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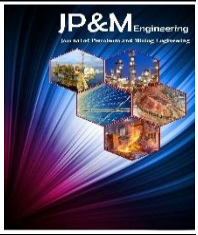

COD, BOD, Oil Content and Heavy Metals Removal from Wastewater Effluents by Coagulation - Flocculation Process

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Abstract

Wastewater effluents from the refineries are considered the major sources, which pollute the environment. Several efforts were carried out to study the possibility of treatment oily wastewater using new materials, to remove contaminates and prevent or minimize its impacts on the environment at low cost. The present study deals with the treatment of the oily wastewater effluents, from El-Nasr Petroleum Company, Suez - Egypt by coagulation flocculation processes. The reagents used in this study were cationic type flocculent of moderate molecular weight Zetag57, kaolinite and modified kaolinite (blended kaolinite with alum) as coagulants. The obtained results showed that kaolinite and modified kaolinite are highly efficient in removal of the contaminants (COD, BOD, Oil content and Heavy Metals) from the oily wastewater. Valuable results were obtained under the following optimal conditions: 3g/l kaolinite; 15 mg/l flocculent Zetag 57 and pH of 7.5. At these conditions, turbidity decreased from 180 to 8 NTU with removal percentage of 95.6%, COD decreased from 4800 to 150 mg/l with removal percentage of 96.9 %, BOD decreased from 1800 to 14 mg/l with removal percentage of 99.2% and Oil content decreased from 1800 mg/l to 0.0 with removal percentage of 100 %. Pb decreased from 14.7 to 0.55 mg/l with removal percentage of 96.3%, Cu decreased from 9.4 to 0.5 mg/l with removal percentage of 94.7%, Zn decreased from 11.5 to 1 mg/l with removal percentage of 91.3%, Fe decreased from 6 to 0.5 mg/l with removal percentage of 91.7% and Cd decreased from 0.2 to 0.0 mg/l with removal percentage of 100%.

Keywords

Oily wastewater, Environmental protection, Coagulation flocculation process, kaolinite, Alum.

Introduction

Wastewater effluents from the refineries are considered as the major sources, which pollute the environment. Several efforts were carried out to study the possibility of treatment oily wastewater using new materials, to remove contaminants such as Chemical oxygen demand - COD, Biological Oxygen Demand - BOD, Oil content and Heavy Metals and prevent or minimize its impacts on the environment at low cost. Coagulation flocculation process is physico-chemical method that widely used in the treatment of wastewater [1, 2]. Among several physico-chemical, chemical and physical methods, adsorption process is one of the effective methods widely used in wastewater systems. Adsorption of oil, COD, BOD, Oil content, and heavy metals using natural adsorbents such as peat, bentonite organo-clay, coal, activated carbon and kaolinite have been studied [3-4]. Nevertheless, these systems require a preliminary treatment using physicochemical treatment to enhance the adsorption. Therefore, in order to simplify the adsorption process, it is necessary to develop a more efficient and environmentally safe adsorbent to remove contaminants from oily wastewater [4-5]. Kaolinite clay is an aluminum hydrous silicate ($Al_2O_3.2SiO_2.2H_2O$) used in many industrial applications due to its unique physical and chemical properties [5]. Kaolinite clay, one of the most common and abundant minerals in nature, is considered as a low cost natural clay adsorbent, and it has been widely used in heavy metal removal. The chemical formula of kaolinite can be written in terms of oxides as Al_2O_3 $2Si_2$ $2H_2O$.The chemical analysis indicates that various ions may substitute in the structure, for example Al^{3+} for Si^{4+} in the silica tetrahedral layer, and Mg^{2+} or Fe^{2+} for Al^{3+} in the alumina octahedral layer [6]. The surfaces of kaolin carry a constant structural negative charge due to the isomorphous substitution of Si^{4+} by Al^{3+} in silica layer, which benefits for the adsorption of heavy metals from aqueous solutions. However, the heavy metal adsorption capability of kaolin is low due to its lower cation exchange capacity (15–75 mmol/kg) [7, 8]. Kaolinite is a 1:1 layer mineral as shown in Fig. 1, one of these layers of the mineral consists of octahedral sheet of alumina and a tetrahedral sheet of silica that share a common plane of oxygen atoms and repeating layers of the mineral are hydrogen bonded together. Due to this structure, the silica/oxygen and alumina/hydroxyl sheets are exposed and interact with different components in the soil [9-10].The outer hydroxyl groups are situated along the unshared plane of the alumina hydroxyl sheet, while the inner hydroxyl groups are located along the plane that is shared with and borders on the silica oxide sheet. Because of chemical bonding between the silica and alumina sheets, the movement of the inner hydroxyl plane is restricted [9-11]. The well-packed structure of kaolinite particles is not easily broken down and the kaolinite layers not easily separated. As a result, most sorption activity occurs along the edges and surfaces of the structure. Kaolinite can form a barrier that is not easily degraded. The naturally occurring sediments and deposits containing an abundance of kaolinite interspersed with other minerals are effective in controlling the migration of dissolved species [9-11]. Because the kaolinite is the least reactive clay, its high pH dependency enhances or inhibits the adsorption of metals according to the pH of the environment [9-11].

