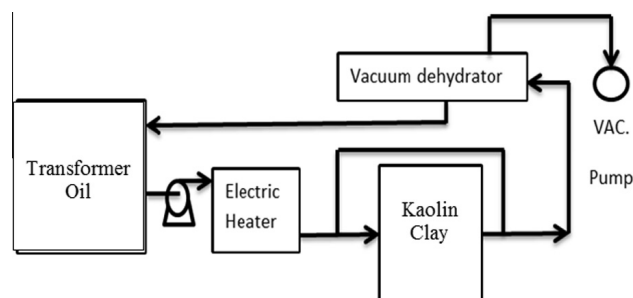
Four aged transformer oils with different sulfur contents were collected from high voltage transformers.

#### 2.3. Kaolin clay

Kaolin used in this investigation was collected from kalabsha quarry in Aswan City, South Egypt, and mainly consists of Al, Si, Fe, Ti and other trace elements. The properties and its constituents were reported [10].

#### 2.4. Copper strips

The copper strips were polished and cut into suitable lengths for the test of corrosion.



**Figure 1** Schematic diagram of oil reclamation unit.

### 2.5. Treatment process

The treatment process was carried out using aged transformer oil samples. The amounts of kaolin clay used were put in impurities removal cartridge. The aged oil samples were heated and passed through the cartridge at 60 °C. Then the oil was introduced into the vacuum chamber to remove undesirable gases after treatment. The treated oil was recycled till maximum removal of free sulfur (four stages). The treated oil samples were withdrawn and analysed according to the standard method of test for copper corrosion.

### 2.6. Determination of copper ions in oil

The copper ions dissolved in oil were quantified using Atomic Absorption Spectrometer, Solar S-4 S- Series Thermo Electron Corporation UK.

### 2.7. Determination of the dissolved copper in the aged transformer oil samples

The test was used for investigating the effect of transformer oil on copper corrosion using test baths. The copper strip was weighted, polished and immersed in 30 ml of oil sample at a temperature of 100 °C. The strip was then removed after 24, 48, 72, 96 and 120 h. The remaining oil samples were conducted to measure the amount of copper ion using Atomic Absorption Spectrometer, Solar S-4 S- Series Thermo Electron Corporation UK.

## 3. Results and discussion

### 3.1. Elemental analyses of aged oil samples

The elemental analyses for (C, H, N and S) were determined by LecoTruspect (CHN) Analyzer, Leco Corporation 3000 LAKE View AVE.ST. Joseph, MI-USA. The results are listed in Table 1.

Table 1 shows the elemental analyses of oil samples (H, N, C and S), as well as, the acidity. The data present in the table are arranged according to sulfur content and acidity. It showed that the largest amount of sulfur is in the oil sample (IV) while the smallest is in the oil sample (I).

### 3.2. Acidity of aged oil samples

The acidity was determined according to ASTM No. D3487. It is observed that the change in acidity showed that the largest

**Table 1** Elemental analyses and acidity of the four samples of aged transformer oil.

Parameter	Oil type			
	I	II	III	IV
Sulfur %	0.30	0.31	0.35	0.39
Hydrogen %	12.86	12.82	12.84	13.28
Carbon %	85.47	85.79	85.47	87.04
Nitrogen %	0.15	0.17	0.18	0.137
Acidity mg KOH/g oil	0.37	0.39	4.23	4.44

amount of sulfur gives more acidity value as in oil sample (IV) while the smallest is in oil sample (I). This may be attributed to the higher sulfur content in the aged oil leading to the formation of more acidic impurities.

