

Treatment of Refinery Industrial Wastewater Using a Hybrid Aluminum Sulfate/Kaolin Coagulant

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Abstract

Conventional coagulation is a difficult process that may have a negative effect on the environment because of the complexity of the harmful substances in industrial wastewater and the nature of the leftover sediment. The goal of the current study is to better understand how to treat turbid and oily industrial wastewater by using combinations of kaolin and aluminum sulphate (alum, the most popular coagulant). Experiments were conducted on oil effluent samples acquired from a refinery plant in Egypt using the standard Jar test at room temperature with a range of pH values and a hybrid coagulant dose. The samples of feed wastewater and treated water were evaluated for turbidity and oil content. The outcomes demonstrate how well an alum/kaolin hybrid coagulant works to reduce the turbidity and oil content of oily wastewater. As a hybrid coagulant, the addition of 19.5 mg/liter alum and 0.7 g/liter kaolin successfully reduced the treated wastewater's turbidity from 230 to 1 NTU with a turbidity removal efficiency of 99.57% . the treated water sample oil content was reduced from 820 to 2 ppm with a removal efficiency of 99.77%.

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Introduction

Water resources are under a lot of stress as a result of population growth and the expansion of industrial activity which makes the industrial sector very concerned about water treatment and reuse. To lessen the impact on the environment, new wastewater treatment technologies urgently need to be developed. Refineries' wastewater is regarded as a significant cause of environmental contamination. The conversion and concentration of natural compounds, as well as their artificial synthesis, can be used to identify the origins of pollution and toxins on earth [1, 4]. The peculiar characteristic of oil, which causes it to create a thin layer on the rapid sections of water, makes oil-related water pollution a very distinct concern. Every year, there are hundreds of little and large oil spills that significantly harm the environment. Minerals, suspended particles, and dissoluble contaminants, as well as petroleum, are all present in the oily effluent that the refineries create [1–5]. Due to the lack of oxygen in the water, oxidative reactions are the most hazardous of these released effluents[1–7].

Additionally, it was discovered that treating industrial wastewater with coagulation/flocculation at different types and doses reduces the hazardous elements in these fluids [8–11]. It believes to be expensively effective when the waste produced by

wastewater treatment units has large concentrations of dangerous substances like phenols, oils, heavy metals, etc. To remove contaminants from wastewater, many different compounds are used. Costly low, kaolinitic clay improved by adding a number of polymers and chemicals is used as a base for treatment products [1–2]. Clay minerals are very efficient in removing some cationic elements from wastewater and can treat oil, sulphate, phosphate, and metals. A significant affinity exists between heavy metals in solution and clay minerals. In addition, clay minerals are frequently utilized to remediate wastewater that is highly colored and turbid. A benefit of clays' ability to absorb organic mixtures is added to their weighing function. Additionally, adding clay minerals to low-level turbid water enhances particle collisions, hastening the formation of settleable floc. The resulting flocs are a complex mixture of suspended materials and condensed contaminants that are electrostatically attracted to one another and held together by Van der Waals forces. The contaminants are made impermeable and non-leachable by being encapsulated at the nanoscale and surrounded by a wall of clay particles [1, 2]. These days, reducing the cost of the chemicals used in wastewater treatment and enhancing the characteristics of the sludge to enable safe utilization are two of the ecological engineer's key goals. The use of kaolin and alum as a hybrid coagulant to treat oily

wastewater was investigated as a possible solution to this problem. The goal of this research is to establish the ideal alum/kaolin hybrid coagulant dose and solution pH for the effective treatment of turbid, oily water samples from industrial refineries.

Materials and Methods

Materials

The kaolin utilized in this study was obtained from the Al-Teah plateau in North Sinai, Egypt. We previously reported on sample homogenization, size reduction, and characterization [7]. According to German regulations and as demonstrated in earlier journals [8–9], the ball mill ground material was dry sieved using a Fritsch shaker. The size fraction with a -250 μm consisting of 92% Kaolinite was retained for treatment experiments. Aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), is obtained from commercial sources. We used diluted sodium hydroxide and sulfuric acid solutions to modify pH values. Industrial effluent samples from an Egyptian oil refinery plant were used in this investigation.

Method

The Jar test standard procedure was used to conduct wastewater treatment tests. One litre of the sample was used for each run. The solution's pH was adjusted using NaOH and H_2SO_4 , and then it was measured with a pH meter. A precise quantity of the hybrid coagulant is then added to the solution, which is stirred for three minutes at 200 rpm (conditioning stage). The solution is then stirred for 10 minutes at a speed of 45 rpm to allow for the coagulation process, and for another 15 minutes to allow for the solids to settle [4, 5]. The turbidity and oil content of the solution are then assessed. First, experiments were carried out utilizing alum in various concentrations ranging from 5 to 50 mg/Litter. Kaolin additions between 0.5 and 2.5 g/Litter were also examined. Hybrid coagulant experiments were carried out to achieve the optimum outcomes for the kaolin runs by increasing the aluminium sulphate inputs. Additionally, experiments were carried out pH values of 6, 6.7, 7.5, and 8.5.

