



## Research article

## Pretreatment of Fuller's earth with nitrogen

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## ABSTRACT

This paper summarizes experimental findings of the regenerative capability of nitrogen on Fuller's earth. Regenerating new oil from aged oil involves several cycles requiring a large volume of Fuller's earth. The use of large amounts of Fuller's earth is not economically profitable for companies that carry out regenerative operations to service transformer oils and can have environmental implications, since Fuller's earth is usually used to reclaim transformer oil in a one-time batch basis then disposed of. To improve the situation, a new technique to reduce the number of regeneration cycles is proposed. It is shown that Fuller's earth can be improved by purging it with continuous flowing of a fluid, preferably dry nitrogen.

## 1. Introduction

Power transformers are essential components in power plants and substations but are also the most expensive ones. Their availability and longevity have a major impact on grid reliability and profitability (Fofana and Sabau, 2008). Oil-immersed transformers contain large quantities of mineral oil and other liquids. These fluids play an imperative part in keeping up the equipment in great condition. Transformer oil's essential capacities are to protect and refrigerate a transformer. A significant problem experienced world-wide by both producers and huge industrial consumers of electrical vitality is the maturing of power transformers. Oil-paper insulation is broadly influenced (36.74%) (Raji and Raju, 2019). It is generally believed that transformer longevity depends on its insulation. In order to increase the service lifetime of transformers to greatest degree, it is vital for control utilities to know their insulation condition. The insulation system deteriorates with time, quickened by lifted temperature and the presence of oxygen, moisture and degradation products. One way to improve the lifetime of transformers is the reclamation of used oils by Fuller's earth. Fuller's earth evacuates acid residues from oil and restores some color. The use of Fuller's earth in the refining of transformer oils continued to be its major use for many years. A survey conducted by the U.S. Geological Survey (USGS) shows that some 27 million tons of clays valued at \$1.6 billion were produced, sold and used

in the country in 2018. Global annual production of fuller's earth in 2018 was approximately 3,300.00 tons (U.S. Geological Survey, 2019). The figures above advocate for the importance of clays industry. The use of large amounts of Fuller's earth is not environmentally friendly, since Fuller's earth is usually used to reclaim transformer oil in a one-time batch basis then disposed of.

However, nitrogen is the foremost commonly utilized gas for blanketing since it is inactive, broadly accessible, and generally reasonable for all intents and purposes of any scales. Other gases, such as carbon dioxide or argon, are also sometimes utilized, although carbon dioxide is more receptive, and argon is approximately five to ten times more costly than nitrogen, depending on the volume, area etc. Blanketing help preventing the access of air/oxygen, moisture or other contaminants to the conservator, slowing down the degradation processes. Through Nitrogen blanketing, a slight positive pressure is created inside the storage containers to prevent the infiltration of air/oxygen and other contaminants causing oxidative degradation and spoilage. Water vapor and oxygen are evacuated from these storages by nitrogen blanketing. Oxidation of the phospholipids, triglycerides, and free greasy acids is avoided, hence making it a basic and successful way of keeping up the purity of the oil (Yanisko et al., 2011; Bebout et al., 2013). This procedure is increasingly used a lot in power transformers. Researchers have created different

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Figure 1. Fuller's earth grounded to fine powder.

strategies to play down accumulation of broken-down oxygen within the oil by using nitrogen (Sabau et al., 2010):

- Nitrogen-Sealed Conservator: Filling the upper side of the conservator with nitrogen avoids contact of the oil with the atmosphere.
- New Nitrogen Blanketing System for Freely Breathing Units: A continuous flow of nitrogen at 99.5% purity is purged on the surface of the oil. The oxygen broken up within the oil is at that point replaced by nitrogen, in this way helps to protect the chemical stability of the oil, upgrading operational security and altogether decreasing preventive upkeep costs.

Continuous purge, pressure control, and concentration control are the three commonly used methods for nitrogen control (Yanisko et al., 2011). Nitrogen blanketing is profitable for improving safety the process, the product quality, which means longer equipment life (Yanisko et al., 2011). In this article a new technique to reduce the number of regeneration cycles is proposed by improving the Fuller's earth process with nitrogen blanketing.