### 3.3. Effect of aged transformer oils on the copper strips structure

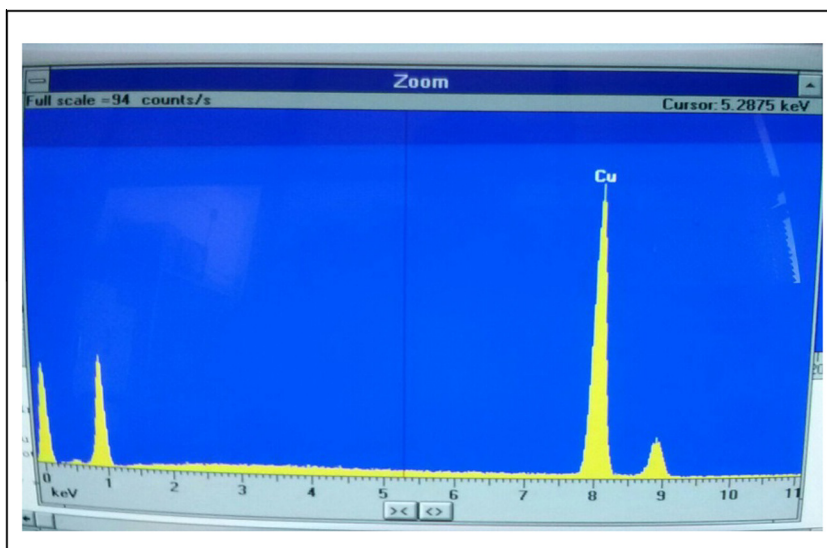
The change in the structure of copper strips by the influence of the four different aged transformer oils containing different concentrations of sulfur element was studied using Energy Dispersive X-ray spectrometer (EDX) ISIS Link Instrument P/C. Oxford Co. Fig. 2 shows the spectrum of copper strip sample after immersing in treated oil with kaolin. It is clearly

seen that the copper strip sample has one peak represented by Cu only.

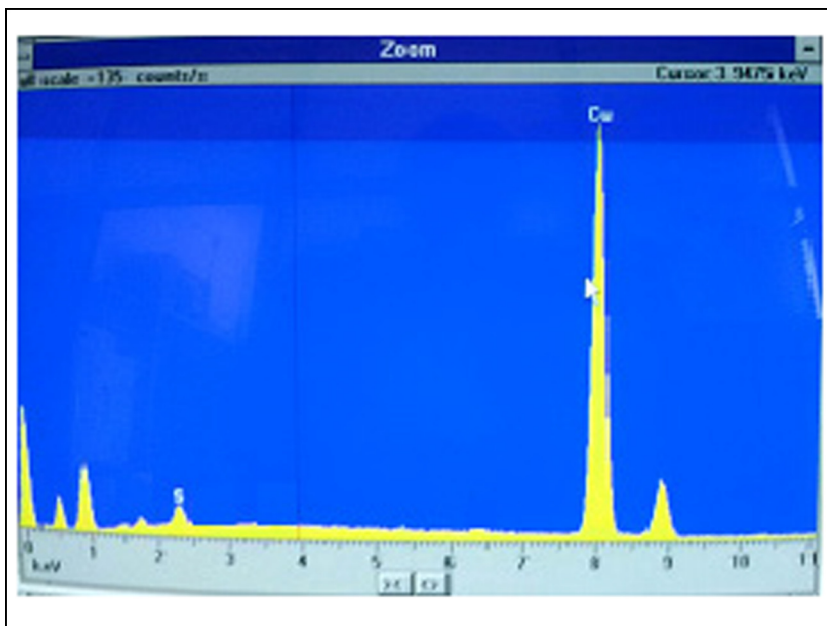
Fig. 3 shows EDX scan of the copper sample after ageing in transformer oil sample (I) which has the lowest amount of sulfur content, at 100 °C for 3 h. The minute sulfur peak is seen at 2.1 keV and copper peak at 7.9 keV.

Fig. 4 shows EDX scan of the copper sample after ageing with transformer oil sample (II) at 100 °C for 3 h. This also shows the deposition of copper sulfide.

