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Wastewater Treatment by Improving the Local Clay Capacity with Chemical and Thermal Activation

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Abstract: Worldwide, liquid effluents are generally discharged into the environment untreated, which, in turn, are affecting humans, animals and plants. Preserving our environment is a priority, especially with the emergence of epidemics in recent years. As a part of our investigation, we aim to treat the wastewater of the Ouargla region by enhancing the adsorption capacity of local clay collected from El-Oued (Elmghaier, south of Algeria) using thermo-chemical activation for the removal of organic pollutants. The clay used was (illite, kaolinite, and quartz 62.0%, 27.0% and 11.1%, respectively). The experiments proved the efficiency of enhancing the adsorption capacity of local clay by thermo-chemical activation in the treatment of urban wastewater to determine the efficiency by the following characteristics: chemical oxygen demand, biochemical oxygen demand, total suspended solids, and turbidity, respectively. Acid-activated clay with sulphuric acid achieved high efficiency on polluted water purification at the ideal concentration (0.75 N) and an adsorption rate of (80.16%, 90.74%, 93.33% and 90.74%), while the result decreased in the optimal concentration of acid activated clay HCl (0.134 N) and the adsorption rate was 73%, 60.92%, 94.31% and 65.57%. The thermal activation effect of the clay studied under optimal temperature conditions (400°C) shows that the adsorption ratio increased with higher temperatures (82%, 65%, 89.56% and 78.65%).

Key words: Clay, chemical activation, thermal activation, wastewater, organic effluents.

Introduction

Since ancient times, man has traditionally used clay in his daily life as household utensils, where he stored drinking water in clay containers to keep its quality, which scientifically infers that clay is a good adsorbent. The adsorption property of clay is attributed to high porosity and surface area, cation exchange capacity, acidity and diversity of active sites (Churchman, 2006; Yuan and Wada, 2012).

Pollution occurs in its various forms, whether air, soil or water pollution as a result of the presence of

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some harmful organic and inorganic substances or due to an increase or decrease in the proportions of some basic components in the environment from their natural ratios. It is worth noting that the problem of water pollution is one of the most important problems, because of the great role of water in daily life and industries. One of the most important techniques that have been used in dealing with this problem is adsorption on clay sediments (Mohammad, 2017) as well as some physicochemical techniques such as coagulation (Jiang et al., 2004), fusion and reverse osmosis, adsorption on activated carbon, or magnesium oxide and clay (Mavros et al., 1994). Adsorption is an effective and well-known process. It has been widely explored as an alternative method compared to other waste removal methods due to the low cost, simplicity of design and ease of operation, moreover, adsorption does not result in the production of any harmful substances. However, its widespread use in wastewater treatment is sometimes restricted due to its high cost (Bergaya et al., 2006). Clay minerals are finding prominence as low-cost adsorbents over the past few decades due to their local availability and ability to be chemically or thermally modified (Murray, 2006). The chemical catalysis method is a one-step and does not consume a lot of time, by treating clay minerals using inorganic (hydrochloric acid, sulphuric acid, phosphoric, nitric) or organic (acids, sterone, oxalic) solutions and in certain conditions (Hussin et al., 2011) where during acid treatment, many changes occur in the structure of aluminosilicates due to the dissolution of structural ions and rearrangement of the structure (Korichi et al., 2009). The extent of these changes depends on various factors such as the geographical origin of the clay, the type of acid used, its concentration, temperature and timing of acid activation (Kooli and Liu, 2013). Several studies was carried on the uses of clay for water depolution. Bentonite clay was used in the adsorption of organic pollutants from industrial wastewater (Smith and Galan, 1995).

Bentonite clay is widely used in the removal of dyes , in this context Hashemian Saeedeh proved that treatment of bentonite with NaCl increases its adsorption capacity at pH=2 in uptaking dye cyanine acid blue (Hashemian, S. 2007). Bentonite clay was also used as a good sorbant in elimination of organic pollutants from water (Smith and Galan, 1995). While, Co(II) ion has been treated by adsorption on clay, Ngomo (2012) used kaolinite and smectite as adsorbents to remove cobalt ions effluents in a discontinuous medium. The researchers (Lund and Nessen, 1986) indicated that adding bentonite clay to raw water removes most of the impurities within the temperature range (20-37 °C) and that a pH value of < 8 is the optimum value for removal. Gersberg et al. (1988) treated urban wastewater by adding bentonite clay as an adsorbent, where they found that the COD value of the treated water was less than 20 mg/L. Francisco indicated that acid activation by HCl or H_2SO_4 of smectite clay from some regions of the State of Brazil showed great efficiency in removing vegetable oils such as soybean, cotton seed and sunflower (Francisco et al., 2001). This work is set to investigate the local clay (El-Oued, Algeria) for treating industrial and domestic wastewater of the National Sanitation Office ONA of Ouargla region in southwest Algeria.

