JEE Journal of Ecological Engineering

Journal of Ecological Engineering 2022, 23(3), 68–73
https://doi.org/10.12911/22998993/145468
ISSN 2299–8993, License CC-BY 4.0

Received: 2021.12.08
Accepted: 2022.01.13
Published: 2022.02.01

$FE_2(SO_4)_3$ and Bentonite Use to Reduce Cod Indicators in Wastewater Containing Detergents

Issayeva Akmaral[1], Abubakirova Azhar[2], Syzdykova Marzhan[2*], Arystanova Saltanat[2], Anlamasova Gulnara[2], Zhumakhanova Roza[2], Leska Boguslawa[3]

[1] Shymkent University, Zhybek Zholy St 131, Shymkent 160031, Kazachstan
[2] South Kazakhstan University named after M. Auezov, Tauke Khan Avenue, 5, Shymkent, Kazakhstan
[3] A. Mickiewicz Poznań State University, Wieniawskiego 1, 61-712 Poznań, Poland
* Corresponding author's e-mail: maksat.marzhan@mail.ru

ABSTRACT
Wastewater pollution with detergents is one of the environmental problems associated with the rational use of water resources. The existing methods of physicochemical wastewater treatment, despite their efficiency, are open to secondary environmental pollution. Biological coagulation/flocculation methods are widely used with the plant waste. The aim of this research was the use of ferric iron obtained by means of the bacterial-chemical method and bentonite to reduce the chemical oxygen demand in the wastewater containing detergents. It was identified that the use of $Fe_2(SO_4)_3$ obtained using the bacterial-chemical method with thionic bacteria *Acidithiobacillus ferrooxidans BIT 1* and bentonite as a clay material is promising. At the same time, it was found that the highest reduction degree in the chemical oxygen demand – 88.1 ± 7.9% in wastewater was noted in the variation where the bacterial-chemical ferric iron in the amount of 1.75 g/L was used in combination with bentonite in the amount of 600 mg/L.

Keywords: wastewater, chemical oxygen demand, ferric iron, bentonite.

INTRODUCTION

The formation of significant wastewater quantities in the Republic of Kazakhstan, contaminated with various detergents, and increased requirements for the quality of treated wastewater determine the use of various methods of their treatment. Synthetic surfactants are a large group of compounds that differ in their structure and belong to different classes. These substances are able to adsorb at the interface and, as a result, lower the surface energy (surface tension). Depending on the properties of surfactants when dissolved in water, they are divided into anionic substances (the active part is anion), cationic (the active part is cation), ampholytic and nonionic, which are not ionized at all [Bhairi, 2007].

The main source of synthetic surfactants involves cleaning agents (detergents) – substances that enhance the washing effect of water. The first detergents were the soaps derived from naturally occurring substances. However now, detergents are usually understood as synthetic substances that are similar in detergent action to soap.

Currently, there are various methods for treating wastewater containing detergents. For instance, one can mention water treatment by adsorption on coals, where the adsorbents used for water treatment must meet a number of requirements: have a large sorption capacity; have high mechanical strength; have a low cost and be easy to regenerate. A large adsorption surface is characteristic of the substances and materials that have a highly developed porous structure or are in a finely dispersed state [Farizoglu, 2011]. In the process of treating wastewater from detergents, the following adsorbents can be used: activated carbons, ion-exchange resins, inorganic precipitates, various types of mineral coals, and polymer sorbents [Slavov, 2017]. A special place is occupied by clay materials, which are used to treat wastewater from heavy metals, oil products, etc.

Wastewater treatment by coagulation, where the effectiveness of such coagulants is considered, is carried out with aluminum sulfate or iron [Suman, 2017; Gu, 2013]. The research was performed to assess the effectiveness of chemical coagulation followed by an improved oxidation process for pretreatment of dairy industry wastewater. Three samples of wastewater were taken and analyzed, which are characterized by some physicochemical parameters to check their potential for contamination. It was found that the COD removal efficiency after the application of $FeCl_3$/lime was 94.2%, while the removal efficiency of $FeCl_3$/polyacrylamide was 70%. The optimal conditions for Fenton's reagent were 30 mL/L H_2O_2 and pH 7.35, which provided 95% of the COD removal. It was concluded that when using the Fenton oxidation process after the coagulation of $FeCl_3$ with lime, a slight improvement in the COD removal from the dairy industry wastewater was found. The effectiveness of coagulation was shown for the treatment of oily wastewater [Altaher, 2011]. The influence of various factors on the processes of coagulation and flocculation, such as temperature, the ratio of various parameters, exposure time, etc., were investigated [Azli, 2020].