2. Background and literature review

Fuller's earth alludes to a class of normally happening adsorbent clays, instead of a particular mineralogical species (IEEE Std C57.637, 2015). In this material there are internal and external polar active sites in which the non-polar components of the oil can pass through without retention in opposition to the polar components or the dissolved decay products in the oil (IEC 60422, 2013). A few clays are appropriate for

such a purpose, such as montmorillonite, kaolinite, sepiolite, bentonite, and palygorskite (attapulgite). Attapulgite clay has been found to be most satisfactory for reclaiming transformer oils because it has the capacity to neutralize acids, adsorb polar compounds, and decolorize to a clear oil (IEEE Std C57.637, 2015). Attapulgite is made of twofold silica tetrahedral chains connected together by octahedral oxygen and hydroxyl groups containing aluminum and magnesium particles in a chain-like structure. Its chemical structure is  $(OH_2)_4(OH)_2Mg_5Si_8O_{20} \cdot 4H_2O$  (Haydn, 1991). Fuller's earth in its fine powder form is shown in Figure 1.

Attapulgite is ordinarily light tan or cream to brown in color in spite of the fact that a few have a blue-green tint. In the structure of this material, there is a charge which is known as moderate. This moderation is in particular due to the three-layer inversion of its structure and also to the replacement in the octahedral layer of aluminum and magnesium by iron. As a result, the minerals generally have an exchange capacity of 40 meq/100g between kaolin and smectites. The inversions have resulted in the presence of the channels or parallel holes in the structure. Another aspect concerns the elevation of the specific surface which is greater than 150 m<sup>2</sup>/g due to the fine particle size and the nature of the elongation of the particles. The charge on the particles, the high surface area as well as the channels in the structure give attapulgite a high absorption capacity hence its wide use in industry.

Also, high viscosity is caused by the elongated lath-like particles, when it is included to any liquid. Owing to its physical viscosity, unlike the chemical one, it is exceptionally steady in many applications. USA is a major producer of attapulgite, more so than South Africa or other countries (Galan, 1996). The drying and treatment by acid activation of attapulgite allows its use in the size from 100 to 200 mesh (Figure 1) in an amount from 12 to 120 g per liter. The oil and paper form the insulation system of power transformers. In service, four main stresses affect the insulation system. These are:

- Thermal (high temperature, overheating, joule effects, etc.)
- Mechanical (vibrations, short circuits, crackles, overloads, etc.)
- Electric (partial discharges, short circuits, overvoltage, etc.)
- Environmental (pressure, oxidation, humidity, pollution, oxygen, etc.).

The combined action of all these factors results in an aging of the insulations. Two types of ageing are preponderant: physical ageing and chemical ageing. The ageing is fundamentally a chemical process that is significantly quickened by heat, oxygen and humidity. It has been shown that the rate of paper degradation (aging), will double with every 1% increase in moisture content in the paper insulation above 0.5% wt./wt.,

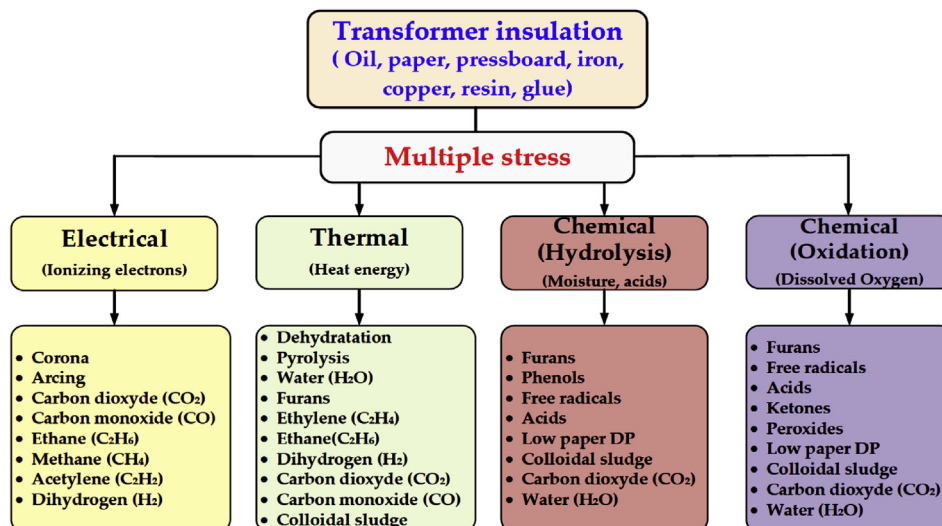


Figure 2. Degradation processes for transformer insulation.

