IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 12, Issue 9 Ser. I (September. 2019), PP 39-51
www.iosrjournals.org

Using of untreated and thermally treated kaolin clayas adsorbent and coagulant in the treatment of Wastewater

H.M. Ismail[1], A.I. Hafez[2], N.A.Khalil[2],A.I. Hashem[3], M.G. Elmalky[4]
[1-]*Ministry of Environment, Egypt.*
[2-] *Egyptian Electricity Holding Company Cairo Egypt.*
[3-]*Chemistry Department, Faculty of Science, Ain Shams University, Cairo Egypt.*
[4-] *Institute of Environmental Studies and Research, Ain Shams University, Cairo Egypt.*
Corresponding Author: A.I.Hafez Ashraf_Hafez40@Hotmail.com

***Abstract**: The capability of kaolin clay (untreated and thermally treated) and combination withferric chloride used as coagulants in wastewater treatment via adsorption, and coagulation-flocculation processes investigated. The optimum conditions (pH and coagulants dosage) identified for the both kinds and in combinations of kaolin clay with ferric chloride. The results obtained that kaolin clay is a good coagulant, which can absorb chemical oxygen demand (COD) biological oxygen demand (BOD), turbidity, total suspended solids (TSS) and some elements from wastewater with a good percentage removal. Using the optimum dosage of the combinations of thermally treated kaolin cay - ferric chloride mixture gave high efficiency removal of oil and grace, ironand turbidity. On the other hand, the effects of contact time indicated that the adsorption capacity of thermally treated kaolin clay was higher than the untreated one.*

***Keywords:** Wastewater treatment; kaolin clay; ferric chloride; coagulation and flocculation.*

Date of Submission: 17-09-2019 Date of acceptance: 02-10-2019

I. Introduction

Industrial wastewaters are still very important in the issue in waste management systems within the world. The COD, turbidity, total suspended solids (TSS), oil and grease, heavy metals and major cations are the main concerns of the characteristics of industrialwastewaters. Generally, high levels of (COD) results in low dissolve oxygen (DO) in water and this can lead to mortality of aquatic life. In addition to that, suspended solids such as organic and inorganic materials can result in the water being contamination of water with dirt anddisagreeableodour. Developing countries pay a high price to import chemicals including polyaluminium chloride and alum for water and wastewater treatment[**El-Kareish GM etal(2018) , M .L Abd l-Wahab et al (2018) , G.O.El-Sayed et al (2016), MY Alkadi et al** (2015) **, AI Hafez et al** (2014)]. Polyaluminium chloride and alum add impurities, such as epichlodine, which are carcinogenic. Besides that, aluminium is regarded as a major poisoning factor in encephalopathy dialysis and one of the factors which might contribute to Alzheimer diseaseWastewater treatment using bentonite, the combinations of bentonite-zeolite, bentonite-alum, and bentonitelimestone as adsorbent and coagulant was investigated[**Syafalni,et al(2013,Al-Bastaki,N & Banat ,F (2003),**]. Some synthetic organic polymers, which has been used as coagulants such as acrylamide, may cause neurotoxicity and strong carcinogenic effects [**Yarahmadi et al., (2009**)]. The use of clay as a natural material has undoubtedly become more popular and widely used as an adsorbent and ion exchange for water and wastewater treatment applications especially for removing heavy metals, organic pollutants, and nutrients **[(Abdelaal, (2004)**]. Clay minerals, such as bentonite and zeolite, are some of the potential alternatives, as they have large specific surface areas with a net negative charge, which can be electrically compensated by inorganic and organic cations from the environment **[(Konig et al., 2012), Anselme,N (1995),Aziz et al (2008)**] compared to polyaluminium chloride. Their sorption capabilities come from their high surface areas and exchange capacities **[(Babel and Kurniawan, (2003)].** The highly effective natural clay mineral, especially in granular form was used for the purification of wastewater and sludge dewatering. Generally, there are two types of bentonite which are sodium bentonite and calcium bentonite. Sodium bentonite is usually a high-swelling type, derived from volcanic ash that is deposited in marine environments. While calcium bentoniteis a low swelling type evolved from volcanic ash deposited in freshwater environments **[(Dwairi and Al-Rawajfeh, (2012)]**. The usage of natural clay minerals such as bentonite and zeolite for water and wastewater treatment are increasing because of their abundance, low price, and adsorption capabilities, as well as, ion exchangeability that is highly capable of adsorbing all kinds of pollutants for some organic and inorganic compounds, including heavy metals in waters **[Guimaraes et al.,(2009)]**. This outstanding capability is due to the presence of the mineral montmorillonite**[(Khenifi et al., (2009)**]. Apart from that, bentonite is a natural material that contains essential compounds such as aluminium, iron and clay materials, which are useful for the treatment of wastewater. Moreover, bentonite is cheaper than chemicals and it fulfills the economic benefits of the operators, as well as ,environmental concerns **[(Al-Qunaibit et al., (2005)].**However, coagulants that are commercialized in the market are mostly chemical-based, which are not environmental friendly and may create adverse impacts on the surrounding environments **[Ozcan et al., (2007)]**. The present study aims to investigate the combination of clay minerals, bentonite and zeolite in comparison with aluminiumsulphate, and zeolite. This study also investigates the comparative suitability of kaolin clay as adsorbents and coagulants for wastewater treatment based on the removal efficiencies of COD, iron, turbidity. Additionally, the effects of pH and dosage were also taken under consideration. There is no data available in the literature concerning the adsorption capability of raw kaolin clay and the combinations with ferric chloride as traditional coagulants.

II. Materials And Methods

2.1-Kaolin source:

Commercial kaolin was used as adsorbent material with the following shapes:
The granular and powder kaolin photographs are shown in Figure (1)

Figure (1) Granular and powder kaolin

The kaolin clay was thermally treated in muffle furnace at 650^0C for four hours to remove any impurities and convert its constituents to metal oxide.

2.2-Industrial wastewater source:

Industrial wastewater samples were taken from boiler air preheater cleaning wastewater system in shoubra El khema power plant Cairo Egypt.

2.3- Chemicals:

All chemicals used in analysis and adjusting water pH were of analytical grade.