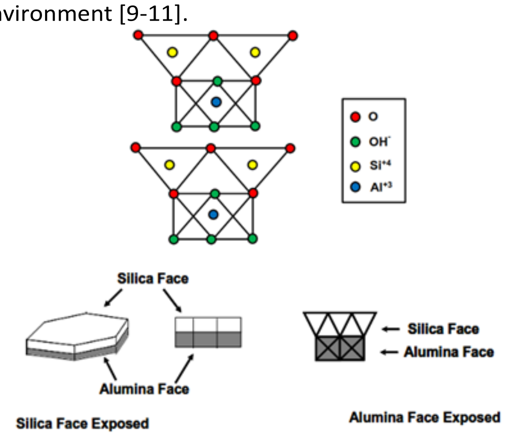

Figure 1 Schematic representation for structure, the organization and ordering of kaolinite particles

The metal adsorption is usually accompanied by the release of hydrogen (H^+) ions from the edge sites of the mineral. Adsorption may also take place on the flat exposed planes of the silica and the alumina sheets [10-11]. The objective of this study was to explore the potential application of using kaolinite clay with flocculent Zetag 57, and alum to treat oily wastewater using coagulation - flocculation process.

Experimental methodology

Materials

Flocculent - Cationic type flocculent Zetag57of moderate molecular weight. Alum- $Al_2(SO_4)_3.nH_2O$, (commercial product) is the most widely used coagulant. pH Modifiers - Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4). Wastewater sample - Table 1 shows the characteristics of oily wastewater sample.

Table 1 Wastewater sample characteristics.

Turbidity NTU	Oil content	COD	BOD	Pb	Cu	Zn	Fe	Cd	pH
	(mg/l)								
180	1800	4800	1800	14.5	9.4	11.5	6	0.2	7.5

Kaolinite clay - The kaolinite clay raw material was collected from El-Teah Plateau, North Sinai-Egypt, then crushed in a lab jaw crusher and ground (dry grinding) in a ball mill to reduce the grain size to – 200µm for the bulk sample (kaolinite particle size -45µm and -200+45µm for silica). Grinding kaolinite causes particles to change their specific surface area (about 15 m^2/g), modifying their pore size distribution and inducing structural changes such as polymorphic transformations, complete or partial amorphization of the material, altered chemical reactivity. When kaolinite is ground, it gradually assumes a more-and-more disordered structure; that is, the background increases as the intensity of the reflections weakens. After 48 h of grinding, only a slight difference in its intensity is observable as compared with the original one. However, after 96 h., the intensity of reflections under XRD is very weak. Nevertheless, after 168 h., only the band and a very broad band are observable [9, 10]. Impurities partially changes into an amorphous like substance, and finally into a perfectly amorphous substance [12-16]. As shown in Fig. 2 grinding process slightly affect alumina quartz phases with amorphization of the others constituents as discussed before and that may be due to short cycle time of grinding process[9-12].

