Chemical Treatment of Oily Wastewater

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Abstract

The general strategy of this study was based on evaluation of the possibility of applying coagulation by chemical coagulant for removal of residual oils from wastewater, as a preliminary treatment prior to biological oxidation. Determination of the optimum conditions for getting the best results for oil removal by studying the different parameters that affect the processes. These parameters are pH, chemical reagent dose and Initial concentration of oil in wastewater. The optimum dose needed for efficient coagulation is about 30-40 mg Γ^1 for alum, ferric chloride and ferrous sulphate. The maximum efficiency obtained between pH 5 and 7 and this matches with the literature. The higher removal efficiency is about of 81% for Ferric chloride in COD removal and about 91.6% of turbidity removal.

Keywords: Coagulation-flocculation process, Oily wastewaters

Introduction

Oily wastewaters are generated in many industrial processes, such as petroleum refining, petrochemical, food, leather and metal finishing. Fats, oils and greases (FOG's) present in these wastewaters have to be removed before the water can be reused in a closed-loop process or discharged into the sewer system or to surface waters. These oily waters are mainly in the form of oil-in-water (O/W) emulsions that pose a great problem in facilities attempting to stay in compliance with discharge limits [1]. Oily wastewater is an abundant and extensive pollution source generated during oil processing. The oil droplets in effluents contain spilled oil, dispersed oil, emulsified oil, dissolved oil, and oil-solid contaminant [2]. The difficulty of separating oil from water depends on the nature of the oil in the water. Spilled oil can be separated from oily wastewater by using gravitational separation technology while dissolved oil may be removed by using biological treatment. However, dispersed oil and emulsified oil occurring in colloidal suspension are very difficult to separate because of the small mean droplet size and chemical stabilization [3].

The main technologies of treating oily wastewater include physical treatment, physical chemistry, chemical demulsifying, biochemistry and electrochemistry [4,5]. The purpose of this work is to study the chemical treatment techniques for removing oil from wastewater. These techniques include chemical coagulation.

A coagulation process has two separate and distinct components or steps. First, particles in the water must be treated chemically to make them "sticky" or unstable. This involves the addition of one or more chemicals in rapid mix tanks. Second, these destabilized particles must be brought into contact with each other so that aggregation can occur. This is done by gentle stirring of the water in flocculation tanks [6].

Coagulation/flocculation is a commonly used process in water and wastewater treatment in which compounds such as ferric chloride and/or polymer are added to wastewater in order to destabilize the colloidal materials and cause the small particles to agglomerate into larger settleable flocs.

Several studies have reported the examination of this process for the treatment of industrial wastewater, especially with respect to performance optimization of coagulant/flocculant, determination of experimental conditions, assess-ment of pH and investigation of flocculant addition [7,8]. Although several studies have been conducted into the treatment of municipal wastewater through granular activated carbons during which COD and some volatile organic compounds, such as chloroform benzene and carbon tetrachloride were adsorbed to the carbon surface [9,10]. The use of adsorbents [11,12], Fenton's reagent [13], wet oxidation [14], coagulation-electrooxidation [15], advanced oxidation with biological oxidation [16] and coagulation/flocculation process have been found to be cost effective, easy to operate and energy saving treatment alternatives [17,18]. Coagulant dosages vary in a wide range aiming at maximum removal efficiency of pollutants using minimum doses at optimum pH [19,20].

The efficiencies of the chemical and the electrochemical break-up of oil-in-water (O/W) emulsions with hydrolyzing aluminum salts were compared. It has been obtained that the efficiency of the processes does not depend directly on the dosing technology, but on the total concentration of aluminum and pH [21].

Materials and methods

Materials

The wastewater used in this study is collected from gas station in El- Mansoura city, Egypt and characterized by measuring the turbidity and COD.

The chemical analysis of the wastewater showed that the concentrations of turbidity, COD, TDS and pH values were 42 NTU, 1279 mg I^{-1} , 1690 mg I^{-1} and 7.7, respectively. The coagulants selected for the experiments were: Al₂(SO₄)₃.18H₂O, Fe (SO₄).7H₂O and Fe₂Cl₃.6H₂O that prepared by dissolving a known quantity in distilled water to obtain a stock solution with concentration of $1 \text{ gm } 1^{-1}$. *Equipments*

Equipments used in this study are mechanical stirrer with various shaking speed, digital PHmeter (Cole-parmer chemadet 5986-50), COD instrument (VELP Scientifica, Eco, Itali), Nephelometric turbidity units (NTU), HACH model 2100A turbid meter and total dissolved solid (TDS), HANNA model Hi 8734.