2.4-Analysis:

2.4-1-kaolin clay analysis:

2.4.1-1 Thermogravimetric Analysis (TGA):

Thermogravimetric analysis of the kaolinperformed using ThermogravimetricdetermenatorLeco: Mac-500.ST.Joseph, Michigan-USA. This apparatus provided a continuous measurement of sample weight at a range of temperatures between ambient and 700^oC.The samples heated in an alumina cell to 700^oC at heating rate of 10^oC/min with nitrogen as the circulating gas.
- Weight loss measured by heating of kaolin at 700^oC until constant weight obtained.
-Elements in kaolin and industrial wastewaterquantified by using Atomic Absorption Spectrometer, Solaar S-4 S- Series Thermo Electron Corporation UK.

2-4-1-2- X-ray analysis of kaolin:

Energy dispersive X-ray spectrometry EDX, of kaolin clay was measuring by (EDX Model ISIS Link Instrument P/C. Oxford Co.).

2.4.2. Industrial wastewater analysis:

- The cation and anionspecies were determined according to ASTM D-4327 ND 6919, respectively using ion Chromatography. The instrument used was Dionex IC model ICS 1100 equipped with high capacity columns (AS9 and CS 12) for anion and cations, respectively.

- Heavy metals were determined using Atomic Absorption Spectrophotometer model Zenit 700p according to ASTM D4691.

- Physical and chemical properties including total dessolved solids (TDS),conductivity , turbidity, pH and others were measured according to the following standards procedures:

- TDS was determined according to ASTM D-1888.
- Conductivity was determined on site using digital conductivity meter WTW 330I according to ASTM D-1125.
- pH was determined according to ASTM D-1293 using digital pH meter model metler Toledo-Seven Go.
- Alkaline species (CO_3^{-2}, HO^{-1}, HCO_3^{-1}) were measured according to ASTM D-3875 calculations were done using Alkalinity calculator Ver. 2.10 (USGS).
- Turbidity was measured in nephelometric turbidity units (NTU) using Helige Digital Direct Reading Turbidmiter.
- Total suspended solids (TSS) was measured by filtering the wastewater samples through a weighed standard glass-fiber filter with 0.2 µm diameter. The residue on the filter was dried at 110ºC. The increase in the weight of the filter represents the total suspended solid.
- Oil and grease were measured according to (EPA 600\4-79\020), gravimetric speratory funnel extraction.
- The organic matter expressed as $KMnO_4$ determined by consumption of $KMnO_4$ in acidic solution.
- The removal efficiency (% Removal) was calculated according the following formula:

% Removal = $(C_0 - C / C_0) \times 100$

Where, C_0 and C = represented for each of oil and grease, organic matter, and turbidity contents of industrial wastewater (produced water) before and after coagulation treatment.

2.6. Water sample specification:

The specifications of wastewater sample are listed in the following table:

Table (1) the specifications of wastewater sample.

No.	Parameters	Result
1.	**PH**	6.2
2.	**Turbidity** (NTU)	16.4
3.	**Color**	Brown color
4.	**BOD (5day,20°C)** (ppm)	420
5.	**COD Dichromate** (ppm)	1775
6.	**Total hardness as $CaCO_3$**(ppm)	560
7.	**Calcium hardness as $CaCO_3$** (ppm)	367
8.	**Magnesium hardness as $CaCO_3$** (ppm)	193
9.	**Total alkalinity $CaCO_3$** (ppm)	137
10.	**Total Dissolved solids** (ppm)	1585
11.	**Total Suspended solids** (ppm)	36
12.	**Oil and Grease** (ppm)	13.55
13.	**Organic matter as ($KMnO_4$)**ppm	27
14.	**Total Phosphorus**(ppm)	0.19
15.	**Total Nitrogen** (ppm)	30.4
16.	**Phenols** (ppm)	0
17.	**Sulfide** (ppm)	0
18.	**Ammonia as Nitrogen**(ppm)	29.5
19.	**Vanadium** (ppm)	0.56
20.	**Mercury** (ppm)	0
21.	**Lead** (ppm)	0.752
22.	**Cadmium** (ppm)	0.003
23.	**Arsenic** (ppm)	0
24.	**Chromium** (ppm)	0.003
25.	**Copper** (ppm)	0.338
26.	**Nickel** (ppm)	0.433
27.	**Iron** (ppm)	5.999
28.	**Manganese** (ppm)	0.433
29.	**Zinc** (ppm)	0.165
30.	**Silver** (ppm)	0
31.	**Boron** (ppm)	0

2.5. Jar Test measurement:

Jar tester containing six (1-liter) beakers in conjugation with multiple stirrers used. Each beaker filled with one liter of raw industrial wastewater and stirred at 100 rpm. The different doses of coagulant kaolin clayadded rapidly and stirred for 3 minutes. The stirring rate then reduced to 50 and 20 rpm for a period of 5 and 10 minutes, respectively to allow complete flocformation, and then stirring stopped. The relative settling rate, floc size and supernatant clarity were recorded. After a settling period of 15 minutes, 250 ml of supernatant water siphoned -off for further analysis.

III. Results and Discussions

When aluminosilicates in kaolin clay arethermally treated, there are many changes of their cations by the effect ofhydronium ions, and there may occur hydrolysis of A1-O-Si bonds. Hydrolysis occurs readily for the most aluminous minerals, and results in complete disintegration to colloidal silica and to aluminum salts. As the silica content increases, colloidal silica is increased. It could be anticipated that as the silica content increases still further the gel will retain more and more of the parent structure. Therefore,highly specific silica-rich sorbents may be obtained and is one of the most siliceous aluminosilicate and accordingly sorbents obtained by acid treatment with hydrochloric acid solutions of the molecular sieve **(Barrer, et al., 1964).**

3.1. Analysis of the untreated and thermally treated kaolin clay:

3.1.1- X-Ray analysis:

Energy Dispersive X-ray spectroscopy (EDX):

The EDX analysis of kaolin clays was carried out in order to investigate their mineralogical nature and chemical composition.