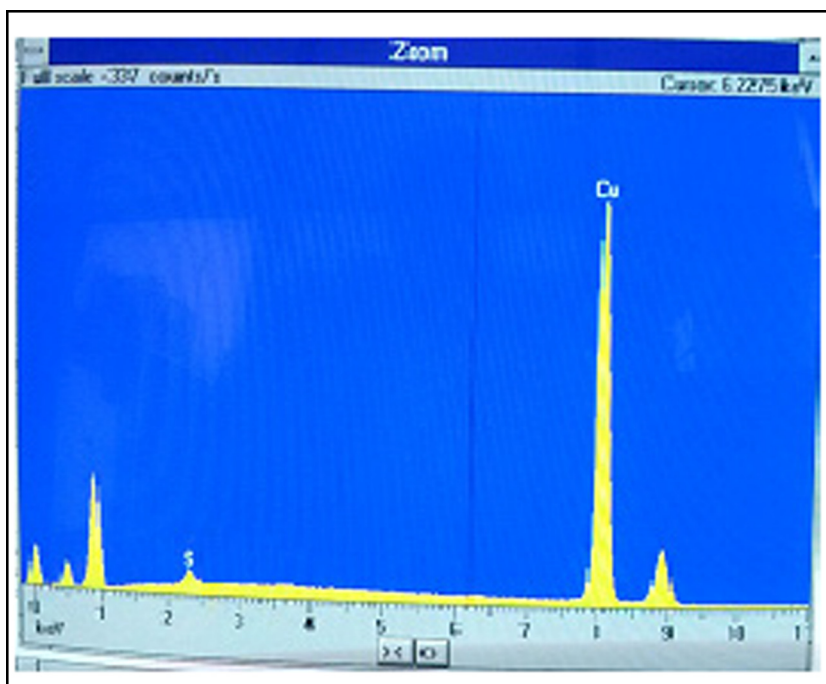
Fig. 5 shows the EDX scan of copper strip sample after ageing in oil sample (III) at 100 °C for 3 h. This indicates copper and sulfur peaks on the aged copper surface. The sulfur peak is seen at 2.3 keV and copper at 7.9 keV.



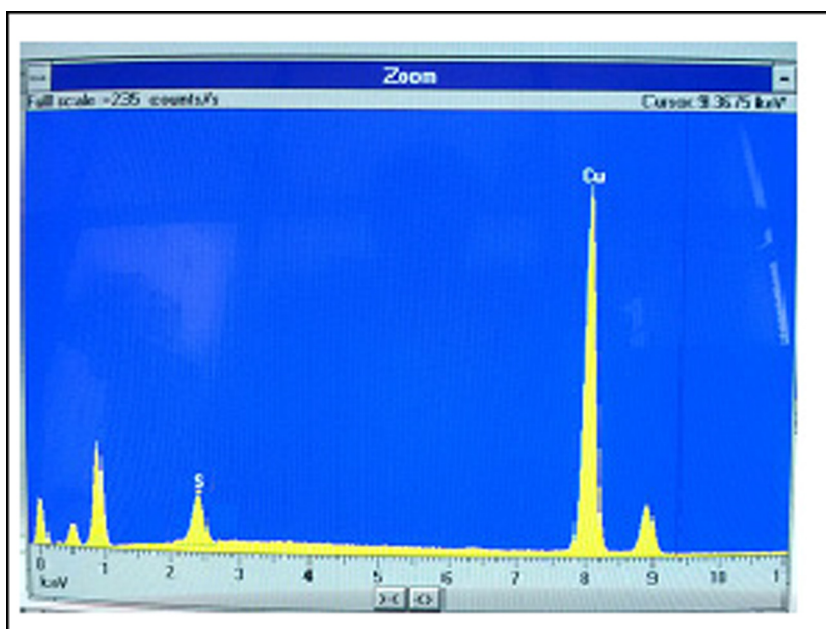
**Figure 2** The EDX spectrum of copper strip sample after treatment.