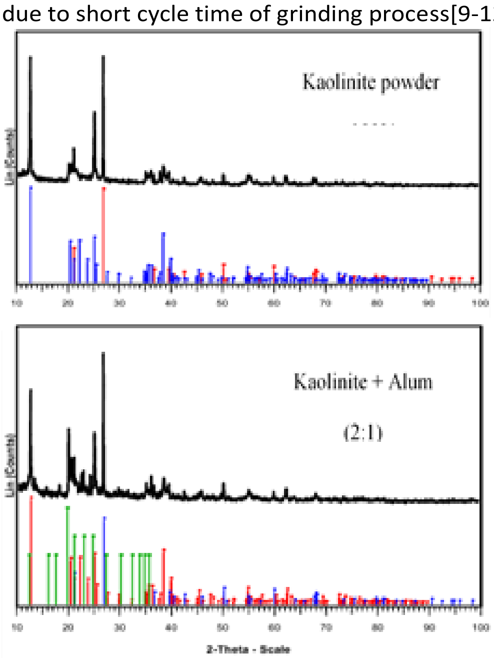

Figure 2 Powder XRD patterns of kaolinite, kaolinite - alum.

Jar Test Apparatus and Procedure of Coagulation Process.

A conventional jar test apparatus was used in the experiments to treat the oily wastewater sample using kaolin, cationic type flocculent of moderate molecular weight Zetag57 and mix of kaolin – alum (2:1). Jar test carried out as a batch test, accommodating a series of six beakers together with six-spindle steel paddles. To evaluate the results, the turbidity of treated water measured in NTU (Nephelometric Turbidity Unit) using turbidity meter and the other parameters (COD, BOD, Oil Contents, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} and Fe^{2+}) were analyzed by El-Nasr Petroleum Company laboratory. Conditioning time for coagulant (kaolin) was 10 min and 30 seconds for flocculants at paddle speed 200 rpm, and then 10 min for flocculation at speed of 45 rpm and settling time – 20 min.

Results and discussion

Effects of flocculent dosage on turbidity, COD, BOD and Oil contents removal.

To carry out this work series of tests were done using Jar test method, at various dosages of Cationic type flocculent Zetag57 of moderate molecular weight and various dosages of kaolinite powder at pH 7.5. The results of turbidity removal were illustrated in **Figure 3** below. **Figure 3** indicates that, as the flocculent dosages increased the turbidity removal increased and also, the increases of kaolinite dosages increased the turbidity removal and best results were achieved at pH 7.5 (NTU: 8), flocculent dosage of 15 mg/l and 3g/l kaolinite, with removal percentage of 96%.

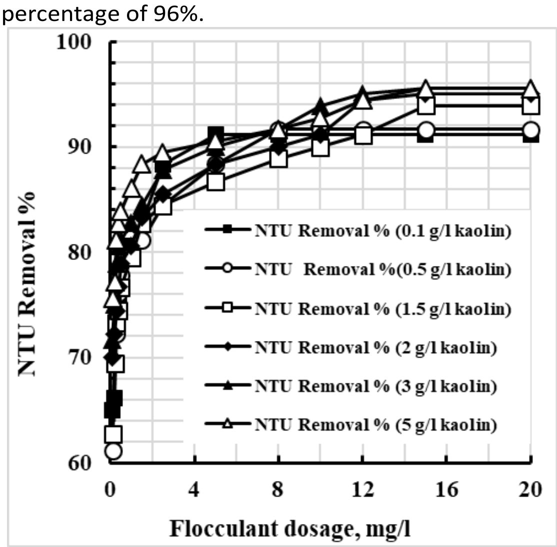

Figure 3 Turbidity removal as a function of flocculent dosages at pH 7.5 and various dosages of kaolinite.

In addition, a series of tests were carried out to treat oily wastewater at pH 7.5 and 15 mg/l flocculent. The results are shown in Fig. 4-a, and 4-b below.