Materials and Methods

The clay was obtained from El-Oued, Algeria having the Illite 62.0%, Kaolinite 27.0%, and SiO_2 11.1% composition (Atia et al., 2018). Analytical graded chemicals including HCl, $AgNO_3$, $PaCl_2$ and H_2SO_4 were purchased from SIGMA-Aldrich. Wastewater (as shown in Figure 1-a) was sampled from the National Sanitation Office ONA station that receives urban wastewater from Ouargla City. The sample was taken during the treatment period from February to May at the entry of the biological disinfection station in a sealed plastic bottle about 3 hours before the analysis. The information provided by ONA on the untreated samples is presented in Table 1, which shows its content in high levels of physicochemical pollution (COD, BOD_5, TSS, Turbidity...). Two main processes were used: activating the clay, and wastewater treatment, which was carried out by conducting five experiments in which the clay resulting from the previous activation process was used.

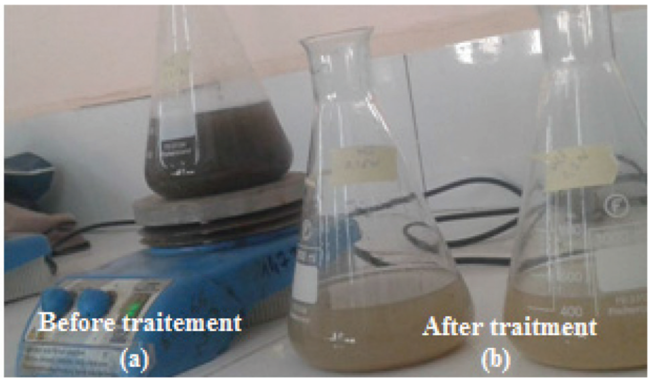

Figure 1: Wastewater before and after the treatment with activated clay.

Table 1: Average pollution standards for wastewater of the city of Ouargla

Parameters	*Domain of variation*
(COD) mg/L	500
(BOD_5) mg/L	190-270
(TSS) mg/L	207-246
(EC) ms/cm	35.1-36
(pH)	7.31-7.4
(T) C°	19.7-20.4
turbidity NTU	82.2-216

Activation of Clay

The clay was chemically and thermally activated according to the protocol of a previous study (Soh et al., 2019).

Chemical Activation

Activation with Hydrochloric Acid (HCl)

About 5 g of purified clay were mixed with 50 ml of hydrochloric acid at the concentrations: (0.134 N, 0.335 N, 0.671 N, 006 N, and 1.342 N) under stirring (200 rpm) at 60°C for one hour. Then, distilled water is added to stop the reaction and let it stagnate. The clay obtained was washed with distilled water by centrifugation until completely free of hydrochloric ions, a filtrate test with a solution of silver nitrate ($AgNO_3$) is necessary until the formation of white precipitate disappears.

Activation with Sulphuric Acid (H_2SO_4)

The same previous process using sulphuric acid with concentrations: (0.1 N, 0.25N, 0.5N, 0.75N, 1N) was carried out. Clay purity is checked by filtering with a $BaCl_2$ solution.

Thermal Activation

The thermal activation of the raw studied clay was carried out according to a previous study (Soh et al., 2019), by burning 2 g of the chemically activated clay in a removable oven (High Therm VMK 39), over a temperature range of 100 to 500°C and then cooled in the dryer for 15 minutes.

Processing Step

During all the treatment processes, a volume of 600 ml of wastewater was taken in order to ensure the measurement of all the treated wastewater properties, by studying the chemical stimulation effect with sulfuric acid and hydrochloric acid. 2 g of treated clay was submerged in 600 ml of wastewater, after two hours of stirring followed by stasis, the required properties were measured. This operation was repeated five times by changing the concentration values of H_2SO_4 from 0.1N to 1N and the concentration of HCl from 0.134N to 1.342N.

