Tuijin Jishu/Journal of Propulsion Technology
ISSN: 1001-4055
Vol. 45 No. 2 (2024)

Sulfide Adsorption on Modified Activated Carbon: Performance and Kinetics

Malee Santikunaporn [1], Suphasuta Dueanchai [2], Channarong Asavatesanupap [3]
[1, 2] Department of Chemical Engineering, Faculty of Engineering, Thammasat School of Engineering, Thammasat University, Pathum Thaina, 12120 Thailand
[3] Department of Mechanical Engineering, Faculty of Engineering, Thammasat School of Engineering, Thammasat University, Pathum Thaina, 12120 Thailand

Abstract:- The investigation of sulfide adsorption in the aqueous phase has been undertaken in response to a growing emphasis on the environment. This research aimed to investigate the adsorption of sulfide on activated carbon derived from the KOH activated on apricot kernel shells. The prepared activated carbons were analyzed using a nitrogen adsorption analyzer, scanning electron microscopy, and the point of zero charges. The nitrogen sorption isotherm demonstrated a microporous structure inside the adsorbent. The adsorption behavior of different adsorbents, including plain and modified activated carbon, found that the modified activated carbon performed significantly better than that of plain activated carbon. The maximum removal was 37.7% on the modified activated carbon at the initial concentration of 50 mg g^{-1} after 600 min of adsorption at 30 °C. Adsorption kinetics demonstrated a good fit between the Langmuir isotherm on plain activated carbon and the Freundlich isotherm on modified activated carbon to describe the experimental data.

Keywords: Sulfide, Apricot kernel shell, Adsorption, Isotherm.

1. Introduction

Due to an increase in environmental awareness all over the world, large industries and municipal wastewater systems are under a lot of pressure to reduce the content of hydrogen sulfide in the wastewater system. Hydrogen sulfide is usually generated from a low-velocity wastewater collection system. The accumulation of sludge solids on the water surface tends to block oxygen, creating an anaerobic condition in the wastewater collection system. In the absence of oxygen, anaerobic bacteria consume and transform sulfate into SO_2, which is then combined with hydrogen to produce hydrogen sulfide. A large amount of sulfate compound is produced in industries such as pharmaceuticals, paper production, distilleries, and food processing. The combination of hydrogen sulfide and humidity can create extremely corrosive solutions that have undesirable effects on any material that is exposed to them.

The generation of hydrogen sulfide is made possible by a group of chemolithotrophic bacteria referred to as dissimilatory sulfate-reducing bacteria (SRB), which compete with the methane production bacteria (MPA) in the wastewater collection system [1]. Under a high sulfate content environment and appropriate thermodynamic conditions, SRB can overshadow MPA activities [2, 3]. Sulfate would then become a terminal electron acceptor, while acetate and hydrogen in the atmosphere are electron donors. This will be the case only when the sulfide concentration is higher than 250 mg L^{-1} [4]. Biological interaction between these two molecules resulted in hydrogen sulfide [5]. Since sulfide has no financial benefit and causes a highly corrosive atmosphere in the reactor, hydrogen sulfide removal methodology is important for large biogas production or wastewater treatment facilities.

Three different techniques were proposed for the reduction of hydrogen sulfide from the system, including biological, chemical, and physical techniques. The biological method involved the oxidation of sulfide to elemental sulfur by the addition of thiobacillus bacteria inside the biofiltration and biotrickling filter systems [6]. The biological process is usually employed in an anaerobic digester for biogas production. However, activation of the sulfate reduction bacteria can take as long as 8 days [7, 8]. On the other hand, the chemical process involved the addition of alkali and metal ions (ferric oxide, ferrous hydroxide, and ferric chloride) to the treatment system

[9]. Hydrogen peroxide was also employed to reduce hydrogen sulfide with a 30% efficiency [10, 11]. However, these two conventional methods lack the ability to recover sulfur from the treatment system. For this reason, researchers are currently investigating the removal of hydrogen sulfide via an adsorption mechanism on heterogeneous support.

Carbon-based materials have recently undergone a significant amount of investigation as an adsorbent due to their large surface area and, more importantly, their ability to be prepared from lignocellulosic biomass via the thermal decomposition method. Khanla et al. [11] suggested a 94% and 99% removal rate of sulfide in air and aqueous solutions when the contaminated medium is exposed to oxygen functional groups on the biochar surface. The highest adsorption capacity of biochar was 160 mg g^{-1} [11]. Analysis of the used adsorbent revealed the deposition of sulfate and sulfur inside the pores. The combined sulfate/sulfur deposited inside the adsorbent is a perfect nutrient for improving land fertility for agricultural activities [12].