Figures (2) and (4) forkaolin clay (untreated and thermally treated), indicate thatthe amounts of aluminum and silicon elements represented by the peaks of Figures (2), (4) are higher compared with other metal elements in all types of kaolin clay. While calcium element represented by the peaks of Figure (4) of thermally treated kaolin clay is higher due to the increase of Al_2O_3, SiO_2, CaO resultswith thermally treated kaolin clay. This makes good coagulant media. In addition, Figure (4) shows other elements present in the different types of kaolin clay such as KandNa, which have small values.

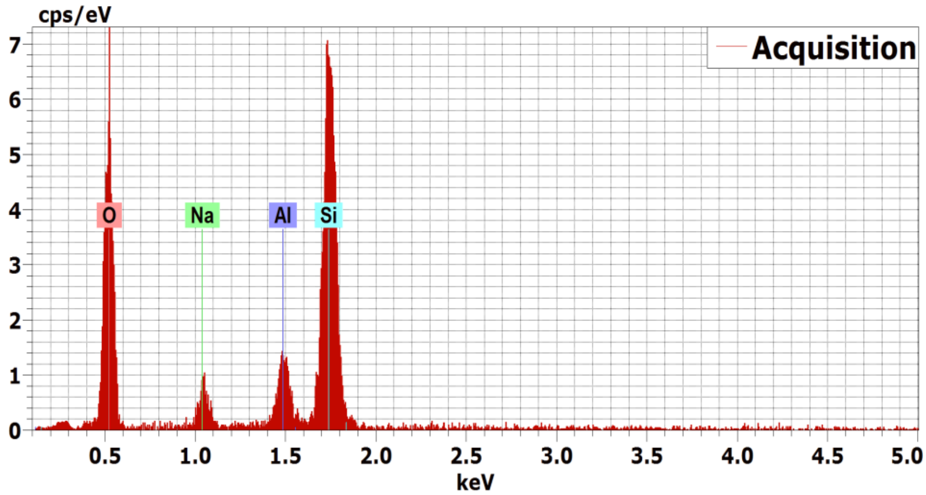

Figure (2) X-Ray analysis (EDX) ofuntreated kaolin clay

Table (2)percentage of metal ion in untreated kaolin clay

Spectrum: Acquisition

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
O	8	K-series	44.74	59.74	71.75	8.5
Na	11	K-series	2.72	3.63	3.04	0.3
Al	13	K-series	4.00	5.34	3.80	0.3
Si	14	K-series	23.43	31.29	21.41	1.2
		Total:	74.89	100.00	100.00	

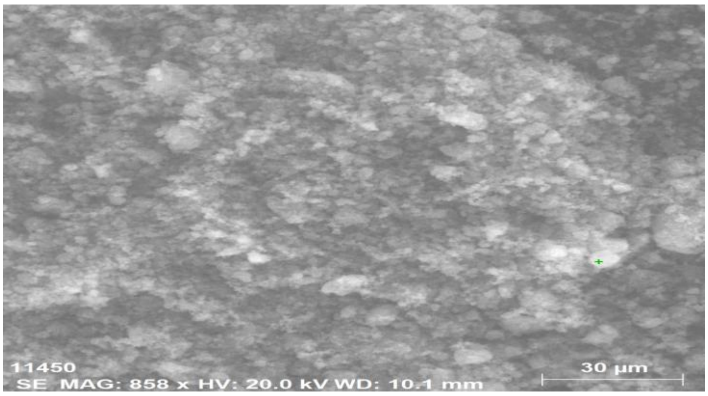

Figure (3) SEM of untreated kaolin clay

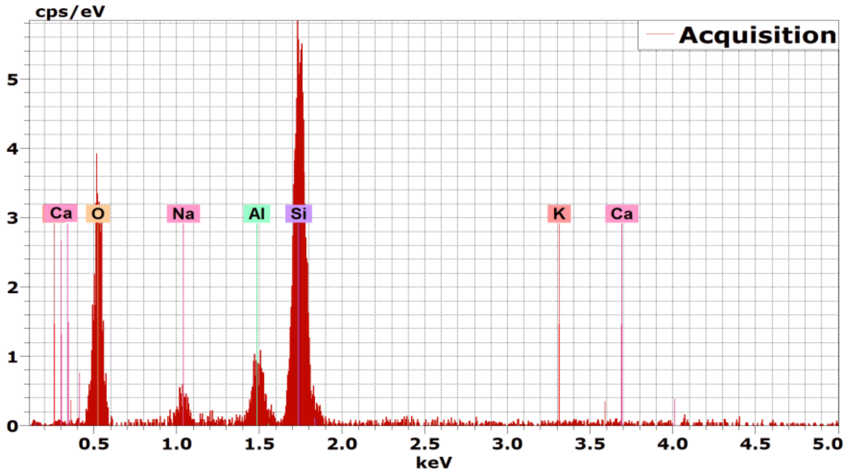

Figure (4) X-Ray analysis (EDX) of thermally treated kaolin clay

Table (3)percentage of metal ion in treated kaolin clay

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	

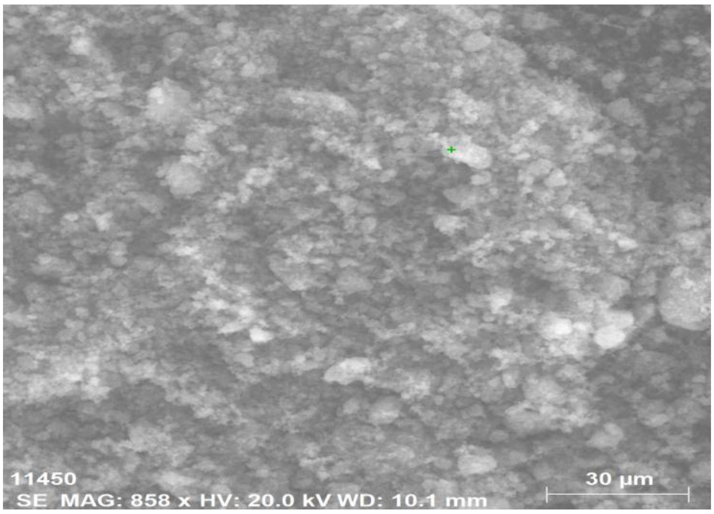

Figure (5) SEM of thermally treated kaolin clay

The percentage of element in the untreated and thermally treated at 650°C of kaolin clayare listed in Table (2) and (3). The tables'show that Al_2O_3 and SiO_2were slightly increased in thermally treated than untreated kaolin clay. It was found that with increasing temperature,the metals oxides increased .Therefore, thermally treated would be more efficient than untreated kaolin clay in adsorption of pollutants.