Fig. 4 (a,b), shows that, as the kaolinite dosages increased the turbidity, COD, BOD and oil contents removal increase. The significant resultsthat achieved at pH 7.5 and flocculent dosage 15 mg/l were in the presence of 3g/l kaolinite. Due to that, turbidity decreased from 180 to 8 NTU with removal percentage of 95.6%; COD decreased from 4800 to 150 mg/l with removal percentage of 96.9 %; BOD decreases from 1800 to 14 mg/l with removal percentage of 99.2% and Oil content decreased from 1800 mg/l to 0.0 with removal percentage of 100 %.From the achieved results shown in Fig. 3 and Fig. 4, it can be seen that, kaolinite play animportant role in the process. When kaolinite fine particles added to the wastewater it works as adsorpant for the dissolved species of COD, BOD, etc. and oil content. This that may be due to that kaolinite clay is characterized by excellent adsorption capabilities for cationic pollutants and in some cases anionic components from wastewater. The obtained results were in agreement with the other reported works [4-11]. The settling of the formed flocs takes place when the specific gravity of the formed flocs is enough. Adding flocculent lead to enhance the settling process by any of the following mechanisms: Enmeshment mechanism; sweep mechanism or enter-particle collusion [13].

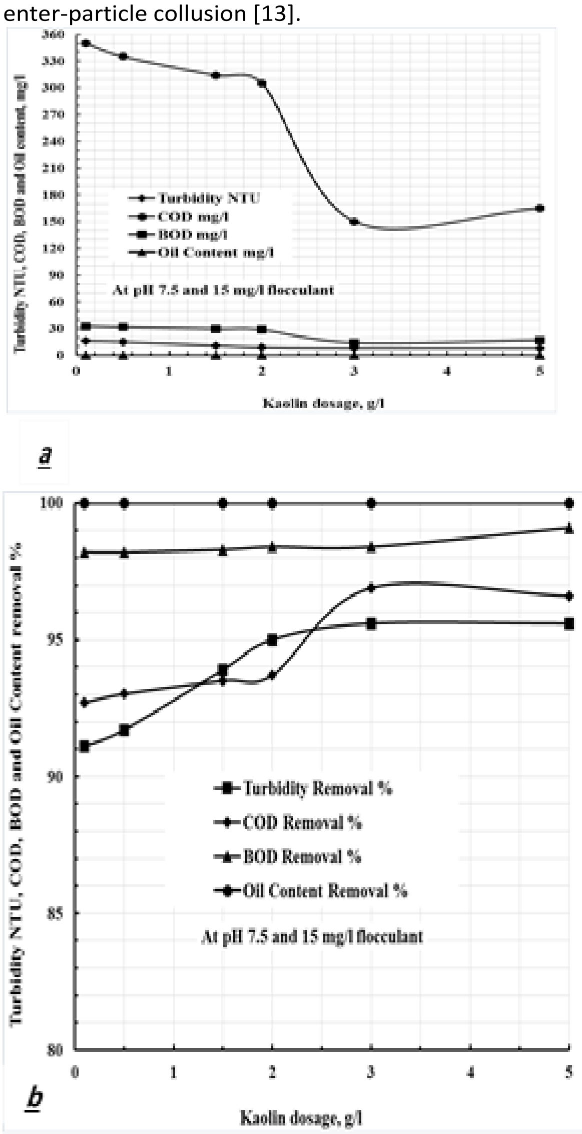

Figure 4 (a, b) Turbidity, COD, BOD and Oil contents as a function of kaolinite dosages: a- Contaminants vs. various kaolinite dosages at pH 7.5 and 15 mg/l of flocculent. b-Contaminants removal percentages vs. kaolinite dosage at pH 7.5 and 15 mg/l of flocculent.

Effects of pH on turbidity, COD, BOD and Oil contents removal.