This research aimed to evaluate the adsorption performance of the prepared activated carbon from the apricot kernel shell. Also, sulfide adsorption isotherms were developed to calculate the adsorption efficiency and describe the adsorption process on the prepared adsorbents.

2. Experimental

A. Materials

Apricot kernel shells (AKS) obtained from Doi Kham Food Products Company were crushed, washed with DI water to remove impurities, and dried at 383 K in an oven for 24 hours. The dried sample was carbonized in an electrical furnace under an oxygen-free environment at 673 K for 1 hour. The carbonized apricot sample (CAS) obtained was then ground into powder form and used as a precursor for activated carbon preparation. All chemicals such as potassium hydroxide (KOH, CARLO ERBA Reagents), hydrochloric acid 37w/v% HCl, CARLO ERBA Reagents), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, QRëC New Zealand), sodium sulfide ($Na_2S \cdot xH_2O$, Ajax FineChem.), sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$, PanReac AppliChem), potassium iodide (KI, CARLO ERBA Reagents), and iodine (I_2, CARLO ERBA Reagents)) were used without any purification.

B. Preparation of Activated Carbon

100 g of CAS was soaked in a concentrated solution of KOH with a CAS:KOH weight ratio of 1:1. The mixture was stirred continuously at 353 K for 2 hours. After that, it was filtered and dried at 383 K for 12 hours. The dried sample was placed inside a horizontal tubular furnace and pyrolyzed under a nitrogen atmosphere using a temperature ramp-up rate of 10 K/min at 1123 K for 2 hours. The pyrolyzed sample was then treated with 0.1 M HCl and washed with DI water to neutralize KOH residuals and contaminants. The final product was then dried again at 383 K for 24 hours.

The dried AC sample was further modified by wet impregnation with 5.0% wt of Al $(NO_3)_3 \cdot 9H_2O$ and stirred for 24 hours. The modified samples were then calcined at 483 K for 1 hour under an oxygen atmosphere. The finished modified activated carbon is denoted as MA.

C. Adsorption Characterization

The elemental analysis of AC and MA was performed by an elemental analyzer (Leco, CN628) at a high temperature. Through the titration technique, we observed the adsorbent surface's affinity towards water by analyzing the point of zero charges (PZC). N_2 adsorption-desorption analysis on the adsorbent samples was carried out at 77 K using an automated gas sorption analyzer (Autosorb iQ, Quantachrome Instruments) following degassing of the samples at 523 K for 6 hours.

D. Adsorption Experiments

The sulfide adsorption by activated carbon prepared from the chemical activation of apricot kernel shells and the modified activated carbon was studied. The stock solution of sulfide was prepared daily from $Na_2S \cdot xH_2O$ during the adsorption study [13]. The study was performed in a batch reactor at a constant temperature of 303 K. For each experiment, 3.0 g of prepared adsorbent was added to 50 ml of solution with various initial concentrations

---

and stirred at 200 rpm for different durations until reaching equilibrium. After adsorption, the adsorbent was filtered out. The remaining concentration was analyzed by the iodometric method [14]. All experiments were conducted in triplicate. Titration was performed between 0.025 N acid-iodine solution and 0.025 N sodium thiosulfate.

E. Isotherm Models

Two different two-parameter isotherm models were used to find a link between the amount of sulfide that was absorbed by each adsorbent and the concentration of sulfide that was measured when everything was balanced. The Langmuir isotherm model is valid for monolayer and homogeneous adsorption without any interaction between particles on a surface [15]. The linear form of the Langmuir isotherm model is given by Eq. (1).

$$\frac{1}{q_e} = \frac{1}{K_L q_m}\frac{1}{C_e} + \frac{1}{q_m} \quad (1)$$

where q_m is the maximum adsorption capacity on a monolayer (mg g^{-1}) and K_L is the Langmuir adsorption constant (L mg^{-1}). A plot $1/q_e$ against $1/C_e$ leads to determined Langmuir parameters that are q_m and K_L from an intercept and slope of a plot, respectively.