In biochemical treatment, the removal of detergents occurs mainly due to the biochemical decomposition of these substances. At the same time, part of the substance is sorbed by activated sludge and removed from the structure during the discharge of excess activated sludge and suspended substances carried out with the treated liquid. In the presence of detergents, the formation of foam is observed in the aerotanks and at the discharge of the treated wastewater to the reservoir. In industrial and urban wastewater treatment plants, well-known methods are widely used for wastewater treatment, according to which first and second stage biofilters are used for wastewater treatment. Hydrogen sulfide salts are added as a source of sulfide ions for treatment of inorganic compounds entering the aero tank [Khongnakorn, 2007; Kamble, 2020].

As an alternative, the use of biotechnological methods of treatment is effective. Thus, the culture liquid of bacteria *Thiobacillus ferrooxidans* can be used as a biocoagulant for the treatment of industrial wastewater from metal ions and some organic pollutants [Issayeva, 2011]. Thionic bacteria *Thiobacillus ferrooxidans* oxidize ferrous iron to ferric iron under acidic conditions. Under favorable conditions, the rate of bacterial iron oxidation is 200–500 thousand times higher than under chemical control conditions. On the other hand, in the south of Kazakhstan there is a bentonite deposit, which can be a promising sorbent for the treatment of the wastewater containing synthetic detergents.

In this regard, the aim of this research is the use of ferric iron obtained by using the bacterial-chemical method and bentonite to reduce the COD in the wastewater containing detergents.

OBJECTS AND METHODS

The research object was the wastewater flowing from Thermal power plant 3 to the local treatment facilities of PetroKazakhstan Oil Products LLP located in Shymkent. Synthetic detergents enter wastewater as a result of boilers rinsing with various detergents. The wastewater samples were taken to plastic containers with tight-fitting lids and placed in a laboratory refrigerator at a temperature of ≤ 4.0°C.

Thionic bacteria isolation and cultivation

The research used the strain *Acidithiobacillus ferrooxidans BIT 1*, which was obtained from the ore waters of one of the deposits of South Kazakhstan. The strain of thionic bacteria *Acidithiobacillus ferrooxidans BIT 1* is grown on Silverman-Lundgren's nutrient medium, which includes, g/L: $(NH_4)_2SO_4$ – 2.0; K_2HPO_4 – 1.0; $MgSO_4$ – 0.5; NaCI – 0.2; $FeSO_4 \times 7H_2O$ – 44.2; the pH of the medium was adjusted to 1.0 with H_2SO_4. The bacteria required for biological leaching were inoculated on the selective nutrient medium in the thermostat of the brand № TS-1/80 SPU TU 9452-002-00141798-97. The process of cultivation was continuously aerated. During the nutrient medium preparation, the scale of the brand "Scout-Pro" was used, and for sterilization, the autoclave of the brand SPGA-100-I-HH was used. The cultivation of microorganisms was carried out at 25°C for 7 days.

The strain *A.ferrooxidans BIT 1* constitutes small gram-negative rod-shaped cells with one polar flagellum, do not form spores, most are strict aerobes. Some species grow at a pH of 0.5 to 9.0. The optimum temperature for growth is about 28–30°C. The content of G+C in DNA ranges from 48 to 68 mol%, the titer of bacteria is of 10^8 to 10^7 cl/mL. With the development of bacteria, the liquid medium, which is initially transparent, acquires an amber hue, which turns into reddish brown to the formation of ferric iron. The colonies on solid media are small (1.0 to 1.5 mm in diameter), round, smooth with deposits of iron oxides. On a liquid medium with sulfur, it forms a uniform turbidity, and the pH of the medium decreases to 1.0–1.5. On solid media with sulfur, it forms small colonies (from 1.0 to 2.0 mm in diameter).

