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Use of Drinking Water Sludge as Adsorbent for H_2S Gas Removal from Biogas

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Abstract

This paper reports the results of a research project, which attempts to produce a low-cost adsorbent material from waste (drinking water sludge). The main objective of this work is to study the characteristics of drinking water sludge for its adsorptive properties including morphology, surface area, porosity and chemical composition. The effect of activation conditions on H_2S gas adsorption efficiency of drinking water sludge was experimented. In this study, raw drinking water sludge was divided into 3 groups. In the first group, drinking water sludge was only oven dried at 105°C. For the other 2 groups, drinking water sludge was soaked in 2.5 M NaOH solution. After soaking, the sludge was divided into 2 groups (group 2 and 3). The second group was washed with distilled water until pH 7; while the third group was not. Biogas from a swine farm was used with an initial H_2S gas concentration in the range of 2,000 - 4,000 ppm. The material analysis showed that more surface area and total volume of sludge can be obtained after activated with NaOH. From the adsorption experiments, it was found that the highest adsorption capacity (q_e) of 87.94 mg H_2S/g adsorptive material can be achieved by using sludge from the third group. Moreover, by adding of 20 wt% iron filing into sludge of the third group the adsorption capacity increased to 105.22 mg H_2S/g adsorptive material. Drinking water sludge can be considered as a high potential energy saving and low cost adsorbent for removal of H_2S.

Keywords: low-cost adsorbent; drinking water sludge; H_2S adsorption; waste utilization

1. Introduction

The use of fossil fuel causes greenhouse gases which lead not only to climate change and global warming problems; on the other hand it will have some negative effects on human health and environment. One of sustainable solutions for these problems is to use energy sources with less total greenhouse gas emission. Biogas is one of this so-called sustainable energy, which is produced by anaerobic digestion process of easily biodegradable organic wastes, e.g. food waste, agricultural waste, manures and night soil (Jam and Xiujin, 2009). To improve the potential of biogas production, co-digestion of organic wastes could have the potential to improve the efficiency of anaerobic digestion process (Cheerawit *et al*., 2012). Khanto and Banjerdkij (2016) studied the biogas production from anaerobic co-digestion of night soil with food waste. The results revealed that up to 56 % methane can be produced and up to 97 % COD can be removed. However, the major problem of this bioconversion process is the production of hydrogen sulfide gas (H_2S), which varies from 0 - 4,000 ppm (Zicari, 2003). H_2S can cause health problems from irritation of eyes and airways, nausea, vomiting and headache (low concentration < 75 ppm) to sudden death by apnea within a few minutes (high concentration > 1,000 ppm) (Deublein and Steinhauser, 2008). Furthermore, H_2S should be removed from biogas prior using in combustion engine and burning utilities to avoid engine damage due to its corrosiveness (Zicari, 2003). Several techniques have been widely used to remove H_2S from biogas, including chemical absorption, water scrubbing, cryogenic, membrane technique, bio-filter and adsorption. However, some of these techniques are often expensive and produce other pollutants to the environment as well. Hence, removal of H_2S from biogas in several industries and biogas farms has been neglected (Pomeroy, 1982; van Lith *et al*., 1997). For these purposes, there are research interests focusing on the production of low-cost adsorbents using waste materials. Bagreev *et al*. (2001) studied the efficiency of sewage sludge-derived materials for H_2S gas adsorption process. They found that the presence of metal oxides in raw sewage sludge was beneficial to the adsorption of H_2S gas. Products of the reactions can be elemental sulfur, metal sulfides and also sulfuric acid. Ros *et al*. (2006) reported that highly porous materials (700 - 1,700 m^2/g) can be obtained by chemical activation of sludge-based precursors with alkaline hydroxides (NaOH and KOH). Ros *et al*. (2007) also reported the experimental results of H_2S