Results

Characteristics of alum treatment

The samples of oily wastewater used in our investigation have a high level of turbidity (230 NTU) and an oil concentration of 820 ppm. The pH was found to be 7.8. The pH of the solution plays a crucial role in the dosage of the coagulant and the alum used in the coagulation process [11–14]. The results of a series of treatment studies employing alum at various pH levels and dosages are shown in Figure 1 along with the related turbidity values. The coagulation process was improved, and the turbidity of the water was decreased, when the dosage of alum was increased. At 19.5 mg/Litter alum, a considerable reduction in turbidity was observed, and a subsequent increase in alum dosage led to a marginally smaller

reduction in water turbidity. We discovered that, at the same alum dosage, turbidity varied according to the pH of the solution. At a pH of 7.5, the best outcomes were obtained. Table 1 demonstrates another relationship between pH and the effectiveness of oil removal during the coagulation phase while employing 19.5 mg/litter alum. At pH 7.5, the best results with the least amount of oil in the treated water could be obtained. These results could be attributable to the low positive charge caused by alum's limited solubility, and its highly polymerized forms could effectively destabilize oil droplets by charge neutralization and by acting as a coagulation bridge at pH values lower than 7.5. Due to alum's highly solubility, its high positive-charged polynuclear complexes produce micro flocs with a greater positive charge, which causes the colloids to re-stabilize and lowers the effectiveness of removing turbidity. As soon as the pH level exceeds 7.5, alum hydrolyses into negatively charged precipitates. As the pH level rises, this re-stabilization of the colloids reduces the efficiency of alum in removing turbidity. The results obtained are in agreement with other reported works and previously published articles [12–16].

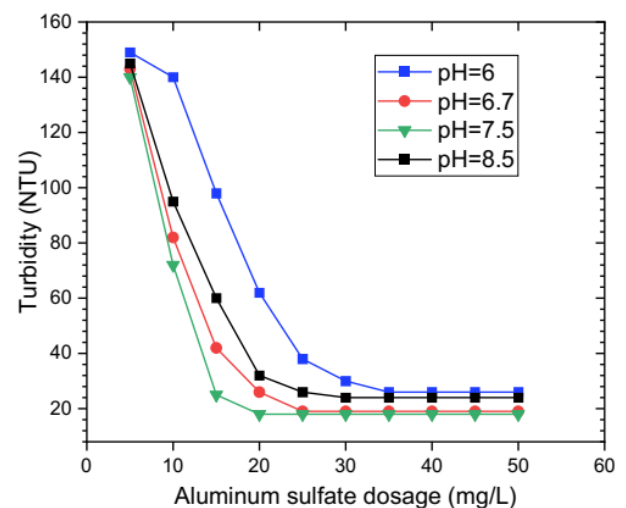


Figure 1 Oily wastewater turbidity as a function of alum dosage at various pH values.

Table 1 Oil content of treated oily water samples at different treatment conditions as a function of solution pH

Solution pH	Oil content (ppm) for different treatments			Optimum results of Oil removal %
	19.5 mg/Litter Alum	0.7 g/Litter kaolin	19.5 mg/Litter Alum + 0.7 g/Litter kaolin	
6	36	14	7.5	99.09
6.7	20	11	3	99.63
7.5	15	13	2	99.77
8.5	24	26	7	99.15

Characteristics of the kaolin treatment

The results of a series of treatment tests with varying kaolin dosage at varying pH levels are shown in Figure 2. The data obtained demonstrate that the pH of the solution and the amount of kaolin both have

an impact on the effectiveness of the coagulation process. When the solution pH is 6.7, the best results can be obtained by treating oily wastewater with 0.7 g/Liter of kaolin.

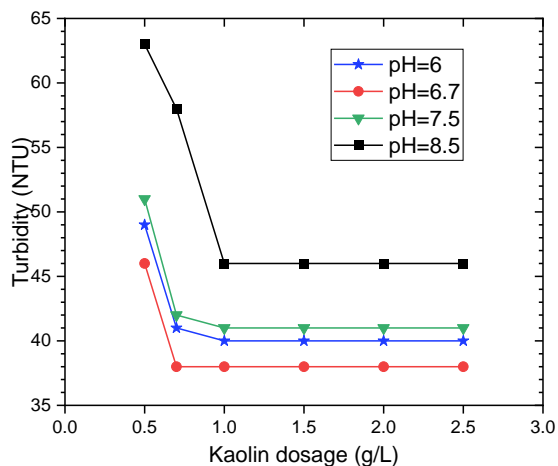


Figure 2 Oily wastewater turbidity as a function of kaolin dosage at various pH values.