Bentonite is a clay mineral sampled from the stratiform bentonite deposit Darbaza in Saryagash district of Turkestan region. The deposit is characterized by poor disseminated sulfide mineralization, localized in limestone conglomerate-breccias and lumpy-layered dolomites of the lower part of the Famennian section. The length of the ore horizon is more than 3 km. The industrial mineralization is isolated in the form of small, consistently overlying lenses. The main ore body is located in the flexure-like fold of Alimbay syncline wing. This is clay containing at least 70% montmorillonite, where the main ore mineral is galena, which forms a fine dissemination and veins in the host rocks. The average lead content is 2.39%. The impurity elements are silver and gold. The ores contain barite (1–6.7%) and manganese (0.2–0.6) (Table 1). A feature of the mineral is its ability to form a dense gel in the presence of water and to limit space. The bentonites from Darbaza deposit have a pH of 6–9.5 and contain less than 2.0% sodium carbonate; the total content of interchangeable sodium and calcium does not exceed 80 IU/100 g.

Table 1. Chemical composition of bentonite, %

Properties	By mass
Al_2O_3	16.6 ± 1.5
SiO_2	52.30 ± 4.9
K_2O	0.92 ± 0.05
Na_2O	1.92 ± 0.1
TiO_2	0.97 ± 0.08
P_2O_5	0.12 ± 0.01
CaO_2	5.49 ± 0.5
MgO	3.05 ± 0.3
Fe_2O_3	5.3 ± 0.4
S	0.38 ± 0.02
Other	12.95 ± 1.2

Note: The content of components in various samples of bentonite can vary while maintaining the ratio of % of the indicators of compounds.

The determination of Fe^{2+} and Fe^{3+} was carried out by using a volumetric trilonometric method in technical solutions, which was distributed to measure the iron content in solutions in the range from 0.1 to 10 g/L.

The values of *pH, COD and* BOD_5 were determined according to standard methods [Abdulkareem, 2020]; the pH measurement was performed using a WTW Multiparameter 340i. In order to determine COD, the closed reflux-colorimetric method (Method 5220 C) was applied, whereas BOD_5 was analyzed according to Method 5210.

Statistical analysis of the results

The experiments were carried out five times in repetitions, the standard deviation was calculated at $0.95 > P > 0.80$ Statistical processing was carried out using the Microsoft Excel statistical software package on "Pentium-IV" PC. The arithmetic mean was determined by the number of measurements and in the general diagnostic group [Loloei, 2019].

The research algorithm represented 3 types of experiments: determination of the pH optimum for wastewater treatment; determination of the optimal ratio of the biocoagulant – ferric iron, obtained by *Thiobacillus ferrooxidans BIT 1*; study of the possibility of using bentonite as a sorbent for detergents.

RESULTS AND DISCUSSION

The analyses of wastewater showed the values of COD – 24.1 ± 2.2 g/L; BOD_5 – 2.9 ± 0.2 g/L. As a result of laboratory studies, it was found that ferric iron in the form of $FeCl_3$ used in production for coagulative wastewater treatment can be replaced with a bacterial suspension *Thiobacillus ferrooxidans* containing $Fe_2(SO_4)_3$. In order to determine the pH optimum for the efficiency of COD and BOD reduction, the $Fe_2(SO_4)_3$ content was at a constant level and amounted to 1.5 ± 0.1 g/L. The effect of different pH values on the COD values in the medium was studied. It was found that the COD and BOD values decreased in inverse correlation with the pH values. An increase in the pH values from 3 to 11 led to an increase in the efficiency of COD removal from 65.8% to 42.9%, while the concentration of COD in wastewater was 10.3 ± 1.0 g/L.