gas removal efficiency with sludge-based materials. The results showed that highly porous materials, a high metallic content and a basic pH of the adsorbents were required to achieve good adsorptive performance. In their study, the maximum loading (x/m) of 456 mg H_2S / g adsorbent can be achieved. Moreover, titration showed that most of H_2S was removed in the form of elemental sulfur, especially by using sewage-sludge-derived material activated with NaOH. Manajit (2008) found that in continuous experiments of 13 days lateritic soils blended with 20 wt% iron filings can remove 100% H_2S (50 ppm inlet H_2S concentration with the maximum loading of 7.34 mg H_2S / g adsorbent). Furthermore, other alternative materials, e.g. soils and clay were also studied for their gas adsorption properties. It was found that alkaline activation also enhanced CO_2 removal efficiency with soils and clay (Aylmore, 1974; Jonge and Mittelmeijer-Hazeleger, 1996; Pires and Pinto, 2010). It was also found that chemical composition of drinking water sludge and clay were quite similar and can be classified as natural inorganic adsorbents (Suriyachart *et al*., 2004). However, studies of drinking water sludge for gas adsorption have been rarely investigated.

The main objective of this work is to study the removal efficiency of H_2S from biogas by using drinking water sludge. The characteristics of drinking water sludge were investigated for its adsorptive properties including morphology, surface area, porosity and chemical composition. The adsorption efficiency of raw and chemical activated (with NaOH) drinking water sludge was experimented. Moreover, the addition of iron filing, which can be considered as a waste product from metal finishing industries, into the selected adsorptive material was also experimented.

2. Materials and Methods

2.1 Preparation of materials

Drinking water sludge used in this study was collected from Banglen Water Treatment Plant in Nakhonpathom, Thailand. It was stored in a dark plastic bag at 4°C and oven dried at 105°C for 24 hr. For all adsorption experiments, adsorbents with the same particle size in the range of 2.36-3.35 mm. (sieve number #6 and #8) were used. Dried drinking water sludge was divided into 2 groups. The first group of drinking water sludge was only grounded and sieved. This sludge will be referred to as “S”.

For the second group of drinking water sludge, activation by NaOH was carried out following the impregnation method, as described elsewhere (Ros *et al*., 2006). One half of this sludge (activated with NaOH) was washed with distilled water until the pH of the washing water was 7 and oven dried at 105°C for 24 hours. It was then grounded and sieved. This drinking water sludge was named as “SAW”.

For the other half of sludge activated with NaOH, after impregnation, the samples were filtered and oven dried at 105°C for 24 hours. It was then grounded and sieved to obtain the same particle size as the others. This drinking water sludge was named as “SANW”.

To study H_2S removal efficiency of drinking water sludge combined with iron filing, 20 wt% of iron filing was then added to the material that has the highest removal efficiency and the highest adsorption capacity, i.e. chosen from S, SAW and SANW (Manajit, 2008).

Iron filing was collected from a metal finishing industry in Samutsongkram, Thailand. The adsorptive material was named as “* + 20% Fe”.

2.2 Characterization of drinking water sludge

The surface area and porosity of raw and chemical activated (with NaOH) drinking water sludge were carried out using Brunauer Emmett Teller (BET) analyzer. The BET was carried out by nitrogen adsorption-desorption method using nitrogen temperature (77 K) with an autosorb BET apparatus (Micrometrics ASAP 2020). The analysis procedure was automated and operated with static volumetric techniques. The samples were first degassed at 473 K for 2 hours before each measurement was recorded. The elemental and morphological analysis was carried out using a combination of Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDX) (Model FEI Quanta 450).

2.3 Experimental setup

For each experiment, 10 g adsorbent was randomly packed in an adsorption column made from PVC plastic with an interior diameter of 2.5 cm and a total bed length of 20 cm. The dimension of the adsorption column is shown in Fig. 1.

The adsorption experiments were carried out at a biogas farm in Lopburi, Thailand and real biogas was used for all experiments. Biogas flow rate into the adsorption column was between 520 - 580 ml/min, while H_2S concentration at the inlet was in the range of 2,000-4,000 ppm. Each continuous experiment was carried out for 8 hours and the throughput volume was between 250,000 - 260,000 ml. Biogas samples were collected from 2 gas sampling points at the gas inlet and gas outlet, see Fig. 1. Gas samples were analyzed using gas chromatograph SHIMADZU GC6890. All measurements were repeated 3 times. Removal efficiency was calculated using equation (1):