3-1-3. Thermogravimetric analysis TGA:

TGA is a thermal analysis technique used to measure the mass-temperature relation of the sample under the program controlled temperature, and to study the thermal stability and elements of materials. The weight loss of kaolin clay against temperature was represented in Figure (5).As it is evident; the results for the samples have three characteristic stages of decomposition. The first stage starts at 100 °C and end at 200°C with weight loss of 3 % this could be recognized due to the moisture content of the sample. The second stage which is related to the main decomposition of the kaolin clay sample. This step ranging from 200°C to300 to 400°C with weight loss of 4 , 6 , 7% respectively assigned to releases of hydration water of interlayer cations and at 400^{o}C is assigned to the degradation of the sample and represented the hydrated hydroxide [Al_2 (Si_2O_5) $(OH)_4$], [Al $(OH)_3$.xH_2O] and others **(Barrer, et al., 1964).**Last stage observedrelated to the decarbonization process, which occurs at 500° C, 600° C and 700^o C with weight losses were 8, 8.3 and 8.3% where the change in weight is very small. A further endothermic change begins near 600° C and persists over a range of temperature. The foregoing reflect the thermal stability of kaolin clay.

TGA Results of kaolin clay

Temperature^{0}C	–	100	200	300	400	500	600	700
Weight %	100	96	94	93	92.4	91.2	91.6	91.6

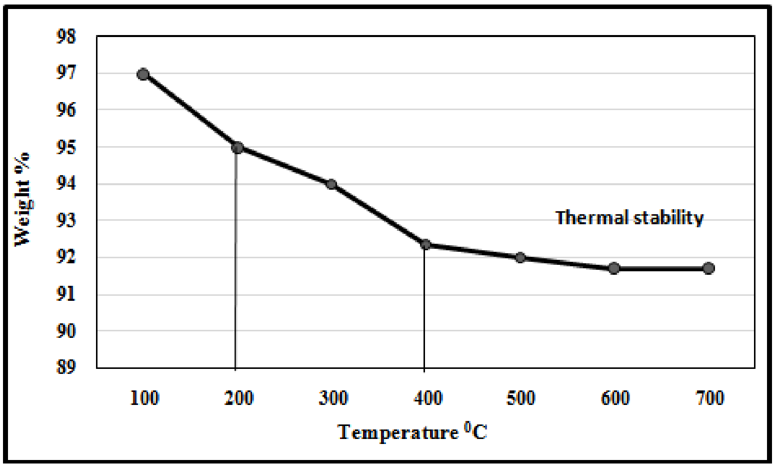

Figure (5) Thermogravimetric analysis of kaolin clay

3.2. Evaluation of the kaolin clay as adsorbent media:

3.2.1. Effect of different kaolin clay dosage on the coagulation performance:

The effect of dosewas done for the two types (untreated, and thermally treated).**Table (4)** showed the variation of dosage concentration (1–8%) on the adsorption performance of the studied sorbent agents using the industrial wastewater.

Table (4): Effect of kaolin clay dosage on turbidity, oil and grease and organic matter removal.

Kaolin Clay Dosage (%)	Untreated kaolin clay			Thermally treated kaolin clay		
	Turbidity (NTU)	Oil and Grease (mg/l)	Organic matter (mg/l)	Turbidity (NTU)	Oil and Grease (mg/l)	Organic matter (mg/l)
Raw Industrial waste water	16.54	13.55	27	16.54	13.55	27
1	12.6	10.17	14.13	9.11	7.17	10.13
2	10.98	9.91	14.09	7.24	6.91	10.09
3	8.62	9.42	13.77	5.48	6.42	9.77
4	5.71	9.20	13.12	3.26	6.20	9.12
5	4.85	8.92	12.19	3.16	5.92	9.11
6	5.74	8.94	12.59	1.22	5.98	9.12
7	4.82	9.11	12.12	1.51	6.11	9.11
8	3.18	9.22	12.45	1.92	6.22	9.1

pH=8 , settling time =45minat room temperature.

It is evident fromtable (4) that the thermally treated kaolin clay, performance increased by increasing its dose where the best flocculation increases by increasing the dosage concentration up to 6 % after which levelling off occurs. Overdosing higher than 6% resulted in the reversal of particle in the stock solution due to the adsorption of excess (sorbent agents) molecules and it is difficult for the particles to form flocs because of electronic repulsion of the adsorbed agents.

Turbidity values for (thermally treated kaolin clay) were (1.22 NTU) compared to (5.74 NTU) for untreated one.Nevertheless, for other parameters such as oil and grease and organic matter the same effect was observed.Thus, the thermally treated kaolin clay gives higher flocculation performance than the untreated kaolin clay.Figures (6-8)show the removal profile for turbidity, oil and grease and organic matter.