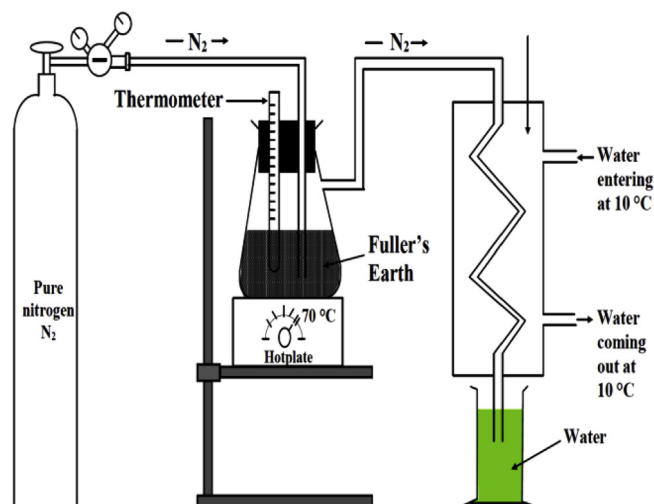


Figure 3. Sketch of the experimental procedure.

which is the optimum moisture content in paper (CIGRE, WG A2.30 TB 349, 2008). The moisture in cellulose thus affects the aging of the celluloses and also the bubbling evolution temperature (high moisture lowers the temperature). Generally, there are three main processes of degradation:

- Hydrolysis: the hydrolysis of cellulose is a catalytic process where the reaction rate depends on dissociated acids or rather  $H^+$  ions that can get into the amorphous zones of the cellulose).
- Oxidation: Oxidation promotes accumulation of additional ageing accelerators such as acids and other contaminants (carbonyls, aldehydes,  $CO$ ,  $CO_2$ ,  $H_2O$  and  $H_2$ ).
- Pyrolysis: pyrolysis is a process that can take place without access to water and/or oxygen, or any other agent to initiate the decomposition. When temperature increases pyrolysis will start to dominate over the normal ageing processes and these ageing rates have a much stronger temperature dependence than ageing at service temperatures.

Figure 2 summarizes a decomposition mechanism for transformer insulation. In case intermittent preventive upkeep measures are not taken, contaminated insulating oil will stop the smooth operation of the transformer. Replacing the used oil with a new oil is not an ideal solution because there is still used oil in the core, the windings and the solid insulation of the transformer. The mixture of the new oil with used oil will quickly reduce performance. It follows that the paper will still be contaminated thereby accelerating the degradation of the transformer. Fuller's earth has the capacity of removing humidity and neutralizing carboxylic acids; it also adsorbs polar compounds and improves coloration of used oil (N'cho et al., 2012). Contact of hot oil with decay products will dissolve them. The oil reclamation is thus done by its passage through fuller's earth. The clean oil, obtained by dissolution and removal of the residues, is warmed up again in the transformer. All the components of the transformer are inhibited by this degradation.

### 3. Experimental arrangement

The experimental procedure of purging the Fuller's earth is shown in Figure 3. It is done through using a pure nitrogen stream to 99.5%. The amount of nitrogen used over a 24 h period was 28.3 L. This duration was selected to guarantee the effective adsorption of nitrogen in the crystal structure of fuller's earth. For this purpose, a bottle of compressed dry nitrogen equipped with a pressure regulator was used to run nitrogen through the Fuller's earth. Throughout the process, the earth was heated to 70 °C with a hot plate. When heated, the cellular structure of fuller's

earth is modified; the pores are enlarged to allow more decay products absorption. This temperature includes conditions beyond the maximum operating temperature allowed (according to IEC loading Guide, 105 °C) (IEC 60076-7, 2018). If the fuller's earth is heated excessively, fusion occurs, thus destroying the cellular structure of the clay and ruining its adsorptive properties. Practically, the oil reclamation occurs when the transformer is in service.

For safety reasons, the nitrogen coming out of the other side was injected into a water tray. In absence of the water tray, the volume of the injected nitrogen would replace a portion of the air present in the room, cause a drop-in oxygen content, and an accumulation of carbon dioxide, which can lead to asphyxiation. After 24 h, the renewed Fuller's earth is collected and used for reclaiming the service aged oil; three cycles are thus realized. For each cycle, the amount of DDP and the microscopic solid suspension is measured. Another sample of the same service-aged oil is also passed three times through Fuller's earth without nitrogen. At each passage, the Fuller's earth is changed. The objective of these operations is to compare the efficiency of the two different clays. The selection of nitrogen is justified by its remarkable properties (Sabau, 1998): it is a chemically inert gas, so it does not affect the insulating properties; it is non-polluting environmentally friendly to the environment; its rate of dissolution in the oil is approximately 1.5% compared to that of air which is 10% by volume.