Results and Discussions

Chemical Activation Effect of Clay on pH Value for Wastewater

The results obtained for the pH values in polluted waters were between 7.63 and 7.4 according to Figure 2, a slight increase in the pH values of water treated with raw clay (8.20) can be distinguished. In general, there is a decrease in pH values after the activation process is estimated at (7.55 - 7.53) for sulphuric acid and (8.33 - 8, 01) for hydrochloric acid. This decrease explains the acid effect on the crystal structure of the clay by replacing the replaceable cations with protons (Steudel et al., 2009), which leads to a modification in physical and chemical properties of clay such as surface enhancement, exchange capacity and surface acidity, thus providing the properties of the influencing adsorbent (Doulia et al., 2009).

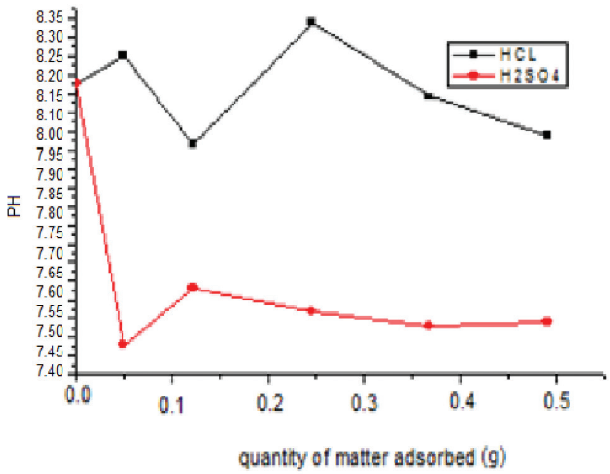

Figure 2: pH changes of wastewater treated with chemically activated clay.

Chemical Activation Effect of Clay on the Change of the Temperature Value for Wastewater

The obtained results show that the temperature values in polluted water ranged between 19.7°C and 20.4°C. In Figure 3, the temperature of wastewater treated with raw clay increases to (25.6°C), after the activation process with sulfuric acid and hydrochloric acid, respectively, to be estimated at 21.3-23.4°C and 23.3-24°C. This increase is explained by the fact that the adsorption process (solid-liquid) is an exothermic reaction (Kamarchou et al., 2015).

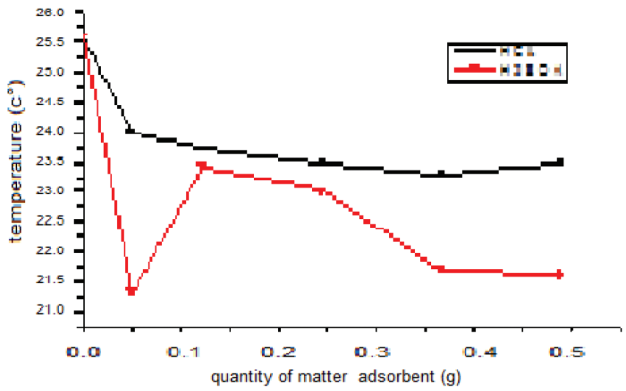

Figure 3: Temperature changes of wastewater treated with chemically activated clay.

Chemical Activation Effect of Clay on the Change of the EC Wastewater Value

According to ONA specifications, the electrical conductivity values (EC) in polluted waters are between 35.55 (35.1 – 36) ms/cm. Figure 4 shows that in treated water with raw clay EC = 44.9 ms/cm. After the activation process by both sulphuric acid and hydrochloric acid treatment EC values are estimated at 33.26 (31.6-33.9) ms/cm and 35.92 (35.7-36.1) ms/cm successfully. These results showed improved effluents with lower conductivity values compared to their respective initial values but still much higher than the Algerian standard values authorised for irrigation, estimated at 3 ms/cm) according to Algerian standards (Official Journal, 2012). The EC values obtained are very high, due to the mixing of the wastewater arriving at the station with the horizontal filtration water of the conne surface layer in the Ouargla region affected by the high value of salinity in the water.

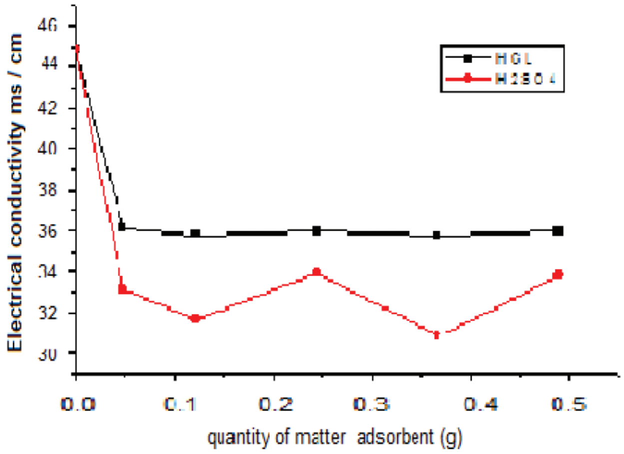

Figure 4: Electrical conductivity values changes of wastewater treated with chemically activated clay.