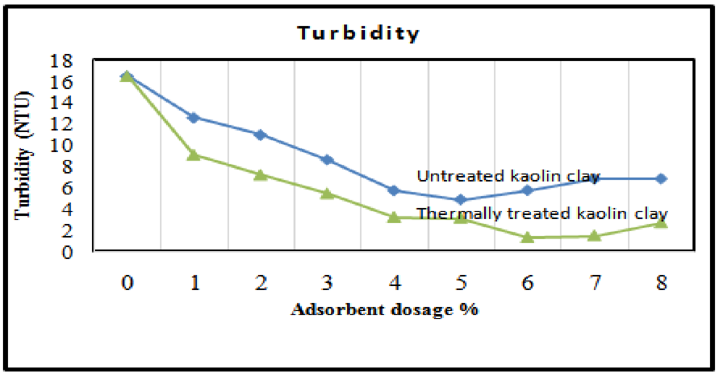

Figure (6) Effect of treated and untreated kaolin clay dosage on turbidity

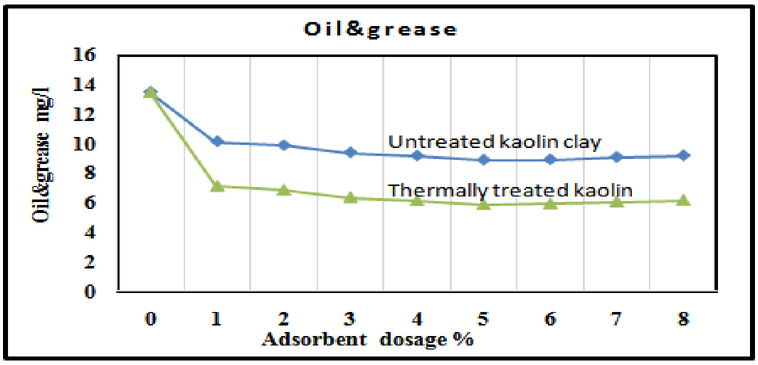

Figure (7) Effect of treated and untreated kaolin clay dosage on oil &grease

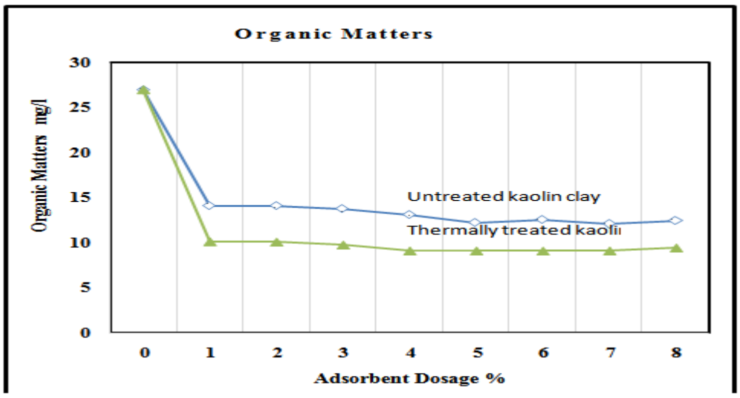

Figure (8) Effect of treated and untreated kaolin clay dosage on organic matters

4.2.3. Effect of different pHon adsorbent performance:

Table (6) shows the effect of the pH of the industrial wastewater on the adsorbent performance (expressed as turbidity value NTU, oil and grease mg/l and organic matter mg/l) of untreated and thermally treated kaolin.

The dosage of the two examined flocculants was adjustedat 6 %. The adsorption performance after 45 min settling time was measured as a function of the turbidity (NTU), oil and grease and organic matter. It is well known that the best flocculation occurs when the net charge at the surface of the coagulant and suspended participles is approximately zero. Suspended matter in water with its negative charge will be absorbed at the kaolin surface as sorbent agent and best adsorption with highly magnitude of negatively charged suspended particles removal was obtained at pH 7.5 - 9.5 for the three examined coagulant substances (untreated and thermally treated kaolin). The adsorption performance for thermally treated and kaolin clay is better than for untreated one.

Table (6): Effect of pH on the turbidity, oil and grease and organic matter removal.

pH	Untreated kaolin clay			Thermally treated kaolin clay		
	Turbidity (NTU)	Oil and Grease (mg/l)	Organic matter (mg/l)	Turbidity (NTU)	Oil and Grease (mg/l)	Organic matter (mg/l)
Raw Industrial waste water	16.54	13.55	27	16.54	13.55	27
6	6.54	10.17	13.13	2.10	6.17	9.13
6.5	6.11	9.91	13.09	2.01	5.91	9.09
7	5.90	9.42	12.77	1.90	5.42	8.77
7.5	5.79	8.98	12.62	1.70	5.20	8.12
8	5.74	8.94	12.59	1.34	5.98	9.10
8.5	5.30	8.94	12.59	1.40	4.98	7.39
9	5.08	8.71	12.12	1.40	5.11	7.12
9.5	5.10	8.72	12.45	1.90	5.22	7.45
10	5.50	9.12	13.66	2.60	5.32	7.66
10.5	5.78	9.25	13.89	2.80	5.35	7.89

Kaolin clay dosage for untreated and thermally treated for settling time 45 min at room temperature
Figures (9-11) show the pH profile for turbidity, oil and grease and organic matter.