Methods

All reactions were performed in batch model, the experiments were conducted at room temperature $(25\pm2^{\circ}C)$. The processes were carried out in 2.0 litter glass beakers. In each beaker the wastewater sample was mixed with chemicals (Coagulant or reagent) depending on the following steps:

- A series of six glass beakers containing 1 liter of wastewater in different proportions.
- All reaction mixture was subjected to rapid stirring (200r.p.m) by using mechanical stirrer for a period of 1 minute.
- The stirrer speed was reduced to 30 r.p.m and the mixture was kept stirred for additional period of 30 minutes.
- Stirring was stopped and the solution was left to stand for about 20 minutes to ensure complete settling of solid materials.
- The remaining oil concentration was determined as COD value.

Results and Discussion

Wastewater calibration curves

The wastewater used in the experiments is differed by the concentration which influences the COD and the turbidity. Fig. 1 indicates the relationship between the pollutants concentration and the Chemical oxygen demand (COD) with accuracy of the data plotted is 99%. Fig. 2 also, indicates the same relation but for the turbidity of pollutants with accuracy of 97.6%.

Determination of coagulants optimum dose

Evaluation and optimization of the coagulation/rapid mixing step of the Wastewater treatment process includes a variety of aspects. Optimal coagulant dosages are critical to proper flocs formation and settling performance.

Maintaining the proper control of these chemicals can mean the difference between an optimized surface treatment plant and a poorly run surface treatment plant.



Fig. 1 Calibration curve of COD of the pollutant concentration



Fig. 2 Calibration curve of Turbidity of the pollutant concentration

Inadequate mixing of chemicals or their

addition at inappropriate points in the treatment plant can also limit performance. The results of the tests were showing the effect of coagulant dosage on removal efficiency of COD and turbidity. Fig. 3, 4, and 5 indicate that the optimum dose needed for efficient coagulation is about 30-40 mg 1^{-1} for each at constant initial concentration pollutants of 500 ml 1^{-1} , and pH about 8.



Fig. 3 Effect of FeCl₃.6H₂O dose on pollutant removal efficiency



Fig. 4 Effect of $FeSO_4.7H_2O$ dose on pollutant removal efficiency



Fig. 5 Effect of Alum dose on pollutant removal efficiency

Effect of Initial pollutants concentration on wastewater treatment

The effects of variation of pollutants concentration on wastewater treatment were displayed in Fig. 6 and Fig. 7. Results indicate that the removal efficiency is about of 81% for Ferric chloride in COD removal and about 91.6% of turbidity removal of the high concentrated pollutants.



Fig. 6 Effect of Initial pollutants COD on removal efficiency



Fig. 7 Effect of Initial pollutants Turbidity on removal efficiency

The ferric and ferrous "hydroxides" form a powerfully co-precipitating "solubility limiting phase" that will trap and drag down numerous regulated material and ions but the powerful of chloride is more than alum and iron sulphate because of high density charge of iron chloride (tri valences).

Effect of pH on wastewater treatment

The levels of pH in water are a way of measuring the amounts of positively charged particles (cations) and negatively charged particles (anions) in the water.

As a result, this factors influence the amount of coagulants which must be used to remove the turbidity in the water. The pH range of the water may be the single most important factor in proper coagulation. The vast majority of coagulation problems are related to improper pH levels. The optimum pH range varies depending on the coagulants used. These lower pH values mean that there are more positively charged particles loose in the water to react with the negatively charged colloids.

In water, the cation and the anion come apart and can interact with other charged particles in the water. The results obtained (Fig. 8 and Fig. 9) indicate that the maximum efficiency obtained between pH 5 and 7 and this matches with the literature.



Fig. 8 Effect of pH on COD removal efficiency



Fig. 9 Effect of pH on Turbidity removal efficiency

Conclusions

Based on the result, the following conclusions were obtained:

- 1. The optimum dose needed for efficient coagulation is about 30-40 mg l⁻¹ for alum, ferric chloride and ferrous sulphate.
- 2. The higher removal efficiency is about of 81% for Ferric chloride in COD removal
- 3. About 91.6% of turbidity removal of the high concentrated pollutants ware obtained by using Ferric chloride

- 4. The maximum efficiency obtained between pH 5 and 7 and this matches with the literature.
- 5. We can recommended ferric chloride as an oily wastewater treatment as a preliminary treatment prior to biological oxidation.

Acknowledgements

The authors Thank Dr. M.M. El-Halwany, Mansoura University for his assistance in the completion of this research.