The role of pH and ferric iron values in the wastewater treatment processes involving coagulation and flocculation was shown by a number of researchers [El-Batrawy,2020; Ostovar, 2020]. For example, the studies by Ayguna Yilmaz [Ayguna, 2020] used a coagulation-flocculation process to treat the wastewater containing detergents. In this case, the degree of treatment of 71% is achieved with the use of 2 g/L of ferric chloride. According to the authors, the pH values are controlled by the types of hydrolysis. When a coagulant is added to wastewater, a number of soluble hydrolysis products are formed. The types of hydrolysis have different charges, positive at acidic pH and negative at alkaline pH values. There are two mechanisms of coagulation: "charge neutralization", when positively charged hydrolyzed particles are absorbed onto the surface of colloidal particles and destabilize stable colloidal particles, as well as "coagulation with flake sweep", where iron hydroxide precipitates formed at high dosages of coagulant physically remove colloidal particles from the suspension. Ayguna Yilmaz [Ayguna, 2020] used ferric chloride in his studies; in contrast, in the discussed experiment trivalent ferric sulfate obtained with the bacterial-chemical method was used. However, the results of the treatment process are quite comparable.

The determination of the optimal amount of added trivalent ferric sulfate was based on the results of laboratory studies, where the preliminary limits of the amount of added coagulant were indicated by the results of studies by Papadopoulos [Ahmad, 2016] who used 1.5 g/L of lime in coagulation-flocculation processes with the COD removal efficiency of 29%, and additional introduction of 1.5 g/L of alum helped to remove COD up to 18%. In the studies by Saravanan [Saravanan, 2017] the use of lime, alum and ferric chloride as a coagulant increased the COD removal by 89%. Research data show that ferric iron can provide higher COD removal efficiency. In this study the $Fe_2(SO_4)_3$, obtained as a result of the oxidative activity of thionic bacteria *Acidithiobacillus ferrooxidans BIT 1*, where metal-containing wastes, such as pyrophoric iron sulfides, can be used as the initial source of ferrous iron etc. [Roy, 2018]. In the present studies, it was found that the optimal amount of $Fe_2(SO_4)_3$ is 1.75 g/L, it is necessary to reduce the COD from 16.1 ± 1.5 g/L to 4.1 ± 0.4 g/L, i.e. the COD removal degree in wastewater is 74.5 ± 0.7% (Fig. 1).

In order to further reduce the COD indicators, it is possible to use additional wastewater treatment processes. Clay materials help to bind small flakes formed during ferric iron use into larger, denser flakes. The effect of bentonite doses on the COD indicators is shown in Figure 2. When using bentonite as a coagulant, the COD values decreased from 4.1 ± 0.4 to 3.9 ± 0.3 g/L in the case of 100 mg/L bentonite addition. A further increase in the bentonite content to 600 mg/L in wastewater leads to a decrease in the COD indicators to 1.9 ± 0.1 g/L, which is