The Freundlich isotherm model is valid for both mono- and multi-layer adsorption on a heterogeneous surface of the adsorbent. The linear form of the Freundlich isotherm model is given by Eq. (2).

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e) \quad (2)$$

where K_F is the Freundlich adsorption constant and n is the surface heterogeneity. Freundlich parameters, KF and n, can be computed from the intercept and slope of a plot $\ln(q_e)$ vs. $\ln(C_e)$.

3. Results And Discussion

Two prepared adsorbents (AC and MA) were used to study the sulfide adsorption performance in water. Physical properties analysis of prepared apricot-activated carbons, the AC was shown in Table 1.

Table 1 Elemental analysis of prepared activated carbons

Parameters		Sample	
		AC	MA
pH_{ZPC}		6.7	6.1
Ultimate analysis (wt%), db			
-	C	80.6	74.5
-	H	2.2	2.9
-	N	0.5	0.8
-	S	0.1	0.1
-	^{a}O	16.6	20.7

^{a}Calculated by difference.

The carbon content was slightly decreased to 74.5 wt% after the modification process, while the oxygen content was slightly increased to 20.7 wt%. However, the sulfur content remains unchanged. pH_{PZC} is one of the main factors affecting the adsorption performance of the adsorbent. When the pH of the solution is at the PZC of the adsorbent, the adsorbent's surface will be globally neutral. However, if the pH of the solution is higher than the PZC of the adsorbent, then the adsorbent's surface will contain a significantly higher positive charge than a negative charge [16]. Therefore, the surface charge of the adsorbents used in this study was determined by the pH drift method. The pH_{PZC} of AC was found at 6.9. For MA, the modification of Al would result in increased acidity of the surface [13]. The surface charge of MA was 6.1, which was lower than AC. Therefore, the surfaces of AC and MA adsorbents will be negatively charged when submerged in a solution with a pH higher than 6.9 and 5.9, respectively. However, the surfaces of AC and MA will be positively charged when submerged in a solution with a pH lower than 6.9 [16].

Table 2 Textural properties of adsorbents

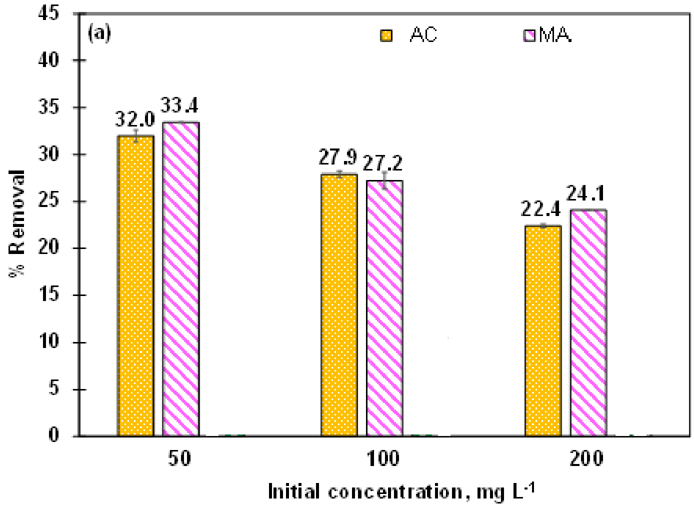
Properties	Samples	
	AC	MA
- BET surface area, $m^2\ g^{-1}$	1041.1	986.3
- Micropore surface area, $m^2\ g^{-1}$	867.2	784.8
- Micropore volume, $cm^3\ g^{-1}$	0.34	0.31

The details of the textural properties of adsorbents determined by an N_2 isotherm adsorption-desorption are presented in Table 2. BET surface area, micropore surface area, and micropore volume of AC are 1041.1 $m^2\ g^{-1}$, 867.2 $m^2\ g^{-1}$, and 0.34 $cm^3\ g^{-1}$, respectively. Impregnation of 5 wt% Al metal on activated carbon was found to decrease the surface area and pore volume.