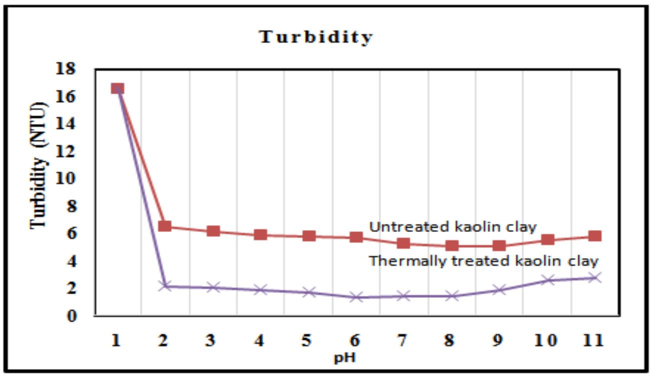

Figure (9) Effect ofpH on the turbidity

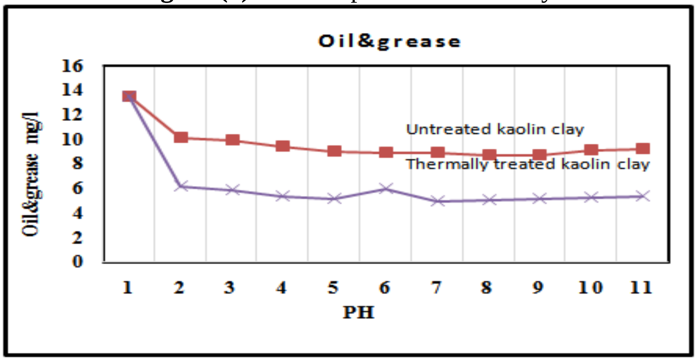

Figure (10) Effect of pH on the oil & grease

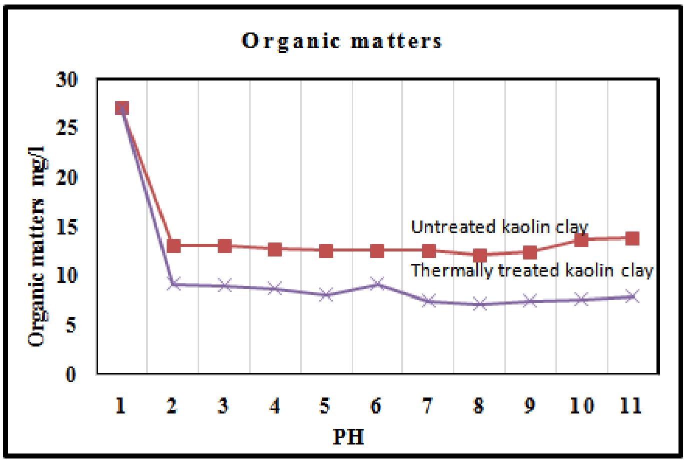

Figure (11) Effect of pH on the organic matters

3.2.4. Effect of different settling times:

Table (7) represents the effect of contact time on the adsorption performance expressed as turbidity value (NTU), oil and grease (mg/l) and organic matter (mg/l), using untreated and thermally treated kaolin clay. The dosage concentrations and pH were adjustedat the previous optimum conditions. It can be seen that by increasing the settling time from 5- 60 min the turbidity, organic matter and oil and grease values were decreased. The more suspended fine particles in water need more time for sedimentation in a colloidal particle. A particle of diameter 0.1 mm needs 38 sec for sedimentation. Meanwhile, particles of diameter $1X10^{-5}$ mm needs 6.3 year for sedimentation **(Faust ,S.D and Aly O.M., 1998).** The turbidity (NTU), oil and grease (mg/l) and organic matter (mg/l) values on using untreated kaolin clay agent are less than that of the values obtained by thermally treated kaolin clay. Therefore, it is evident that the removal % of turbidity, oil and grease and organic matter using thermally treated Kaolin clay are greater than untreated which means that thermally treated has the more effective action for adsorption performance.

Table (7): Effect of Settling time on the turbidity, oil and grease and organic matter removal in water.

Time (min)	Untreated kaolin clay			Thermally treated kaolin clay		
	Turbidity (NTU)	Oil and Grease (mg/l)	Organic matter (mg/l)	Turbidity (NTU)	Oil and Grease (mg/l)	Organic matter (mg/l)
Raw Industrial waste water	16.54	13.55	27	16.54	13.55	27
5	7.74	11.97	14.13	2.80	7.17	11.13
10	6.77	10.31	13.99	2.01	6.99	10.09
15	6.10	9.92	13.37	1.90	6.72	10.07
20	5.99	9.48	13.22	1.80	6.60	9.92
30	5.94	9.14	12.99	1.44	6.28	9.50
45	5.74	8.94	12.59	1.34	5.98	9.10
60	5.74	8.94	12.59	1.34	5.98	9.10

Kaolin clay dosage for untreated and thermally treated for pH 8 at room temperature.

Figures (12-14) show the settling time profile for turbidity, oil and grease and organic matter.

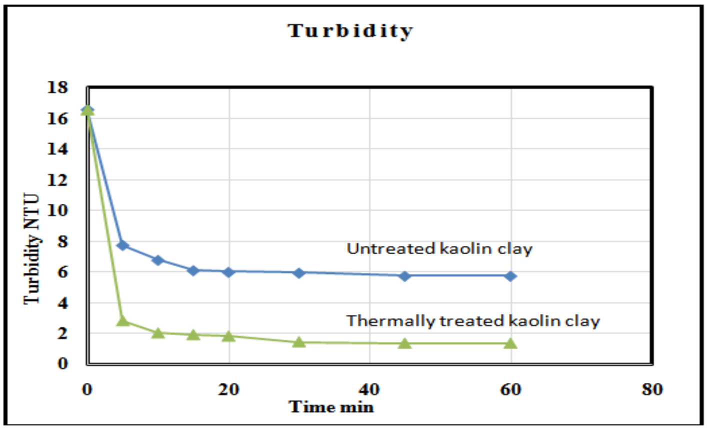

Figure (12) Effect of Settling time on the turbidity

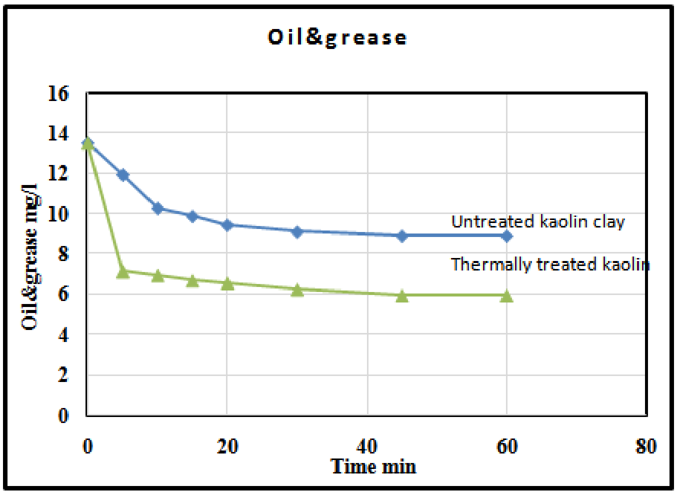

Figure (13) Effect of Settling time on the oil &grease

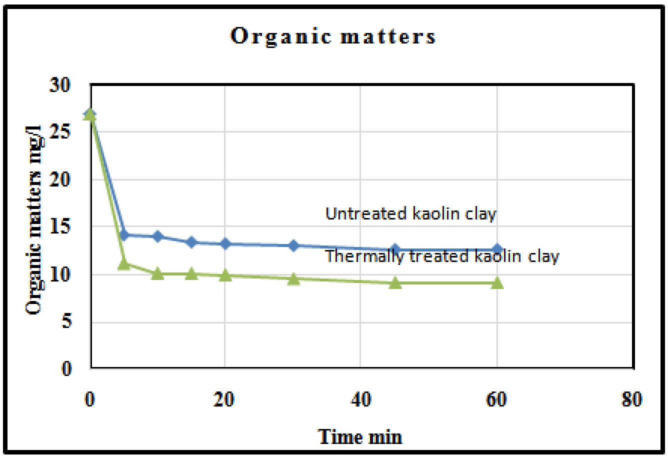

Figure (14) Effect of Settling time on the oil &grease

4.3. Evaluation of combination of ferric chloride as conventional coagulant and kaolin clay:

The data listed in Tables (8 and 9) show the effect of different ferric chloride doses (20 to 40 ppm) combined with untreated and thermally treated kaolin concentrations on the turbidity values of industrial wastewater. The flocculation and adsorption action were determined at optimum conditions of 45 min settling time and pH 8 at room temperature. The results clarify the following aspects:

Increasing kaolin concentrations of the three examined sorbents agents were accompanied by observed increase of the flocculation performance of the treated industrial wastewater up to 4%. A point of interest is that ferric chloride used in best water flocculation with a concentration of 35-40 ppm gives turbidity values 2.74 and 2.76 (NTU). In addition, from our previous data best flocculation for our studied compounds was 6 ppm. Combination between ferric chloride and the studied two sorbent agents is associated by definite decrease of its concentration to (25 ppm) for ferric chloride and 4% for the studied two sorbent agents. Moreover, the quality of clarification is more improved than that obtained for each component alone. For instance, the turbidity value (NTU) for 4% dosage for thermally treated and untreated kaolin 3.26 and 5.74 (NTU) respectivelywere obtained. Turbidity value of 1.11and 2.42 (NTU) for 4% of thermally and untreated kaolin clay respectively was reached with (25 ppm) ferric chloride. Nevertheless, the data obtained from Tables (8), (9) show that at constant ferric chloride concentration (25 ppm) the variation of flocculation performance as turbidity function follow the following sequence:
Thermally treated kaolin + 25ppm ferric chloride >untreated kaolin+25ppm ferric chloride >25 ppm ferric chloride.

Table (8): Effect of combination between ferric chloride and thermally treated kaolin clay at different dosages on the turbidity removal.

thermally treated kaolin dosage %	**Turbidity (NTU)**				
	Ferric chloride concentration				
	20 ppm	**25 ppm**	**30 ppm**	**35 ppm**	**40 ppm**
0	**2.92**	**2.87**	**2.70**	**2.74**	**2.76**
2	**1.49**	**1.40**	**1.43**	**1.45**	**1.47**
4	**1.35**	**1.11**	**1.24**	**1.26**	**1.29**
6	**1.25**	**1.15**	**1.19**	**1.21**	**1.23**
8	**1.37**	**1.21**	**1.24**	**1.26**	**1.28**

Industrial wastewater sample of (13 NTU), pH8 and settling time 45 min.

Table (9): Effect of combination between ferric chloride and untreated kaolin clay at different dosage on the turbidity removal.

Untreated kaolin dosage %	**Turbidity (NTU)**				
	Ferric chloride concentration				
	20 ppm	**25 ppm**	**30 ppm**	**35 ppm**	**40 ppm**
0	**2.92**	**2.87**	**2.70**	**2.74**	**2.76**
2	**2.72**	**2.57**	**2.60**	**2.62**	**2.64**
4	**2.63**	**2.42**	**2.46**	**2.50**	**2.54**
6	**2.54**	**2.38**	**2.41**	**2.46**	**2.50**
8	**2.59**	**2.51**	**2.54**	**2.56**	**2.58**

Industrial wastewater sample of (13 NTU), pH 8 and settling time 45 min.

3.4. Characteristics of treated water:

To explain clearly the importance of this study a collective Table was made to compare the characteristics of industrial wastewater taken as a control, with that independently treated with (25 ppm) of ferric chloride and 4% of two studied different kaolin's. It can be seen that the conductivity upon using ferric chloride caused a decrease of its value to (1357µS) compared with that of the industrial wastewater (1375µS).While, treated and untreated kaolin showed a slight increase when mixed with ferric chloride.

The turbidity of the treated water was considerably decreased by using mixture of ferric chloride and treated kaolin and reached to lowest turbidity values of (1.5 NTU) against a value of (2.3 NTU) obtained using combination of ferric chloride with untreatedkaolin. The total alkalinity was affected by treatment with ferric chloride,kaolin or their admixture and the recorded values were 109, 118, 111,122, 114, 121 and110 ppmrespectively, while that of industrial wastewater was 137 ppm. With respect to the total hardness, BOD, COD and oil and grease,the treatment by treated and untreated kaolin or their mixture with ferric chloride affected them.In addition, each of Ti and Cr also affected by such treatment.

Table (10): Variation of water characteristics at the optimum dosage of ferric chloride and different prepared flocculants concentration and their combination

Parameters	Industrial waste water	Ferric chloride (35ppm)	Untreated Kaolin (6%)	Untreated Kaolin (4%) + 25ppm ferric chloride	Thermal treated kaolin (6%)	Thermally treated Kaolin (4%) + 25ppm ferric chloride
pH	6.2	5	6	7	8	7.3
Conductivity (µS)	1357	1375	1366	1371	1360	1372
Turbidity (NTU)	16.54	2.9	3.8	2.3	2.6	1.5
Total alkalinity as $CaCO_3$	137	109	118	111	122	114
Calcium hardness as $CaCO_3$	367	358	257	256	250	256
Organic matter as $KMnO_4$	27	14.61	13.93	13.72	13.85	13.64
COD	1775	1384	994	923	905	958.5
BOD	420	344.5	315	273	264.6	243.6
Oil and Grease ppm	13.55	8.24	4.93	4.73	4.51	3.72
Ti ppm	0.004	<0.001	<0.001	<0.001	<0.001	<0.001
Cr ppm	0.003	<0.001	<0.001	<0.001	<0.001	<0.001

3-5. Benefits of Study

The study was carried out in accordance to economical side and environmental impact as follows:

1- Using of kaolin can help companies save money through:

- Operation costs.
- Reduce truck traffic (solid form).
- Reducing the problems of environmental impacts of solid waste.
- Using of kaolin clay in other purposes as softener.
- The obtained results in this work revealed that, thethermally treated of kaolin clay makes it suitable for the treatment of wastewater with good efficiency.