**Figure 3** EDX scan of copper sample after ageing with transformer oil(I) at 100 °C for 3 h.



**Figure 4** EDX scan of copper sample after ageing with transformer oil(II) at 100 °C for 3 h.



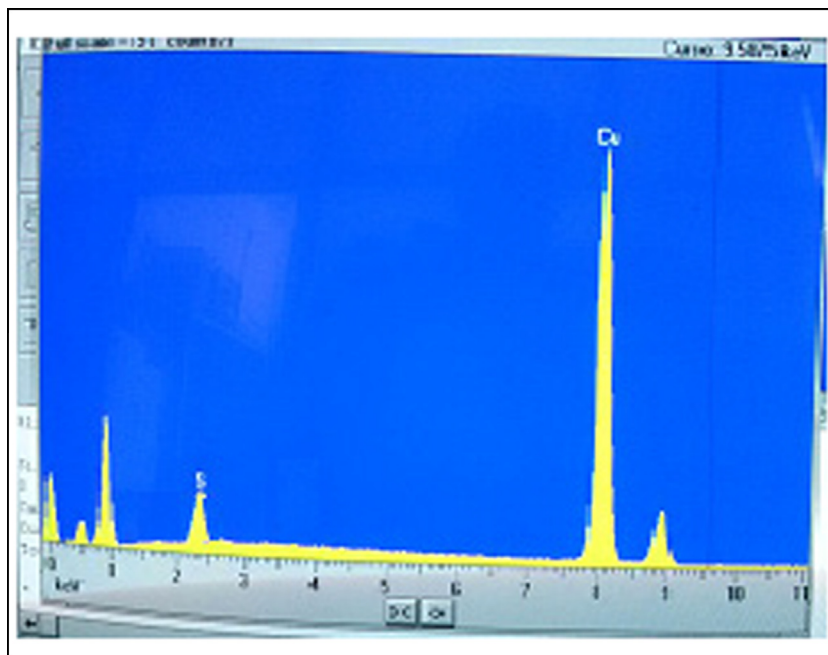
**Figure 5** EDX scan of copper sample after ageing with transformer oil(III) at 100 °C for 3 h.

Fig. 6 shows EDX scan of copper sample after ageing with transformer oil sample (IV) at 100 °C for 3 h. This also shows a significant large peak of sulfur at 2.3 keV and copper at 7.9 keV representing the deposition of copper sulfide.

#### 3.4. Corrosion on copper strip

The copper strip corrosion test (ASTM D 130) is commonly used as a specification for liquid petroleum products [11].

The test is designed to indicate the presence of components that may be corrosive to copper that come into contact with the oil. While the test is very simple to perform, its interpretation can be subjective. Furthermore, the test is generally assumed to be due to sulfur compounds. The polished copper strips were immersed in the aged oil for three hours at 100 °C. Then the effect of oil on the copper strip was detected. The colour and tarnish level are assessed using the corrosion standards according to standard method



**Figure 6** EDX scan of copper sample after ageing with transformer Oil (IV) at 100 °C for 3 h.

of test ASTM D 130 (2004) [11,12]. This is a qualitative method that is used to determine the level of corrosion of petroleum products.

The test was used to determine the effect of transformer oil on copper corrosion using test baths. At elevated temperatures, a copper strip that has been polished was immersed in 30 ml of oil sample. The strip was then removed after 3 h and tested for corrosion and a classification number is given. A comparison study between ASTM copper strips **1 – 4** and corrosion standard was determined as shown in Fig. 7.

### 3.5. Effect of kaolin clay treatment on acidity removal of tested oil

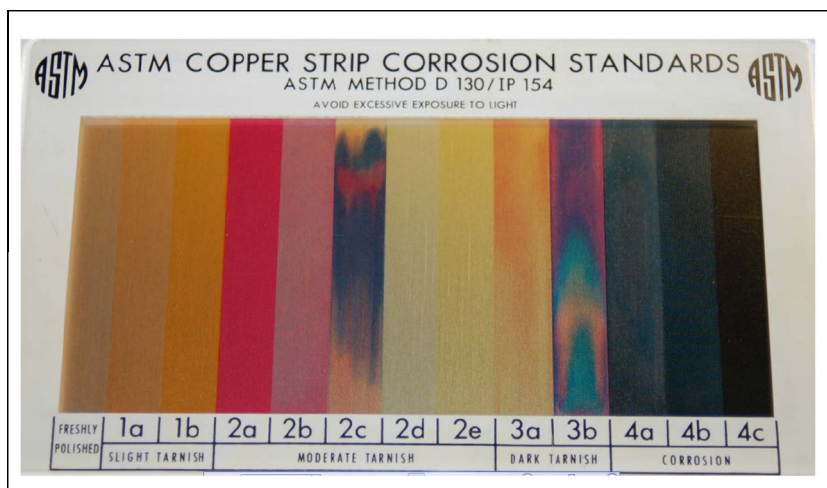
The degradation of oil produces some dissolved acids which may cause damage to the paper and copper windings. Also elemental sulfur is the most corrosive against copper, followed by hydrogen