Chemical Activation Effect of Clay on the Change of the Value of the Turbidity for Wastewater

The results in Figure 5 show a high turbidity removal efficiency value of polluted water, Figure 1-b, where the raw clay achieved an average turbidity removal efficiency of 55.25 % (75%-35.5%). Improving the capacity of the clay by chemical activation caused an increase in these percentages to reach an average removal of 76.60% (61.52-74.690 %) with sulphuric acid and 46.97% (26.39%-65.57%). Given the best percent turbidity removal was 90.75% for the amount of adsorbent (0.36 g/g), which corresponds to the concentration of 0.75 N for sulphuric acid, as for hydrochloric acid, the best turbidity removal percentage was 65.57% for the amount of adsorbent (0.49 g/g), which corresponds to the concentration of 0.134N, through the ratios obtained, we conclude that sulphuric acid has a greater ability to improve the ability of clay to remove pollutants compared to hydrochloric acid.

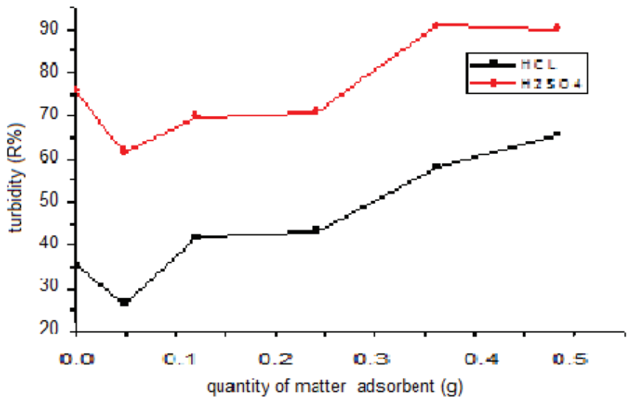

Figure 5: Turbidity values changes of wastewater treated with chemically activated clay.

Chemical Activation Effect of Clay on the Change of the Value of the Suspended Material (TSS) from Wastewater

Figure 6 shows a high efficiency in removing suspended matter from polluted water. The percentage of the sample purification using mud was 79.27%. This percentage increased after the chemical activation process of clay, where the average removal was 84.09% (77.89-93.33%) for clay treated with sulphuric acid and (79.26-94.31%) in the case of treatment with chloridric acid with an average of 89.37 %. It was found that the best percentage of removing suspended matter with sulphuric acid was 93.33% for the amount of adsorbent (0.36 g/g), which corresponds to a concentration of 0.75 N. When using hydrochloric acid, the best removal percentage was 94.31% for the amount of adsorbent

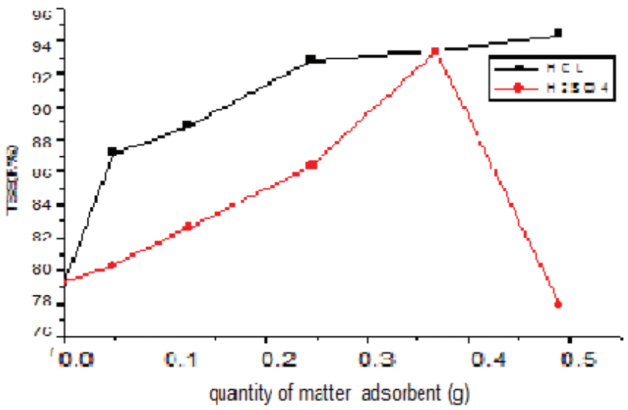

Figure 6: Changes in the value of suspended matter (TSS) of wastewater treated with chemically activated clay.

(0.49 g/g), which corresponds to the concentration of 0.134 N. Through the obtained ratios, we conclude that the two acids have a capacity that is considered close in order to enhance the ability of the clay for removal.