3-6. Environment Impacts:

It is well known fact that the environment is affected by produced water and sludgeas a solid wastes. The main goal of this work is to use kaolin clay in theremoving of organic matters, oil and grease and heavy metals from produced wastewater. By this way, it can decrease environmental impacts from disposal of more than one of hazardous wastes represented in produced water in addition to save cost of disposal process and waste sludge after treatment.

IV. Conclusions

The target of this work was to investigate the potential of using kaolin clay (untreated and thermally treated) and in combination with ferric chloride in the treatment of industrial wastewater. The results obtained revealed that these sorbents induced a considerable reduction in the turbidity, organic matter, (BOD), (COD) and total suspended solid (TSS) and eliminate considerable amounts of oil and grease from industrial wastewater.

It is evident, therefore, that kaolin clay as an available cheap natural material, compare with other commercial materials used in the field of industrial wastewater treatments.

References

[1]. **Abdelaal, A.M., (2004),**"using a natural coagulant for treating wastewater". Eighth International Water Technology Conference, IWTC8, Alexandria, Egypt.

[2]. **AI Hafez, FM Tera, ESE El-Shereafy, MM Kayaty(2014)** "Synthesis and application of cationic rice starch as a flocculants for water treatment" Journal of Advanced Scientific Research, Issue 4 (6) , p 156-168

[3]. **AI Hafez, NA Khalil, AI Hashem(2014)** "Synthesis and characterization of cationic chitosan nanoparticles as coagulant in water treatment" Journal of Advanced Scientific Research 4(6) p 126-146.

[4]. **Al-Bastaki, N., and Banat, F., (2003),**"Combining ultrafiltration and adsorption on bentonite in a one-step process for the treatment of coloured waters". Resources, conservation and recycling, 41, p 103-113.

[5]. **Anselme, N., SubbaNarasiah, N., and Brian, G.T., (1995),**"Active agents and mechanism of coagulation of turbid water using MoringaOleifera". Wat. Res., 29, p 703-710

[6]. **Al-Qunaibit, M.H., Mekhemer, W.K., and Zaghloul, A.A., (2005),**"The adsorption of Cu (III) ions on bentonite – a kinetic study". Colloids Interface Sci., 283, p 316-321.

[7]. **Aziz H.A., Adlan M.N., and Ariffin K.S., (2008),**"Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr (III) removal from water in Malaysia: Post treatment by high quality limestone". Biores. Tech, 99, p 1578-1583.

[8]. **Barrer, R.M., and Makki, M.B., (1964) "**Molecular sieve sorbents from clinoptilolite". Canadian Journal of Chemistry, NRC Research Press. 42(6),p 1481-1487.
[9]. **Dwairi, R.A.A., and Al-Rawajfeh, A.E., (2012),**"Removal of cobalt and nickel from wastewater by using Jordan low-cost zeolite and bentonite". Journal of university of chemical technology and metallurgy, 47(1), p 69-76.
[10]. **El-KareishGM , Hafez AI , Tera FM (2019) "**Improving Petroleum Industrial Waste Water Quality Using Cationic Modified Rice Starch**"** International Journal of Chemical Sciences 16 (4), 1-9**.**
[11]. **Faust, S.D. and Aly, O.M., (1998).** In "chemistry of water treatment", 2nd edition, Lewis Publication, Boca Raton, London, chapter.6, p. 369-466.
[12]. **G.O.El-Sayed , A.I. Hafez , H.M.Zahr El-Deen (2014)** "Extraction of Calcium and magnesium ions from Water-Treatment-Plant Sludge for Reusing in industrial water Treatment" International Journal of Advanced Scientific and Technical Research 6 (5) ,p 491-510.
[13]. **Guimarães J.L. E., Frollini, C.G. da Silva, F. Wypych, K.G. Satyanarayana (2009).**
[14]. "Characterization of banana, sugarcane bagasse and sponge gourd fibers of Brazil" journal of Industrial Crops and Products 30, 407–415.
[15]. **Khenifi, A., Zohra, B., Kahina, B., Houari, H., and Zoubir, D.,(2009)**, "Removal of 2,4-DCP from wastewater by CTAB/bentonite using one-step and two-step methods": A comparative study. Chem. Eng. J., 146, p 345-354.
[16]. **Konig, T.N., Shulami, S., and Rytwo, G., (2012),**"Brine wastewater pretreatment using clay minerals and organ clays as flocculants". Applied clay science, 67(68), p 119-124.
[17]. **M .L Abd l-Wahab , A.I HAfez , F.M Tera , K.I . El-Nagar (2018)** "Carbamated corn cobs as a natural coagulant for water treatment. International Journal of Advanced Scientfic and technical Research 4 (8), 74-84**.**
[18]. **MY Alkadi, T Razek, AI Hafez, ME Moursy(2015)** "CATIONIC MODIFIED RICE STARCH FOR DRINKING WATER PURIFICATION".Journal of Advanced Scientific Research 6 (2), p 10-13.
[19]. **Ozcan, A., Omeroglu, C., Erdogan, Y., and Ozcan, A.S., (2007),**"Modification of bentonite with a cationic surfactant: An adsorption study of textile dye Reactive Blue 19". Journal of hazardous materials, 140, p 173-179.
[20]. **Syafalni, Rohana Abdullah, Ismail Abustan, AimiNadiahMohd Ibrahim (2013),** "Int. J. of Env. Sci. Volume 4 No.3, 380.
[21]. **Yarahmadi, M., Hossieni, M., Bina, B., Mahmoudian, M.H., Naimabadie, A., and Shahsavani, A., (2009),** Application of MoringaOleifer Seed Extract and Polyaluminium Chloride in Water Treatment. World app. Sci. j, 7 (8), p 962-967.

H.M. Ismail" Using of untreated and thermally treated kaolin clayas adsorbent and coagulant in the treatment of Wastewater"IOSR Journal of Applied Chemistry (IOSR-JAC) 12.9 (2019): 39-51.