sulfide, mercaptans, sulfides, disulfides and other organic sulfur compounds. As a result, all the necessary conditions exist properly in a power transformer for the degradation of the oil (see Fig. 8).

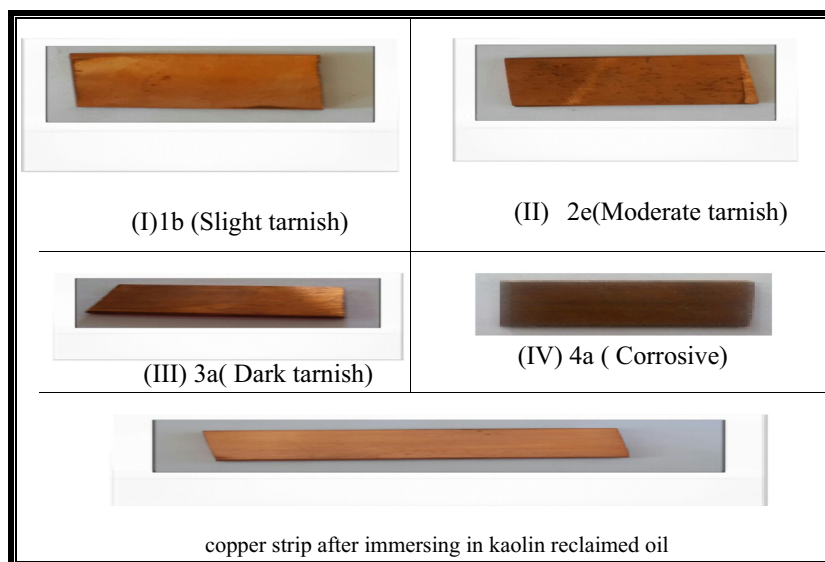
The effect of kaolin clay on the removal of acidity is represented by Fig. 9. It is evident that the acidity decreased by increasing the number of passing stages at 60 °C (stage time is ½ h). The maximum decrease of acidity was after 4 stages, it reached 0.1 mg KOH/g of oil for oil (I), while the other samples II, III and IV reached to 0.14, 0.17 and 0.18 mg KOH/g respectively.

### 3.6. Effect of aged transformer oils on the dissolution of copper

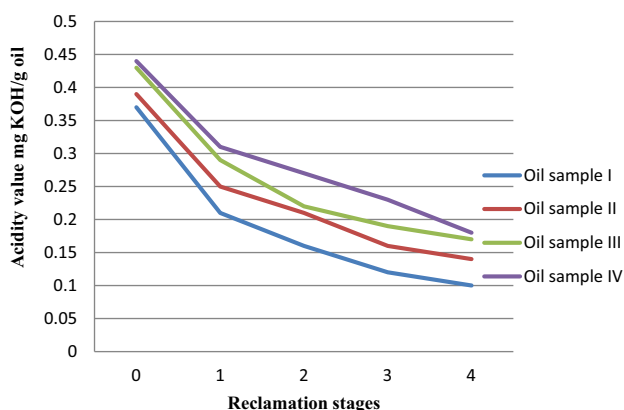
Table 2 shows the amount of copper as (mg/kg) present in the four oil samples after immersing of copper strips at different times of 24, 48, 72, and 120 h.



**Figure 7** Corrosion standards according to EN ISO 2160 and ASTM D 130.



**Figure 8** Shows a photograph of the copper strip after ageing in oil I, II, III and IV, and after kaolin treatment.



**Figure 9** Variation of total acid value with the four stages using kaolin clay at 60 °C for oil samples I, II, III, and IV.