Figure 1 shows the percentage removal of sulfide from two different adsorbents with an initial concentration of 50, 100, and 200 mg L^{-1} at a temperature of 303 K for 120 and 600 min. As seen in Figure 2, the percentage removals on AC at the initial concentrations of 50, 100, and 200 mg L^{-1} were 32.0, 27.9, and 22.2 at 120 min and 34.2, 33.8, and 30.4 at 600 min, respectively. Also, the percentage removals of MA at initial concentrations of 50, 100, and 200 ppm were 33.4, 27.2, and 24.1 at 120 min and 37.3, 27.2, and 24.1 at 600 min, respectively. At 600 min, the amount of sulfide adsorption obtained on AC and MA adsorbents at the same initial concentration was nearly the same, as shown in Figure 2. It can be concluded that the adsorption performance of MA is a little higher than that of AC, which is a parent precursor for MA preparation.

To further study the effect of time on the adsorption activity, the prepared adsorbents (AC and MA) were experimentally performed at 303 K by varying the initial sulfide concentrations of 50 and 100 mg L^{-1} with a constant adsorbent dosage of 30 g L^{-1}, and the results are shown in Figures 3(a) and 3(b).

For all adsorption conditions on both AC and MA, the percentage removal of sulfide initially increased rapidly for the first 120 minutes due to the abundance of sites on the adsorbent. After the first period of adsorption, the percentage removal increased slightly and reached the highest amount at the concentration. The percentage removal increased from 23.2 to 34.1 when the contact time increased from 30 to 480 min, and at the 100 mg L^{-1} initial concentration, the percentage removal increased from 22.8 to 33.8 as the contact time increased from 30 to 600 min. Like AC, at 50 mg L^{-1}, the percentage removal on MA



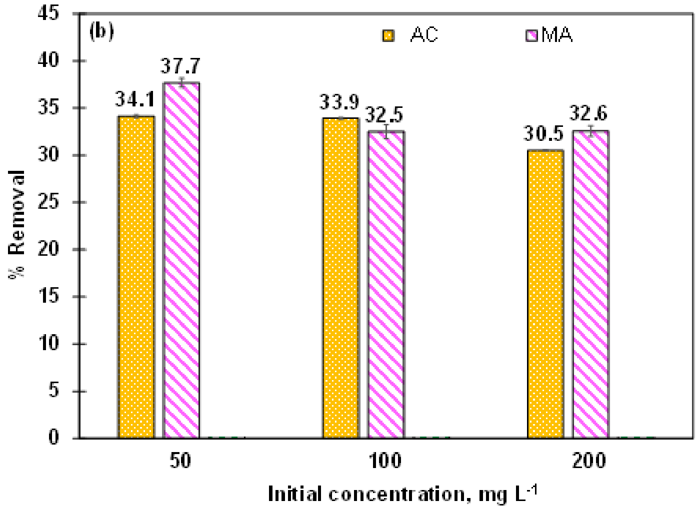


Figure 1. Effect of adsorbents on sulfide removal on various initial concentration at (a) 120 min and (b) 600 min.

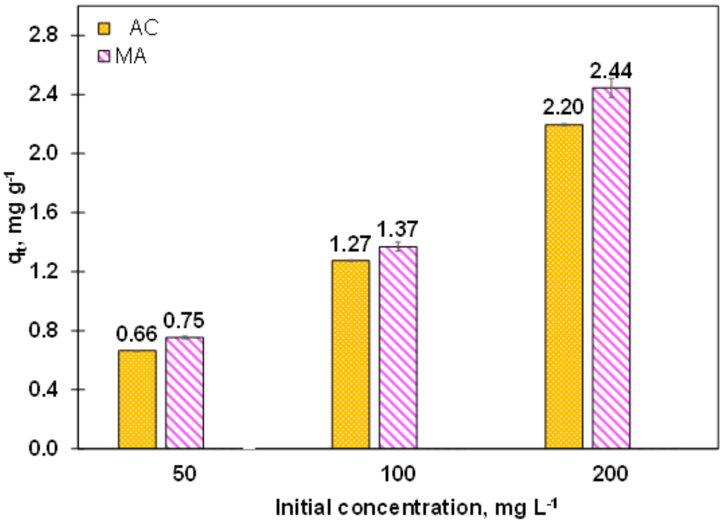
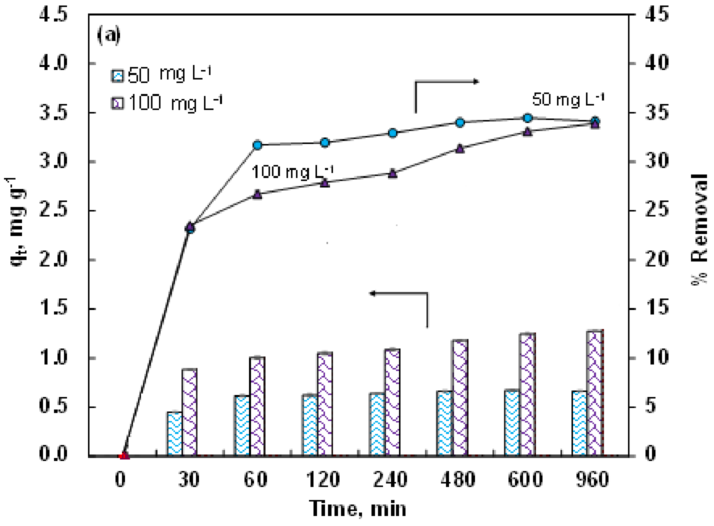