Chemical Activation Effect of Clay on the Change of the Value of (BOD_5) from Wastewater

Figure 7 shows that there is a high efficiency in removing the biochemical oxygen demand (BOD5) from polluted water, as the clay achieved an average removal rate of 57.04%, which shows the effectiveness of the removal process with raw mud. We noted the increase of those percentages after enhancing the clay's ability by chemical activation process, which gives an average removal of 85.68% (72.22-90.74%) with sulphuric acid and (60.92-38.94%) for chloridric acid with an average of 52.6%. The best percentage of biochemical oxygen demand removal was at 90.74% for the amount of adsorbent (0.36 g/g), which corresponds to the concentration of 0.75 N for sulphuric acid. For chloridric acid, the best percentage of removal was at 60.92% for the amount of adsorbent (0.49 g/g), which corresponds to the concentration (0.134 N). The results obtained show that sulphuric acid has a greater ability to further enhance the ability of clay to remove compared to hydrochloric acid.

The obtained results show high efficiency of activated clay, especially with sulphuric acid (90.74%) to remove the biochemical oxygen demand compared to the activated carbon method, where a return of 87.55% was recorded (Kamarchou et al., 2015).

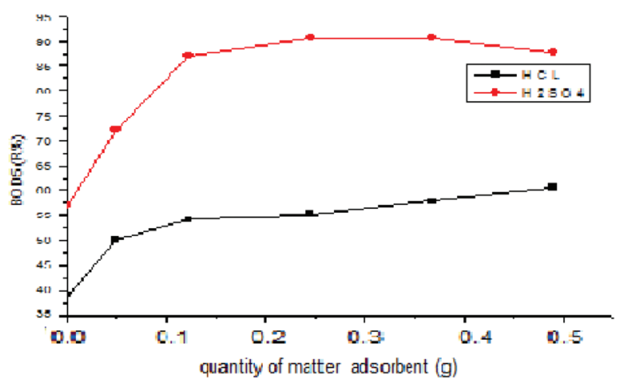

Figure 7: Changes in the value of the biochemical demand for oxygen (BOD_5) of wastewater treated with chemically activated clay.

Chemical Activation Effect of Clay on the Change of the Value of (COD) from Wastewater

The results obtained, in Figure 8, show that there is a high efficiency in removing chemical oxygen demand (COD) from polluted water, as the mud achieved a removal rate of 71%, which indicates the effectiveness of the removal process with raw clay. To note the increase of that percentage after enhancing the clay's ability by chemical activation process, where we obtained an average removal of 75.02% (72.6%-80.16%) with sulphuric acid. As for the clay treated with hydrochloric acid, the removal percentage ranged between 69% and 73%, with an average of 71%.

In order to compare which of the two acids is better for the activation process, we found that the best percentage of suspended matter removal was at 80.16% for the amount of adsorbent (0.36 g/g), which corresponds to the concentration of (0.75 N) for sulphuric acid, while for chlorine acid In water, the best removal rate was at 73% for the amount of adsorbent (0.49 g/g), which corresponds to a concentration of (0.134 N). And through the results obtained, we conclude that sulphuric acid has a greater ability to

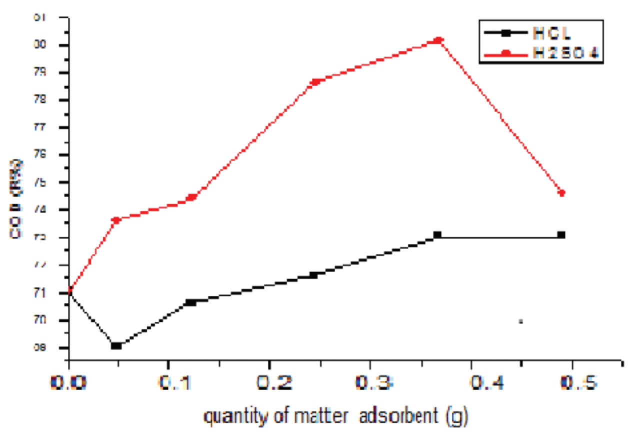

Figure 8: Changes in the value of the chemical demand for oxygen (COD) of wastewater treated with chemically activated clay.

enhance the ability of clay to remove compared to chlorine acid+water.

On the other hand, the activated carbon method recorded a yield of 86.90% (Kamarchou et al., 2015) higher for removing chemical oxygen demand compared to activated clay, especially with sulphuric acid (80.16%).

The optimum conditions for chemical activation were determined, from sulfuric acid with a concentration of 0.75N, and on this basis, we performed a heat treatment process according to those conditions.

Effect of Activated Clay with Sulphuric Acid and Heat on the Efficiency of Changing Physical Properties (pH, T, EC)

From Figure 9, the values of the physical properties of pH, T and EC remained constant at all temperatures from 500°C to 100°C for water treated with chemically activated and thermally activated clay, and this indicates that the activation thermal temperature does not change the physical properties, the change is only related to particle size and heating system (Bergaya et al., 2006).