**Table 2** Concentration of dissolved copper in oil (mg/kg).

Ageing Time (h)	Amount of copper in oil (mg/kg)			
	I	II	III	IV
24	0.41	1.41	1.65	2.05
48	0.48	1.48	1.76	2.34
72	0.66	1.66	1.82	2.65
96	0.95	1.95	1.98	2.88
120	1.10	2.11	2.23	3.21

#### 4. Conclusion

The results obtained in this investigation reveal the following:

- 1- EDX- Patterns of copper strip before and after immersions in the aged transformer oil samples investigated indicated scattered deposits due to the copper sulfide deposited on the copper surface.

- 2- The formation of copper sulfide can be ascribed to the reaction between the metal and corrosive sulfur components in the aged oil.
- 3- The dissolution of copper was found to increase by increasing the sulfur content in the oil.
- 4- Kaolin was proved to be effective as an adsorbent for treating aged transformer oil. It has high efficiency in the removal of corrosive sulfur components.
- 5- The procedure described here for the treatment of aged transformer oil represents an important inexpensive method since kaolin is a natural material abundant in many locations of Upper Egypt.

#### References

- [1] M.A. Abdel wahab, M.M. Hamada, A.G. Zeitoun, G. Ismail, A newly modified forced oil cooling system and its impact on in-service transformer oil characteristic, *IEEE Trans. Power Del.* 18 (3) (2003) 827–834.
- [2] B. Garcia, J.C. Burgos, A.M Alonso, J. Sanz, A moisture-in-oil model for power transformer monitoring-Part I: theoretical foundation, *IEEE Trans. Power Del.* 20 (2) (2005) 1417–1422.
- [3] A.C. Laurentino, A.L. Parize, M.C.M. Laranjeira, A.R. Martins, N.M. Mayer, V.T De Fávere, Regeneration of insulating mineral oil by carbonated amorphous Calcium Phosphate–Chitosan Adsorbent, *Process Saf. Environ. Prot.* 85 (B4) (2007) 327–331.
- [4] L. Nasrat, M. Abdelwahab, G. Ismail, Improvement of used transformer oils with activated bentonite, *J. Eng.* 3 (2011) 588–593.
- [5] J. Hajek, M. Dahlund, L. Pettersson, Quality of oil makes the difference. ABB discovers the solution to transformer breakdowns, *ABB Rev.* 3 (2004) 61–63.
- [6] P. Wiklund, M. Levin, B. Pahlavanpour, Copper dissolution and metal passivators in insulating oil, *IEEE Electr. Insul. Mag.* 23 (2007) 6–14.
- [7] F. Scatiggio, M. Pompili, R. Bartnikas, Oils with presence of corrosive sulphur: mitigation and collateral effects, in: *In Proceedings of the IEEE Electrical Insulation Conference, 2009*, pp. 478–481, Montreal, Canada.
- [8] F. Scatiggio, M. Pompili, R. Bartnikas, Effects of metal deactivator concentration upon the gassing characteristics of

- transformer oils, *IEEE Trans. Dielectr. Electr. Insul.* 18 (2011) 701–706.
- [9] Lance R. Lewand, *The Role of Corrosive Sulphur in Transformers and Transformer Oil*, Doble Engineering Company, USA, 2002.
- [10] A.I. Hafez, N.S. Gerges, Kh.E. Elnagar, S.E Mohamed, A.I. Hashem, Reclamation of old transformer oil using kaolin clay, *Int. J. Adv. Sci. Tech. Res.* 4 (5) (2015) 752–769, July–August.
- [11] ASTM D 130, 2004. Standard Test Method for corrosiveness to Copper from Petroleum Products by copper Strip test. American Society for Testing Materials. Strip Test. European Committee for Standardization.
- [12] International standard ISO 2160: Petroleum Products- Corrosiveness to Copper–Copper strip test third ed., 1998, pp. 9–15.