Figure 2. Effect of initial concentration on the sulfide adsorption capacity on various adsorbents at 600 min.



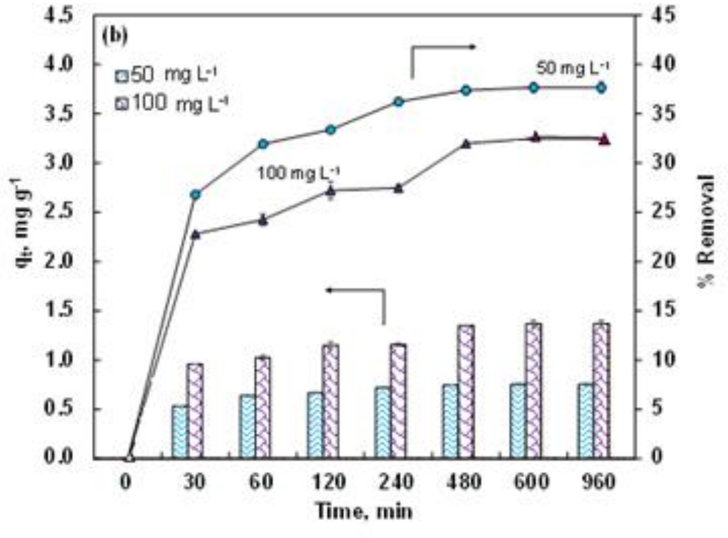
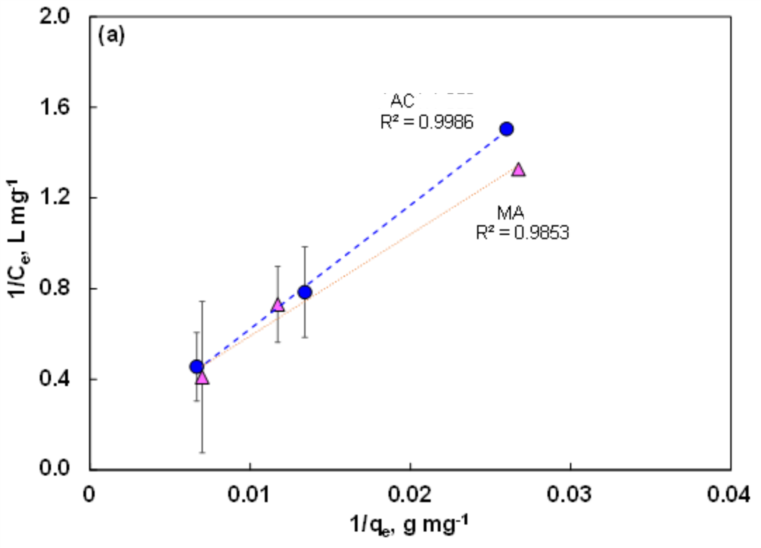


Figure 3. Effect of time on sulfide removal of (a) AC and (b) MA on different initial concentration.

increased from 28.2 to 38.4 when the contact time. For AC, at 50 mg L^{-1}, the initial time increased from 30 to 480 h, and at 100 mg L^{-1}, the percentage removal increased from 22.5 to 33.6 as the contact time increased from 30 to 600 min. The time to reach the maximum removal was altered depending on the initial concentration. The lower the initial concentration, the faster the time to reach adsorption equilibrium. The equilibrium time for AC and MA adsorbents was found to be 480 and 600 min for 50 and 100 mg L^{-1}, respectively.