The obtained results demonstrate that the pH of the solution and the amount of kaolin both have an impact on the effectiveness of the coagulation process. When the solution pH is 6.7, the best results can be obtained by treating oily wastewater with kaolin at a concentration of 0.7 g/Liter. Regardless of the quantity of kaolin utilized, the water turbidity was still higher than it was in the alum scenario. Additionally, Table 1 demonstrates that the pH level of the treated wastewater is a major determinant of the effectiveness of oil removal. A satisfactory outcome could be obtained at a pH range between 6 and 7.5. As the pH value rises, there is an increase in the amount of leftover oil in the treated water. Comparing kaolin to alum, it is more effective at removing oil. These outcomes might be a result of the properties of kaolin and its propensity to absorb dissolved gases and oil. Excellent adsorption properties for cationic contaminants and, in some situations, anionic components from wastewater are characteristics of kaolinitic clay [1-8].

Characteristics of the hybrid (kaolin/aluminium sulphate) coagulant technique

As a function of the dose of aluminium sulphates at 0.7 g/Liter kaolin additions at various pH values, the treated wastewater's turbidity is shown in Figure 3 at various pH levels. The turbidity of the treated wastewater has been significantly reduced as a result of the hybrid alum/kaolin application. When 19.5 mg/liter of alum and 0.7 g/liter of kaolin are added to water with a pH of 7.5, a very low turbidity of 1 NTU can be attained. Additionally, compared to the application of either alum or kaolin alone, the pH-related changes in the solution had less impact. At pH 7.5 and 19.5 mg/Liter of alum, the lowest turbidity (NTU: 1) was achieved. In addition, as shown in Table 1, the oil content in the treated water was reduced to an extremely low level of 3 ppm.

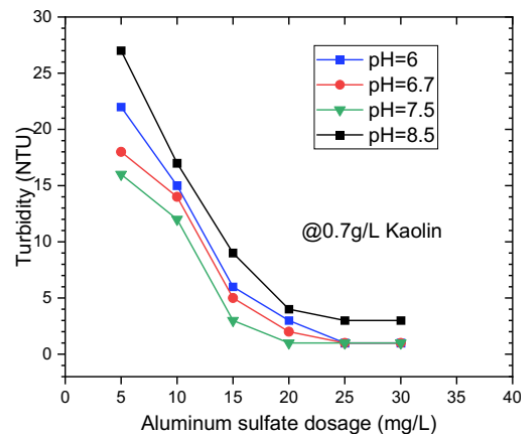


Figure 3 Oily wastewater turbidity as a function of alum dosage at 0.7 g/L kaolin and various pH values.

The following steps can be used to explain the increased coagulation results: Clay substance kaolin often appears as a colloidal size. These crystals are negatively charged due to the ionic substitutions at various locations within their structures, and as a result, exchangeable cations are "adsorbed" on their surface. Organic mixes, heavy metals, oils, and other substances that cause turbidity and colour in wastewater are known as "oily wastewater concerns," and kaolin particles act as nuclei to adsorb these substances from wastewater. Additionally, the presence of kaolin increases the likelihood of particle collisions, which has the effect of hastening the production of settleable floc. By gathering the flocs particles produced by the coagulation of kaolin in a net bridge from one surface to the next and binding the individual particles into big agglomerates, the addition of alum coagulant to the process would boost the settling rate [12–20]. The final mass is a complicated mixture of encapsulated contaminants and clay particles held together by electrostatic and van der Waals interactions. Because the contaminants are enclosed and protected by a wall of kaolin particles, they are resistant to external leaching.

Conclusions

According to the results, oily wastewater can be efficiently treated by coagulation applying alum/kaolin hybrid coagulant because of the synergistic interaction between alum and kaolin. The treated wastewater's turbidity was successfully reduced from 230 to 1 NTU with the addition of 19.5 mg/liter of alum and 0.7 g/liter of kaolin, and the oil content was reduced from 820 to 3 ppm. When hybrid alum/kaolin is utilized, the impact of pH on both kaolin and alum treatment is considerably reduced. The hybrid coagulant based on clay minerals has the potential to be less expensive and less harmful to the environment because the toxic material will be encapsulated inside the clay flocs.