To fulfil that work, a series of tests were done at varied pH values and constant dose of 3 g/l kaolinite and 15 mg/l flocculent. Fig. 5 shows the results of studying the effect of pH on turbidity, COD, BOD and oil content removal. From the obtained results shown in Fig. 5, it is clear that, the best results obtained at pH 4, where, the turbidity removal of 98.3 %, 98.5 % COD, 99.6 % BOD and 100 % Oil content, while the obtained results at pH 7.5 were, turbidity removal of 95.6 %, 96.9 % COD, 99.2 % BOD and 100 % Oil content. However, the obtained results at pH 9 were, 97.8 %, 93.1 % COD, 98.2 % BOD and 100 % Oil content. The results reveal that, as the pH of the process increases toward basicity the contaminants removal slightly decreases except oil content, which its removal was not affected. It is clear, that clays tend to carry negative charges in water and oil droplets tend to adsorb hydroxide ions (OH^-) from the surrounding water. These results may be due to the characteristics of the kaolinite and its affinity to adsorb oil and dissolved organic gases. The adsorption is usually accompanied by the release of hydrogen (H^+) ions from the edge sites of the kaolinite and decrease the pH of the solution toward iso-electric point of that species [4, 14, 15, 17, 18].

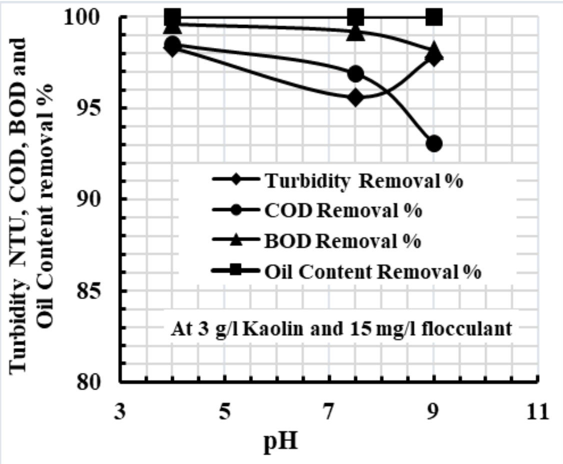

Figure 5 Turbidity, COD, BOD and Oil content removal percentages as a function of pH at 3 g/l kaolinite and 15 mg/l flocculent.

The obtained results indicated that the acceptable pH value from the point of view of industrial application could be pH 7.5.

Effect of kaolinite + alum on turbidity, COD, BOD and Oil contents removal.

To study the effects of mixing kaolinite with the other known coagulant, like alum, a series of tests were done using three values (2, 3, 10 g/l) of modified kaolinite (kaolinite: alum - 2:1) at pH 7.5 and 15 mg/l flocculent. Fig. 6 shows the obtained results.

The results indicates that, the effects of modified kaolinite on the treatment of oily wastewater is similar to using kaolinite. The obtained results from using modified kaolinite were, COD 96.5%, BOD 99.1%, Oil content 100 % removal, except for turbidity removal, it was 98.3% greater than that achieved by using kaolinite (95.6 %) and that may be due to the function of alum and its capacity as coagulant.

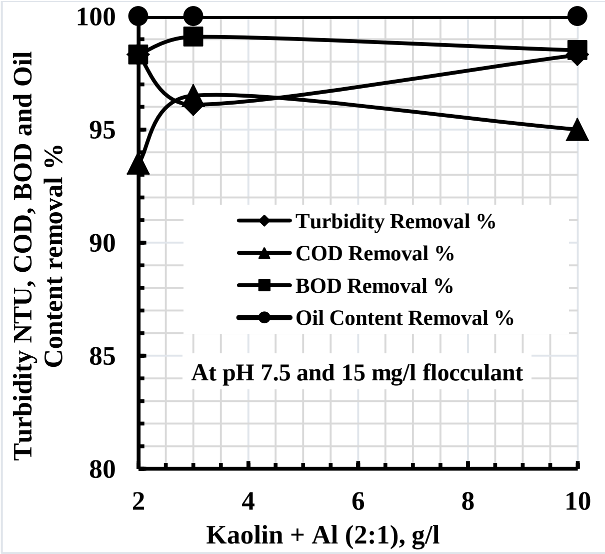

Figure 6 Turbidity, COD, BOD and Oil contents removal percentages as a function of kaolinite + alum (2:1) at pH 7.5 and 15 mg/l flocculent.

Studying the possibility of heavy metals removal from wastewater.