Efficiency of Sulphuric Acid and Heat Activated Clay in Removing Organic Pollutants

Figure 10 shows the effectiveness of chemical and thermal activation in removing organic pollutants, as it is noted that the removal rate increases with increasing temperature until it reaches 400°C, so the removal percentage of COD, BOD5, TTS and Turb, respectively, becomes 82%, 65%, 89.56% and 78.65%. Then the removal rate begins to decrease after 400°C, due to the decrease in the surface area due to the damage to the clay structure by collapsing its interspaces, which makes the particles closer to each other (Önal and Sarıkaya, 2007).

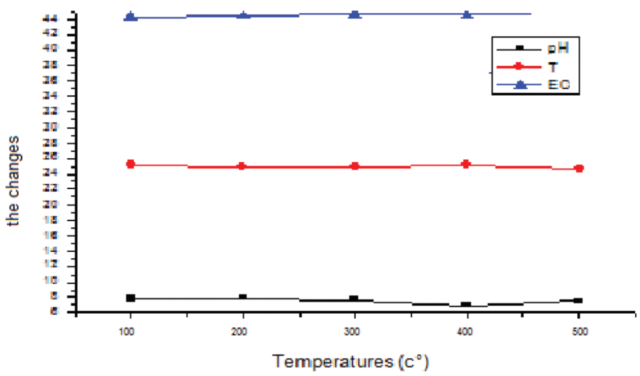

Figure 9: Changes of physical properties (pH, T, EC) of wastewater treated with chemically and thermally activated clay.

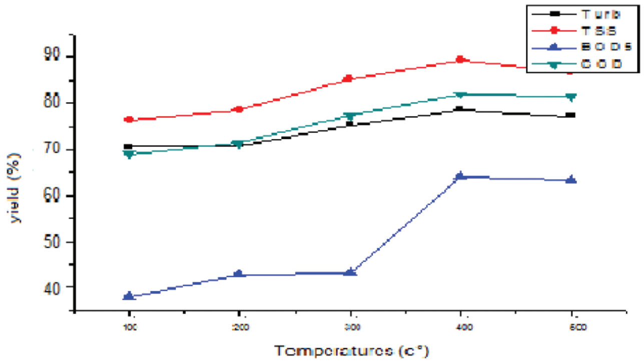

Figure 10: Efficiency of sulfuric acid and heat activated clay in removing organic pollutants.

Similar results were obtained by Önal and Sarıkaya (2007), where they examined the thermal activation of bentonite in the temperature range from 100°C to 1300°C and observed that the surface area increased with increasing temperature and then decreased at temperature of more than 400°C.

Conclusions

The performance of chemically and thermally activated clay in the treatment of effluents was studied and assessed by the removal of pollutants in ONA (Ouargla) wastewater. The acidified clay showed higher de-pollution efficiency versus raw clay. The thermal removal of organic pollutants from wastewater by observing: COD, BOD_5, TSS and turbidity and determining the best experimental conditions for chemical and thermal activation.

The results of the wastewater analyses have shown good efficiency due to the use of crude clay by eliminating pollutants for: COD, BOD_5 and TSS, and turbidity, respectively, 71%, 46%, 51.45% and 60%. Sulphur-activated clay has shown increased effectiveness in removing pollutants from the wastewater at its optimal dose of adsorbent (0.36 g/g), corresponding to the concentration of 0.75 N for COD (80.16%) BOD5 (90.74%), TSS (93.33%) and (Turb) 90.74%. The clay activated with hydrochloric acid was less efficient in removing pollution for the amount of adsorbent (0.49 g/g), which corresponds to the concentration of 0.134 N where organic pollutants have been eliminated in the proportions of COD (73%), BOD5 (60.93%), TSS (94.31%) and Turb (65.57%).

From obtained results, we conclude that sulphuric acid has a greater capacity to improve the elimination compared to the chloridric acid in water. Thermal activation has shown that adsorption increases with increasing temperature, to give the best absorption rate at 400°C, therefore, the elimination rate for (COD, BOD5, TSS and turbidity), respectively, 82%, 65%, 89.56% and 78.65%. Especially, the best dose in chemical stimulation with sulphuric acid was 0.75 N. Finally, it has been able to exploit an available natural resource which has a major impact on improving the environment and can be applied on the ground. Finally, it has been able to exploit an available natural resource which has a major impact on improving the environment and can be applied on the ground.

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