The relative amount of DDP in transformer oils was assessed by UV-vis spectrophotometry according to the ASTM D6802 (ASTM D6802-02, 2010). The increasing concentration of DDP in aged/used oils shifts the absorbance curve to longer wavelengths while new/unused oils are nearly transparent to a monochromatic or polychromatic beam of light in the visible spectrum.

The DDP were determined by Thuramed T60 UV-Vis Spectrophotometer. The DDP in the samples was determined by the numerical integration of the region underneath these absorbance curves.

A turbidity meter technique developed by ASTM (ASTM D6181-03, 2005), was used to determine quantitatively the number of sludges in fluids that are present in new and service aged oils. The interaction between an incident light wave and a suspended particle defines the principle of measurement. This generates optical phenomena such as reflection, scattering, adsorption and refraction. The intensity of the particle as well as its size, type, shape, refractive index are at the origin of a scattering of the incident light in all directions. A quantitative assessment of particles in the fluid is carried out by diffusion at 90°. Mitigation-angled photodetectors may help improve the accuracy when the particles are in correlation with the nephelometric and certain angles. NTU is the unit of turbidity and signifies Nephelometric Turbidity Units. Measuring the turbidity of insulating liquids is done with a ratio turbidimetric optical in accordance with turbidity standards. The increase of contaminants (such as sludges) in the fluid is ascertained by the increase in turbidity. The water droplets or gas bubbles which are other sources of turbidity are removed. It is worth recalling that before colloids appear in service conditions, the first sign will be the drop of the in the interfacial tension (IFT) followed by an increase of the total acid number (TAN) and dissolved decay products (DDP) (Hadjadj et al., 2015). In this contribution, the TAN, which is by and large utilized to reflect the oxidation performance of mineral oils, was correlated with turbidity and DDP. The achievability of utilizing of UV/Visible spectrophotometer (DDP) and turbidity as a diagnostic tool and oil quality classification was then confirmed.

These techniques (DDP and turbidity) are quick and accurate enough in reflecting the oxidation performance of mineral oils. Therefore, in the present work to monitor the colloidal and soluble particles with reclamation, the related amount of DDP and turbidity are adopted.

### 4. Results and discussions

Two distinct kinds of Fuller's earth from different producers, were utilized to reclaim the same service-aged oil: a Normal Fuller's earth and

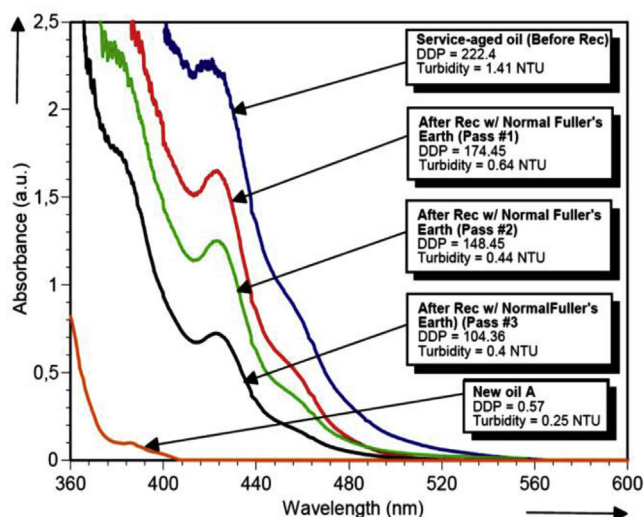


Figure 4. DDP and turbidity values obtained with Normal Fuller's earth during the three cycles of reclamation.

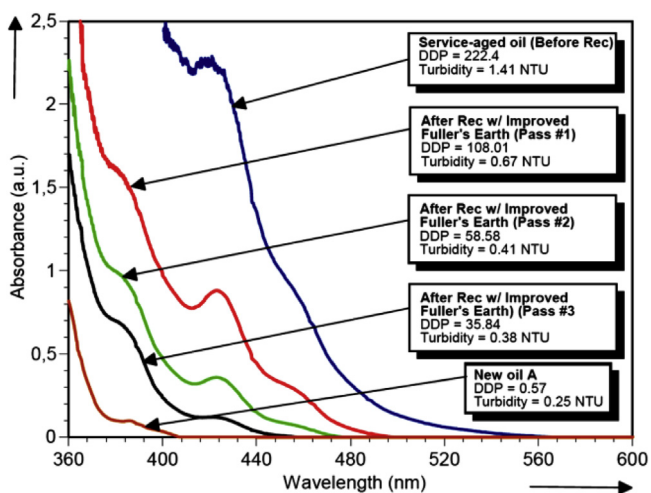


Figure 5. DDP and turbidity values obtained with Improved Fuller's earth during the three cycles of reclamation.