As discussed above, the concentration gradient is the main driving force for the adsorption process [17]. The larger concentration gradient results in a higher driving force for the process. As previously discussed, the maximum adsorption capacities obtained from AC and MA were 0.67, 1.24, and 2.20 mg g^{-1} and 0.75, 1.36, and 2.44 mg g^{-1} for 50, 100, and 200 mg L^{-1} as the initial concentrations, respectively.

To understand the adsorption process, the experimental data tested on the prepared adsorbents at 303 K were fitted with two different two-parameter isotherm models, including Langmuir and Freundlich, as shown in Figure 4. The adsorption parameters for two isotherm models were listed in Table 4. Focusing on the correlation coefficients ($R^2 > 0.99$), the experimental data on AC and MA adsorbents were fitted well by the Langmuir and Freundlich isotherms, respectively. This suggests that the surface of the AC is homogeneous with no interaction between adsorbate and adsorbent, while the MA is heterogeneous due to the surface modification with Al seen from the surface characterization.



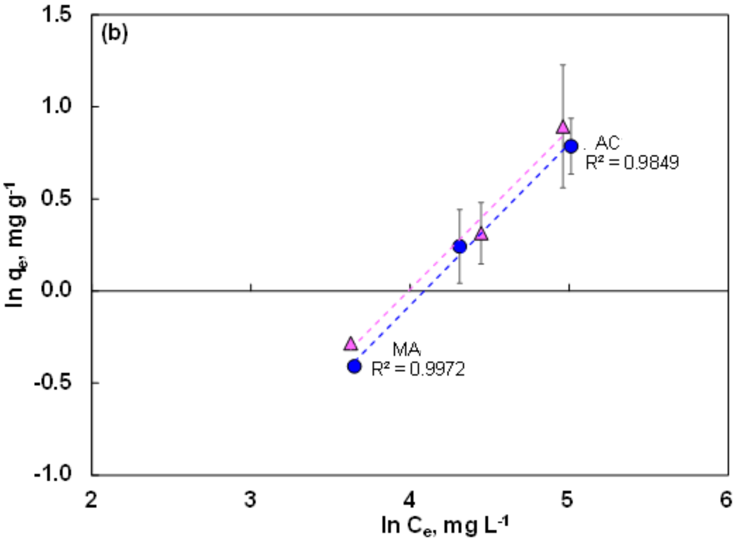


Figure 4. Adsorption isotherms of the prepared adsorbents tested at 303 K: (a) Langmuir isotherms and (b) Freundlich isotherm.

Table 4 Adsorption parameters for two isotherm models

Adsorption models	**Adsorbents**	
	AC	**MA**
Langmuir		
- $K_L, L\ mg^{-1}$	0.004	0.003
- $q_m, mg\ g^{-1}$	5.794	7.042
- R^2	0.999	0.985
Freundlich		
- n	1.151	1.140
- $K_F, mg\ g^{-1}(L\ mg^{-1})^{1/n}$	0.031	0.060
- R^2	0.985	0.997

4. Conclusion

This study investigated the sulfide adsorption performance of an activated carbon-based adsorbent. The adsorbent was synthesized by the KOH activation of apricot kernel shell char at a CAS:KOH ratio of 1:1 and a pyrolysis temperature of 1123 K, including surface modification with an aluminum precursor. This preparation procedure can provide a high surface area and micropore volume of the adsorbent; its surface area and micropore volume decreased, but the average pore size increased after modification. Also, the adsorption performance of plain activated carbon (AC) and modified activated carbon (MA) was investigated through parametric studies of contact time and initial concentration. MA provided the highest adsorption capacities for all studied conditions. This shows the potential application of using the carbon-based adsorbent in water treatment. Data analysis showed that the Langmuir isotherm can best describe the sulfide sorption behavior on plain activated carbon, whereas the Freundlich isotherm can best describe the sorption behavior on modified activated carbon.

Acknowledgements

This work was partially supported by Thammasat University.

References

[1] T.P.H. van den Brand, K. Roest, G.H. Chen, D. Brdjanovic and M.C.M. van Loosdrecht, “Occurrence and activity of sulphate reducing bacteria in aerobic activated sludge systems,” World J Microbiol Biotechnol. vol. 31, no. 3, pp. 507-516, 2015.