References

- [1] C. Jose, G. Gemma, J. M. Benito, Water Purification and Management (2011) 1
- [2] J.A. Brierley, C.L. Brierley. Hydrometallurgy 59 (2001) 233
- [3] G.H. Chen, G.H. He, 31 (2003) 83
- [4] R.J. Hunter, Academic Press, New York (1981)
- [5] L. Zhu, Y.Y. Pan, Shanghai Environmental Sciences 16 (1997) 38
- [6] Metcalf, Eddy, Inc, fourth edition (New York: McGraw-Hill, 1999)
- [7] A.A. Tatsi, A.I. Zouboulis, K.A. Matis, P. Samara, Chemosph 53 (2003) 737
- [8] H.I. Abdel-Shafy, S.E. Abdel-Basir, Environ. Manage. Health 2 (1991) 19
- [9] R.R. Bansode, J.N. Losso, W.E. Marshall, R.M. Rao, R.J. Portier, Bioresour. Technol. 94 (2004) 129
- [10] M. Ahmedna, W.E. Marshall, R.M. Rao, Bioresour. Technol. 71 (2000) 113
- [11] A. Pala, E. Tokat, Water Res. 36 (2000) 2920
- [12] C. Guohua, Sep. Purif. Technol. 38 (2004) 11
- [13] N.S. Martinez, J.F. Fernandez, X.F. Segura, A.S. Ferrer, J. Hazard. Mater. B101 (2003) 315.
- [14] C.M. Hung, J.C. Lou, C.H. Lin, Chemosph 52 (2003) 989
- [15] Y. Xiong, P. Strunk, H. Xia, X. Zhu, H. Karlsson, Water Res, 35 (2000) 4226
- [16] P.R. Gogate, A.B. Pandit, Environ. Res. 8 (2004) 501
- [17] O.S. Amuda, I.A. Amoo, O.O. Ajayi, J. Hazard. Mater. B129 (2006) 69
- [18] D. Bromley, M. Gamal El-Din, D.W. Smith, Penang, Malaysia (2002) 215
- [19] Y. Watanabe, Y. Kanemoto, K. Takeda, H. Ohno, Water Sci. Technol. 27 (1993) 201
- [20] J. Szpak, D. Woods, K. Bouchard, Water Qual. Res. J. Can. 31 (1996) 51
- [21] P. Canizares, F. Martinez, C. Jimenez, C. Saez, M.A. Rodrigok, J. Hazard. Mater 151 (2008) 44

الملخص العربى

المعالجة الكيميائية لمياه الصرف التى تحتوى على زيوت

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تهدف هذه الدراسة إلى تطبيق المعالجة الكيميائية لسوائل الصرف التي تحتوى على الزيوت من خلال تطبيق عملية الترويب والترسيب وذلك باستخدام بعض المروبات مثل (كبريتات الحديدوز وكلوريد الحديديك وكبريتات الالمونيوم) وتحديد أنسب الظروف لإتمام عملية الترويب والترسيب ومن العوامل التي تم دراستها درجة حامضية المحلول وجرعة المروب والتركيز الابتدائي للزيوت وقد أوضحت النتائج أن أفضل الظروف لإزالة الزيوت تكون عند رقم الأس الهيدروجيني 5 و7 وأن الجرعة المتلى من المروبات المستخدمه لإعطاء كفاءة اعلى للتخلص من الزيوت تكون حوالي 00- 40 مجم/ لتر. كما ان عملية الترويب والترسيب اعطت كفاءة اعلى للتخلص من المواد العضوية عن طريق قياس الاكسجين الكيمياني الممتص (COD) حيث وصلت نسبة الإرالة إلى 81% وكذلك اعلى كفاءة للتخلص من العوار العروبية على كفاءة للتخلص من المواد العضوية على حليقة للتخلص من العكارة الكيمياني الممتص (COD) حيث وصلت نسبة الإزالة إلى 81% وكثر وكذلك اعلى 2016% عند المياه التي تحتوى على تركيزات عالية من الملوثات حيث وصلت نسبة الإزالة إلى 91% عند المياد التي تحتوى على تركيزات عالية من الموثات حيث وصلت نسبة الإزالة إلى 91% علي كفاءة المواد العضوية عن طريق قياس المحارة المياد التي تحتوى على التخلص من المواد العضوية عن طريق قياس المحارة الكيمياني الممتص (COD) حيث وصلت نسبة الإزالة إلى 81% وصلت نسبة الإزالة إلى 91% على كفاءة للتخلص من العكارة المواد التي تحتوى على تركيزات عالية من الموثات حيث وصلت نسبة الإزالية إلى 91% مريوبية الموليد الموادية إلى 91.6%