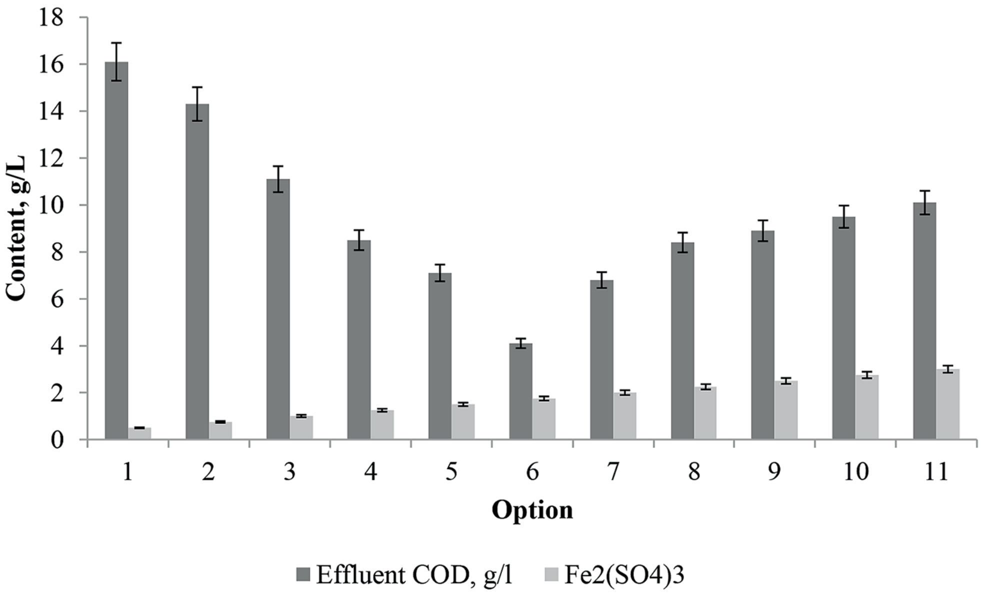

Figure 1. Effect of added $Fe_2(SO_4)_3$ doses to reduce the COD content

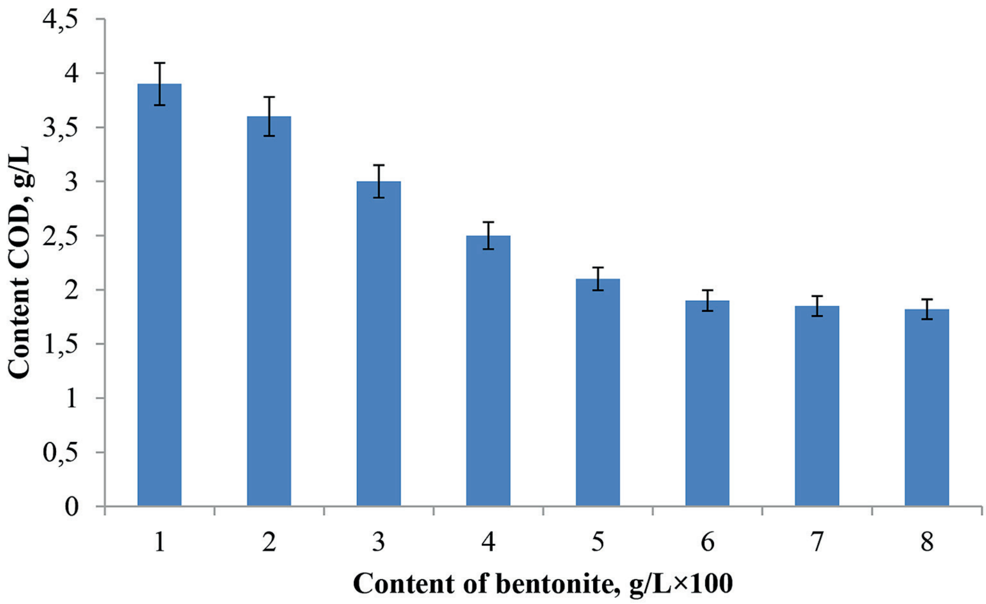

Figure 2. Effect of different added bentonite doses to reduce the COD content

88.1 ± 7.9% of the decrease in the initial COD indicators. This amount of bentonite was the optimal one required for the maximum efficiency of wastewater treatment from COD.

A further increase in the amount of added bentonite did not lead to a significant decrease in COD. Moreover, judging by the data from Demirci [1998] the use of bentonite for wastewater treatment is not only efficient, but also economically justified.

CONCLUSIONS

As a result of the studies, it was found that the coagulation process can be used for preliminary treatment of the wastewater containing detergents with a high COD content and low BOD values. At the same time, the prospect of using $Fe_2(SO_4)_3$ obtained with the bacterial-chemical method by means of thionic bacteria *Acidithiobacillus ferrooxidans BIT 1* was established. It was found that the highest COD reduction degree – 88.1 ± 7.9% in wastewater was noted in the variation where the bacterial-chemical ferric iron in the amount of 1.75 g/L was used in combination with bentonite in the amount of 600 mg/L. At the same time, the use of bentonite is justified not only by the cleaning efficiency, but also by its economic feasibility.