[2] G. Muyzer and A.J.M. Stams, “The ecology and biotechnology of sulphate-reducing bacteria,” Nat Rev Microbiol. Vol. 6, no. 6, pp. 441-454, 2008.

[3] C. Plugge, W. Zhang, J. Scholten and A. Stams, “Metabolic Flexibility of Sulfate-Reducing Bacteria,” Front Microbiol. Vol. 2, no, 81, 2011.

[4] S.K. Bhattacharya, V. Uberoi and M.M. Dronamraju, “Interaction between acetate fed sulfate reducers and methanogens,” Water Res. Vol. 30, no. 10, pp. 2239-2246, 1996.

[5] S.K. Khanal and J-C. Huang, “Effect of High Influent Sulfate on Anaerobic Wastewater Treatment,” Water Environ. Res. vol. 77, no. 7, pp. 3037-3046, 2005.

[6] K. Promnuan and S. O-Thong, “Biological Hydrogen Sulfide and Sulfate Removal from Rubber Smoked Sheet Wastewater for Enhanced Biogas Production,” Energy Procedia. vol. 128, pp. 569-574, 2017.

[7] H.K. Namgung, H. Ahn and J. Song, “Development of a two-phase bioreactor for the biological removal of hydrogen sulfide from biogas,” Energy Procedia. vol. 14, pp. 1143-1148, 2012.

[8] M. Andreides, L. Pokorná-Krayzelová, J. Říhová Ambrožová, E.I.P. Volcke and J. Bartáček, “Key parameters influencing hydrogen sulfide removal in microaerobic sequencing batch reactor,” Biochem Eng J. vol. 168, pp. 107951-107967, 2021.

[9] S. Mudliar, B. Giri, K. Padoley, D. Satpute, R. Dixit, P. Bhatt and et al., “Bioreactors for treatment of VOCs and odours,” J Environl Manage. vol. 91, no. 5, pp. 1039-1054, 2010.

[10] A. El Brahmi and S. Abderafi, “Hydrogen sulfide removal from wastewater using hydrogen peroxide in-situ treatment: Case study of Moroccan urban sewers,” Mater Today: Proc. vol. 45, pp. 7424-7427, 2021.

[11] F.R. Oliveira, K.C. Surendra, D.P. Jais, H. Lu, G. Unal-Tosun, S. Sung and et al., “Alleviating sulfide toxicity using biochar during anaerobic treatment of sulfate-laden wastewater,” Bioresour Technol. vol. 301, pp. 122711, 2020.

[12] J. Kanjanarong, B.S. Giri, D.P. Jaisi, F.R. Oliveira, P. Boonsawang, S. Chaiprapat and et al., “Removal of hydrogen sulfide generated during anaerobic treatment of sulfate-laden wastewater using biochar: Evaluation of efficiency and mechanisms,” Bioresour Technol. vol. 234, pp. 115-121, 2017.

[13] T.S. Kazeem, S.A. Lateef, S.A. Ganiyu, M. Qamaruddin, A. Tanimu, K.O. Sulaiman and et al., “Aluminium-modified activated carbon as efficient adsorbent for cleaning of cationic dye in wastewater,”. J Clean Prod. Vol. 205, pp. 303-312, 2018.

[14] D.F. Goerlitz and E. Brown, “Methods for the determination of inorganic substances in water and fluvial sediments,” in R.L. Wershaw, M.J. Fishman, R.R. Grabbe and L.E. Lowe, Techniques of Water-Resources Investigations of the United States Geological Survey Book 5, Chapter A3; 1972.

[15] O.M. Bankole, A.S. Ogunlaja, M.A. Adeyemo, S.E. Olaseni, O.S. Adanlawo, K.I. Ojubola and et al., “Simple ultrasound-heating process for preparation of magnetite-sulphur adsorbent for rapid uptake of phosphate ion in solution,” Int J Environ Anal Chem. Vol. 11, p. 1-24, 202.

[16] P. Tengvall, “4.6 Protein interactions with biomaterials,” In: P. Ducheyne, editor. Comprehensive Biomaterials II. Oxford: Elsevier, pp. 70-84, 2017.

[17] I.A.W. Tan, L.L.P. Lim, K.T. Lim, Removal of atrazine from aqueous solutions using HNO3 treated oil palm shell-based adsorbent, J Civ Eng., vol. 4, no. 3, pp. 17-20, 2013.