References

- [1]. Yaser Rasouli, Mohsen Abbasi, Seyed Abdollatif Racemiform, Investigation of the in-line coagulation-MF hybrid process for oily wastewater treatment by using

- novel ceramic membranes, *Journal of Cleaner Production*. Vol. 161 (2017) 545-559.
- [2]. Tao Yang, Bo Qiao, Guo-Chao Li, Qi-Yong Yang, Improving Performance of Dynamic Membrane Assisted by Electrocoagulation for Treatment of Oily Wastewater: Effect of Electrolytic Conditions, *Desalination*. Vol. 363 (2015) 134-143.
- [3]. Bingnan Yuan, Ling Li, Vignesh Murugadoss, Sravanthi Vupputuri, Jinwu Wang, Nasim Alikhani and Zhanhu Guo, Nanocellulose-based Composite Materials for Wastewater Treatment and Waste-oil Remediation, *ES Food Agrofor*. 1 (2020) 41-52.
- [4]. E.A. Mazlova, S.V. Mescheriakov, A.M. Abdelaal, Determination of 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, Moscow, Russia, 4-7 June 2002.
- [5]. A. M. Abdelaal, Using a Natural Coagulant to Treat Wastewater, Eighth International Water Technology Conference, Alexandria, Egypt, 26-28 March 2004.
- [6]. L. N. Potseeba, L. V. Gandorena, and P. S. Shtondena, Advanced Technology on Oily wastewater treatment, *Chemistry and Technology of Fuel and Oil*. 6 (1997).
- [7]. A.M. Abdelaal, COD, BOD, Oil Content and Heavy Metals Removal from Wastewater Effluents by Coagulation-Flocculation Process. *Journal of Petroleum and Mining Engineering*, 19(1) (2017) 57-62.
- [8]. A. F. Muhammad, M. S. El-Salmawy, A. M. Abdelaal, Potential for upgrading El-Nakheil oil shale by froth flotation, *Oil Shale*. 30 (1) (2013) 48-59.
- [9]. A. F. Muhammad, M. S. El-Salmawy, A. M. Abdelaal, S. Sameah, EL-Nakheil oil shale: material characterization and effect of acid leaching, *Oil Shale*. 28 (4) (2011) 528-547.
- [10]. J. C. Vaughn, G. J. Turre, and B. L. Grimes, Chemical and Chemical Handling. In: *Water Quality and Treatment, a Handbook of Public Water Supplies*, Prepared by the American Water Works Association, Inc., Third Edition, McGraw-Hill Book Company. (1971).
- [11]. S.V. Bodrezov, V.E. Gamov, and K.M. Morozova, Wastewater Sludge Treatment, *Water Supply, and Sanitary Technology*. 3 (1993) 12-14.
- [12]. U.A. Feofanov, L.F. Smirnova, New Forms of Flocculants, *Water Supply and Sanitary Technology*. 7 (1995).
- [13]. D. R. Brink, S. Choi, M. Al-Ani, and D. W. Hendricks, Bench-Scale Evaluation of Coagulants for Low Turbidity Waters, *Journal AWWA*. April (1988).
- [14]. Muthia Elma, Amalia Enggar Pratiwi, Aulia Rahma, Erdina Lulu Atika Rampun, Mahmud Mahmud, Chairul Abdi, Raissa Rosadi, Dede Heri Yuli Yanto and Muhammad Roil Bilad, Combination of Coagulation, Adsorption, and Ultrafiltration Processes for Organic Matter Removal from Peat Water, *Sustainability*. 14 (2022) 370.
- [15]. G. Peter and S. Fisher, Using poly aluminium coagulants in water treatment, PTY Ltd will, Australia. (2001).
- [16]. Nomthandazo Precious Sibiya, Sudesh Rathilal and Emmanuel Kweiner Tetteh, Coagulation Treatment of Wastewater: Kinetics and Natural Coagulant Evaluation, *Molecules*. 26 (2021) 698.
- [17]. M. C. Jesse, and A. H. Sidney, Coagulation and Flocculation; *Water Quality and Treatment, Handbook of Public water supplies*, American Water Works Association, Inc., 3rd eds. McGraw Hill Book. (1971).
- [18]. C. D. Cancela, E. R. Taboada, and F. S. Rasero, Adsorption of cyanazine on peat and montmorillonite clay surfaces, *Soil Science*. 150 (1990).
- [19]. D. A. Laird, P. Y. Yeen, W. C. Koskinen, T. R. Steinheimer and R. H. Dowdy, Sorption of atrazine on soil clay components, *Environ. Sci. Technol.* 28 (1994).
- [20]. M. Jeffery and P. E. Harris, Leachate Treatment Options for Sanitary Landfills, *Intercontinental Landfill Research Symposium*, Lulea University of Technology, Lulea, Sweden. December 11-13 (2000).