A series of tests carried out at pH 7.5 with 15 mg/l flocculent and 3g/l kaolinite. The optimum results concerns heavy metals removal percentages from wastewater were indicated in Fig. 7. The results of heavy metals reduction from wastewater were; Pb^{2+} decreased from 14.7 to 0.55 mg/l at removal percentage of 96.3%; Cu^{2+}decreased from 9.4 to 0.5 mg/l at removal percentage of 94.7%; Zn^{2+}decreased from 11.5 to 1 mg/l at removal percentage of 91.3%; Fe^{2+}decreased from 6 to 0.5 mg/l at removal percentage of 91.7% and Cd^{2+}decreased from 0.2 to 0.0 mg/l at removal percentage of 100%. The results reveal that, we can achieve significant removal percentages of heavy metals from wastewater by using kaolinite. These results may be due to; metal adsorption usually accompanied by the release of hydrogen (H^+) ions from the edge sites of the mineral. Adsorption may also take place on the flat exposed planes of the silica and the alumina sheets [8-9]. Metal adsorption by kaolinite could affect the mechanical and charge properties of soil. Where Pb^{2+}, Zn^{2+} Fe^{2+} or Cd^{2+} substituted for H^+.

Modification of the chemical structure and physicochemical properties of kaolinite may be subjected to grinding. The forces that hold the kaolinite layers together are hydrogen bonding and attractive van der Waals forces. Metal adsorption on the broken edges of the kaolinite may change the van der Waals attractive forces, but exactly how they are changed is not known. With the adsorption of divalent cations of Pb, Zn, Fe and Cd, the double layer thickness decreases, repulsive forces decrease and flocculation of the kaolinite flocs increase [11, 19].

The very good results obtained may be due to the following mechanism: Kaolinite clay mineral that usually in aqueous solution occurs as colloidal size. These colloids are negatively charged as a consequence of ionic substitutions at several sites within the kaolinite structures and, as a result, exchangeable cations are "adsorbed" on their surface. In our case of oily wastewater (Turbidity, Chemical oxygen demand COD, Biological Oxygen Demand BOD, Oil content and Heavy Metals), colloidal kaolinite particles work as a nuclei adsorbent for the organic compounds, heavy metal and oils from the wastewater. Furthermore, the addition of kaolin provides increased opportunity for particle collisions, resulting in rapid formation of settleable flocs, particularly, with using flocculent.

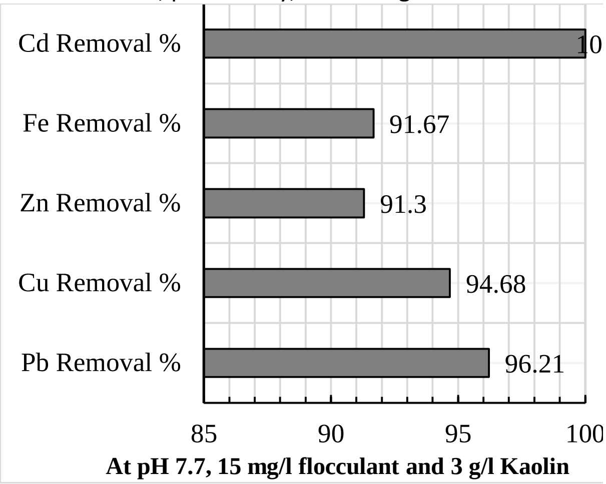

Figure 7 Optimum results of heavy metals removal percentages of wastewater at pH 7.5 with 15 mg/l flocculent and 3g/l kaolinite.

Conclusion

The following conclusions could be obtained from the present study:

- Kaolinite and modified kaolinite have a very good property to remove contaminants - COD, BOD, Oil content and Heavy Metals (Pb^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}) from oily wastewater. The best results were obtained under the following optimal conditions: 3g/l kaolinite, 15 mg/l flocculent Zetag 57 and pH of 7.5.
- The optimal removal percentages were COD – 96.9%; BOD- 99.2%; Turbidity NTU – 95.6%; Oil content- 100%; Pb^{2+}- 96.3%; Cu^{2+}- 94.7%; Zn^{2+}- 91.3%; Fe^{2+}-91.7% and Cd^{2+}- 100%. The obtained results indicated that, using kaolinite as a coagulant not only work effectively and economically, but also, encapsulated toxic matters (the color of flocs seems as no change after sedimentation process) inside the crystals of clay and that makes it environmentally acceptable.