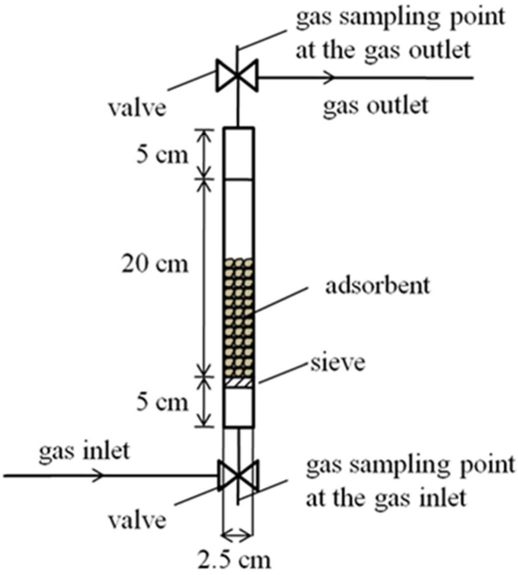


Figure 1. Adsorption column

$$\text{Removal efficiency (\%)} = \frac{C_i - C_o}{C_i} \cdot 100\% \quad (1)$$

Where, c_i and c_o are the inlet and outlet H_2S concentration (ppm), respectively.

The adsorption capacity can be defined as the amount of H_2S adsorbed by the adsorptive materials (q_e) and was calculated using equation (2):

$$q_e = \frac{V \cdot (C_i - C_o)}{m} \quad (2)$$

Where, V is the throughput volume of biogas, m is the mass of adsorptive material used and c_i and c_o are the inlet and outlet H_2S concentrations, respectively.

3. Results and Discussion

3.1 Characterization of drinking water sludge

Surface area and pore size of adsorbents are among important parameters that describe the quality of adsorbents as they affect directly their analysed retention abilities. Table 1 shows some physical properties of raw and chemical activated (with NaOH) drinking water sludge. It can be seen that more surface area and total volume can be obtained by activation with NaOH. Similar results were also reported by Ros *et al*. (2006).

Fig. 2 shows the adsorption isotherm of both raw and chemical activated (with NaOH) drinking water sludge prepared for this study. The results indicated that both are the isotherm of Type III, which explains the formation of multilayers and the adsorption is not limited even at high relative pressure ratio (P/Po).

The elemental analysis and morphological structures of raw drinking water sludge obtained are illustrated in Fig. 3. Raw drinking water sludge comprised about 55 wt% of O, 27 wt% of Si, 10 wt% of Al, 4 wt% of Fe and about 4 wt% of other metals. This was comparable with the analysis data of drinking water sludge from the other three drinking water treatment plants in Bangkok (Suriyachart *et al*., 2004).

Scanning electron microscope (SEM) morphology of sludge S, SAW and SANW with magnification of (a) 30, (b) 1,000 and (c) 5,000 are shown in Fig. 4 in order to compare surface and pores of each adsorptive material before the experiments.

As can be clearly seen from Fig. 4, by the magnification of 30 the surface of S and SAW/SANW are quite different. The surface of S is relatively smooth, while those of SAW and SANW are quite rough. This could be due to the reaction with NaOH. For higher magnifications, the difference between their morphological structures cannot be easily seen. Nonetheless, more small pores can be seen for SANW with magnifications of 1,000 and 5,000, compared with the other two.

Table 1. Physical properties of drinking water sludge

Physical property	Raw drinking water sludge	Drinking water sludge activated with NaOH
BET surface area (m^2/g)	70.80	90.51
pore width (nm)	11.35	16.03
pore volume (cm^3/g)	0.2008	0.3627