Improved Fuller's earth. The service-aged oil reclaimed in this study comes from a ageing power transformer commissioned in 1984 and with the following characteristics: 47 MVA, 161/26.5 kV. The terms "Normal Fuller's earth" and "Improved Fuller's earth" mean respectively normal Fuller's earth and normal Fuller's earth treated with nitrogen. Figures 4 and 5 show the absorbance curves obtained for each Fuller's earth during the 3 cycles of regeneration. They reflect the amount of DDP and colloidal suspensions in the oil after each pass-through Fuller's earth. The amount of dissolved decay products removed by Fuller's earth having undergone a continuous flow of nitrogen is remarkable. Clearly, Improved Fuller's earth shows higher efficiency than Normal Fuller's earth. Figure 6 shows the reclamation rate for each type of Fuller's earth. The rate of reclamation is the amount of DDP removed after each Fuller's earth passage. An initial DDP of 222.4 is increased to 108.01 for Improved Fuller's earth, and 174.45 for Normal Fuller's earth.

Improved Fuller's earth carries a reclamation rate of 52%, 73.66%, 83.88% respectively for the 1st, 2nd and 3rd cycle against 21%, 33.25% and 46.92% for Normal Fuller's earth. These results reflect the effectiveness of this process. To validate these results, the reproducibility test was performed.

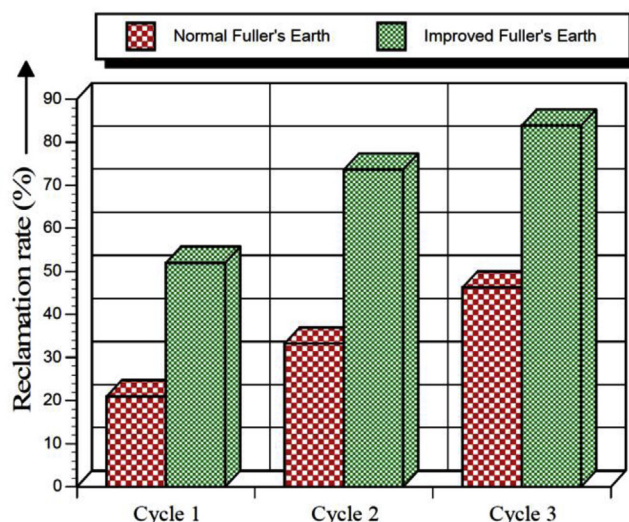


Figure 6. Reclamation rate achieved by both Fuller's earth types during each cycle of reclamation.

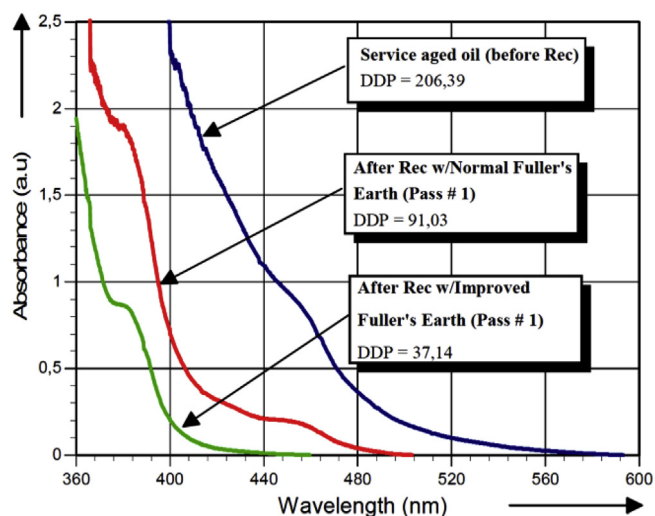


Figure 7. Reproducibility test of the two Fuller's earth types. DDP: Dissolved Decay Products.

For this test, however, a single cycle of reclamation was performed on an aged oil other than that used initially. The two Fuller's earth types were compared again. Figure 7 shows the results for reproducibility where Improved Fuller's earth achieved a regeneration rate of 82% compared to 55.89% with Normal Fuller's earth, as shown in Figure 8.