REFERENCES

1. Abdulkareem L., Al-sareji O.J., Obaid Z., Abdulhusain N., Satyi S. 2020. Removal of COD and TOC from domestic wastewater by using alum and peels of sunflowers seeds as natural coagulant. Eurasian Journal of Bio Sciences, 14, 2011–2014.
2. Ahmad H., Lafi W., Abushgair K., Assbeihat J.M. 2016. Electrocoagulation and Biological Techniques for the Municipal Wastewater Treatment. Int. Journal of Appl. Eng. Res., 11, 11014–11024.
3. Altaher, Hossam, Qada, Emad, Omar, Waid. 2011. Pretreatment of wastewater streams from petroleum/petrochemical industries using coagulation. Advances in Chemical Engineering and Science, 1, 245–251.
4. Ayguna A., Yilmazb T. 2010. Improvement of coagulation-flocculation process for treatment of detergent wastewaters using coagulant aids. International Journal of Chemistry and Environmental Engineering, December, 97–101.
5. Azli F., Azoddein A., Abu Seman M.N., Hamid A., Tajuddin T., Nurdin S. 2020. Treatment of Petroleum-Based Industrial Wastewater Using Electrocoagulation Technology. Advances in Waste Processing Technology. Springer Nature Singapore: Pte Ltd, 49–59.
6. Bhairi S.M., Mohan C. 2007. Detergents: A guide to the properties and uses of detergents in biological systems. In: EMD Biosciences; 20–21 November; San Diego, CA, 43.
7. Demirci S., Erdogan B., Ozcimder R. 1998. Wastewater treatment at the petroleum refinery, Kirikkale,

Turkey Using Some Coagulants And Turkish Clays As Coagulant Aids. Water Research, October, 3495–1499.

8. El-Batrawy O., El-Sonbati M., El-Awadly E., Hegazy T. 2020. Study on ferric chloride coagulation process and fenton's reaction for pretreatment of dairy wastewater. International Current Science, 10, 366–370.
9. Farizoglu B., Uzuner S. 2011. The investigation of dairy industry wastewater treatment in a biological high performance membrane system. Biochemical Engineering Journal, 10, 1016–1021.
10. Gu L.Y., Wang N., Zhu D., Zhang S., Huang H., Yuan Z., Wang M. 2013. Preparation of sewage sludge based activated carbon by using fenton's reagent and their use in 2-naphthol adsorption. Bioresour. Technol., 146, 779–784.
11. Issayeva A.U., Bishimbayev V.K., Uspabayeva A.A., Taskarayeva A.A., Bishimbayev K.V. 2011. Method for biological wastewater treatment. Innovation Patent, 24863, 11.
12. Kamble P., Pandit A. 2020. Significant study of effect of aeration intensities on membrane bioreactor performance. International Journal of Scientific and Research Publications, 11, 203–209.
13. Khongnakorn W., Wisniewski C., Pottier L., Vachoud L. 2007. Physical properties of activated sludge in a submerged membrane bioreactor and relation with membrane fouling. Purif. Tech., September; 125–131.
14. Loloei M.H., Alidadi G., Nekonam K., Kor Y. 2019. Study of the coagulation process in wastewater treatment of dairy industries. International Journal of Environmental Health Engineering, 2, 17–21.
15. Ostovar F., Abedinzadeh N., Pourkarim S., Mirblooki H., Yazdi M. 2021. Desalination and water treatment combination of coagulation and oxidation processes for treatment of real fish canning wastewater. International Current Science, 10, 203–207.
16. Roy C.K., Jahan M.A., Rahman S.S. 2018. Characterization and Treatment of Textile Wastewater by Aquatic Plants (Macrophytes) and Algae. European Journal of Sustainable Development Research, 2, 29–30.
17. Saravanan J., Priyadharshini D., Soundammal A., Sudha G., Suriyakala K. 2017. Wastewater Treatment using Natural Coagulants. International Journal of Civil Engineering, 4, 40–42.
18. Slavov A.K. 2017. Wastewaters general characteristics and treatment possibilities. Food Technology and Biotechnology, 10, 17113–17120.
19. Suman A.T., Ahmad K. 2017. Dairy wastewater treatment using water treatment sludge as coagulant: a novel treatment approach. Environ. Dev. Sustain., 10, 100–113.