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References

[1] Xiaoping, L.I., Chunjuan, Z., and Jiongtian, L., Adsorption of oil from Wastewater by coal: characteristics and mechanism, Mining Science and Technology, 20 (2010) 0778–0781.

[2] Zhou, Y., Liang, Z., and Wang, Y., Decolorization and COD removal of secondary yeast wastewater effluents by coagulation using aluminum sulfate, Desalination, 225 (2008) 301–311.

[3] AhmadA, A.L., Sumathi, S., Hameed, B.H., Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: Equilibrium and kinetic studies, Water Research, 39 (2005) 2483–2494.

[4] Panpanit, S., and Visvanathan, C., The role of bentonite in Uf flux enhancement mechanisms for oil/water emulsion, J. Membr Sci., 184 (2001) 59–68.

[5] Asmatulu, R., Removal of the Discoloring Contaminants of an East Georgia Kaolin Clay and its Dewatering, Turkish J. Eng. Env. Sci., 26 (2002) 447 – 453.

[6] Miranda-Trevino1, J. C., and Coles. C. A, Kaolinite properties, structure and influence of metal retention on pH, Applied Clay Science, 23 (2003) 133–139.

[7] Schofield R.K., Samson H.R., Discussions of the Faraday Society18 (1954) 135.

[8] Olphen H.V., An Introduction to Clay Colloid Chemistry: For Clay Technologists, Geologists and Soil Scientists. Interscience, New York, 1963.

[9] Lyklema J., Fundamentals of Interface and Colloid Science, Volume II: Solid Liquid Interfaces. Academic Press, 1995.

[10] Huertas, F., Fiore, S., Huertas, F., and Linares, J., Experimental study of the hydrothermal formation of kaolinite, Chemical Geology, 156 (1999) 171–190.

[11] Gonzalez Garcia, F., Ruiz Abrio, M.T., and Gonzalez Rodriguez, M., Effects of Dry Grinding on two kaolins of Different Degrees of Crystallinity, clay minerals, 26 (1991) 549-565.

[12] R.L Frost, E Horvath, E Mako and J Kristof, Modification of low- and high-defect kaolinite surfaces: implications for kaolinite mineral processing, Journal of Colloid and Interface Science, 270(2) (2004) 337-46.

[13] Abdelaal, M., Using a Natural Coagulant to Treat Wastewater, Eighth International Water Technology Conference, (2004) Alexandria, Egypt, 26-28 March.

[14] Madhavi, T.P., and Kumar, R.R., Utilization of Natural Coagulant for Reduction of Turbidity from Wastewater, Int. J. Chem. Tech Res, 5 (3) (2013) 1119-1123.

[15] William A., Jury R.. H., Soil Physics, 6th edition, John Wiley and Sons Inc., Hobken, New Jersey, pp 14 -17 (2004).

[16] Mazlova, E.A., Mescheriakov, S.V., and Abdelaal, A.M., Determination The Optimum Parameters For The Coagulation Flocculation Process Used in Wastewater Treatment Using A Model of Bentonite, 5th International Congress 'Water Ecology and Technology', ECWATECH, (2002). Moscow, Russia, 4-7 June.

[17] Hogg, R., Flocculation and Dewatering of Fine-Particle Suspensions, Coagulation and flocculation-Theory and Applications, 2nd ed., Taylor and Francis, Boca Raton, 2005, p. 805-850.

[18] Moon-SunK.andJaygwanG.C., Removal of Copper (II) Ion by Kaolin in Aqueous Solutions, Environ. Eng. Res. Vol. 7,No. I, pp. 49-57 (2002).
[19] Jorge C. M., and Cynthia A. C., Kaolinite properties, structure and influence of metal retention on pH, Applied Clay Science, 23 (2003) 133–139.