This performance was established by leaving the Fuller's earth under a continuous flow of nitrogen for 3 days. This reflects into a rapid change from a DDP of 206.39 to a DDP of 37.14 for Fuller's earth improved with nitrogen. This result shows again the effectiveness of the process discovered. Using this Improved Fuller's earth would require a reduced number of passes involving the transformer. Moreover, a reduced requirement of Fuller's earth in reclaiming aged oils would certainly have a beneficial environmental effect.

In common, the chemical and physical properties of clays can be altered to extend their normal capacity adsorbent and give particular characteristics for some applications (Beltran-Pérez et al., 2015). The effectiveness of the Improved Fuller's earth method is probably due to the presence of pure nitrogen. Exchange of metal ions and complex metal cations into the interlayer of clay minerals is possible (Dipak, 2018). Substitutions are possible, especially for attapulgites: substitution of Si by

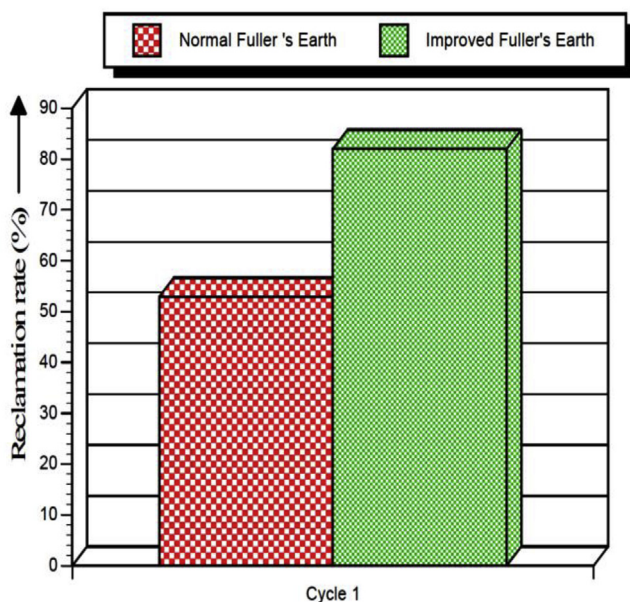


Figure 8. Reclamation rate after reproducibility test.

Al in the tetrahedral position and of Mg by Al or  $\text{Fe}^{3+}$  in the octahedral position (Le Berre, 1989). Substitutions, stacking state of leaflets and impurities are likely to influence the surface properties of clay minerals. The most important of these surface properties is the ability to adsorb the mineral and organic substances with which these materials are in contact. This adsorption may be of the molecular type (surface complexation) or of the macroscopic type (ion exchanger) (Errais, 2011). The nitrogen can only react directly with magnesium to form magnesium nitride ( $\text{Mg}_3\text{N}_2$ ) (Sabau, 1998). It follows that by interacting with the Fuller's earth, it sees its crystalline structure modified. The new crystalline structure of Fuller's Earth would certainly carry the  $\text{Mg}_3\text{N}_2$  function. This change in the crystal structure of the renewed Fuller's earth would certainly explain the observed differences in the absorbance curves of both compounds. The efficiency of oil reclamation depends on the structural characteristics of the crystal lattice and the origin of the material which composes the Fuller's earth (Bleaching Clay, 2019).

## 5. Conclusion

In this research, a new proposal for improving the properties of Fuller's earth is presented. Three highlights result from this study:

- the adsorption power of nitrogen-improved Fuller's earth is more effective than normal Fuller's earth;
- the adsorption power of nitrogen-improved Fuller's earth saves two cycles of regeneration for the same result which is economically profitable for companies that carry out regenerative operations to service transformer oils;
- the gain of two regeneration cycles can considerably reduce the amount of Fuller's earth used. Usually this inexpensive material is used only once before it is discarded in landfills. Reclamation units allowing 300–500 reactivations of the Fuller's Earth are also available (<http://www.enervac.com/wp-content/uploads/2018/08/E575-R-Brochure-2017.pdf>).

The proposed technique can complement those units by improving regeneration efficiency. Hence, a decreased necessity of Fuller's earth in reclaiming aged oils would doubtless be beneficial to environmental protection since there would be less of Fuller's earth to discard.

## Declarations

### Author contribution statement

Janvier Sylvestre N'cho, Issouf Fofana & Abderrahmane Beroual: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

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