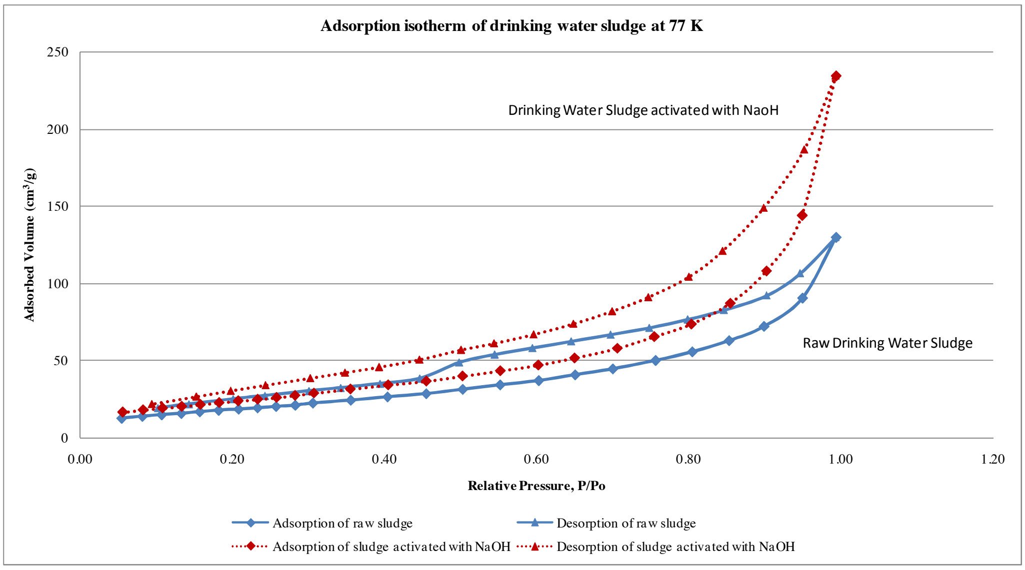
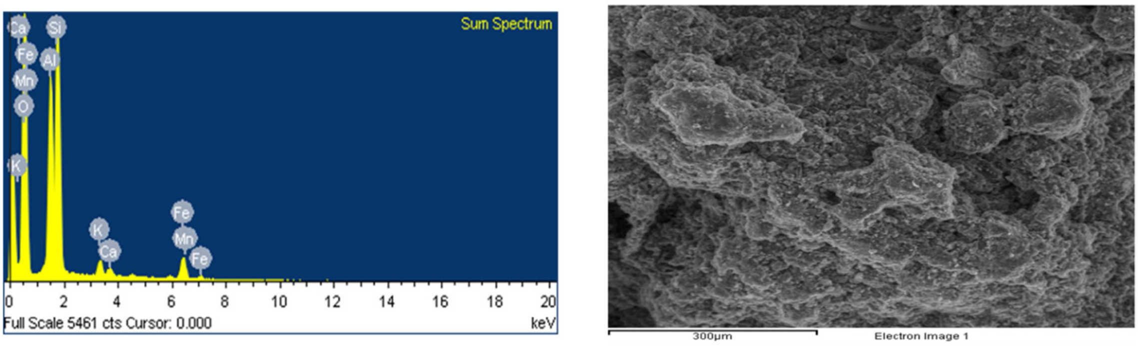


Figure 2. The BET plot of raw and chemical activated (with NaOH) drinking water sludge

3.2 *Adsorption experiments*

The removal efficiency (%) and the amount of H_2S adsorbed by the adsorptive material (q_e) were used to investigate the performance of the adsorptive materials. Fig. 5 shows the removal efficiency of S, SAW, SANW, and SANW+20%Fe. The throughput volume of each experiment ranged between ca. 250,000 - 260,000 ml. The initial concentration of H_2S varied between 2,000 - 4,000 ppm.

The maximum removal efficiency obtained from S, SAW and SANW were 86.58, 98.17 and 99.99 %, respectively. Furthermore, it can be seen in Fig. 5 that the removal efficiency of SANW was above 99 % for almost the whole experiment time, whereas at the end of the experiment (throughput volume of biogas above ca. 226,000 ml or ca. 7 hours throughput time) the removal efficiency dropped to 90.8%. The experiments also showed that by using SANW the outlet concentration of H_2S was lower than 1 ppm for throughput volume up to ca. 226,000 ml (ca. 7 hours throughput time). For higher throughput volumes from ca. 226,000 to 258,000 ml, the outlet concentration increased from 4.8 to 255 ppm. Biogas with H_2S concentration lower than 100 ppm can be used for internal combustion engines, while for upgraded natural gas the H_2S concentration must be lower than 4 ppm (Zicari, 2003). The results of adsorption capacity (q_e) from the beginning to the end of the experiments showed that SANW also had the highest q_e value of 87.94 mg H_2S/g adsorptive material compared with SAW (81.38 mg H_2S/g adsorptive material) and S (72.64 mg H_2S/g adsorptive material).



a)

b)

Figure 3. The EDX and SEM analysis of raw drinking water sludge: a) spectrum and b) SEM

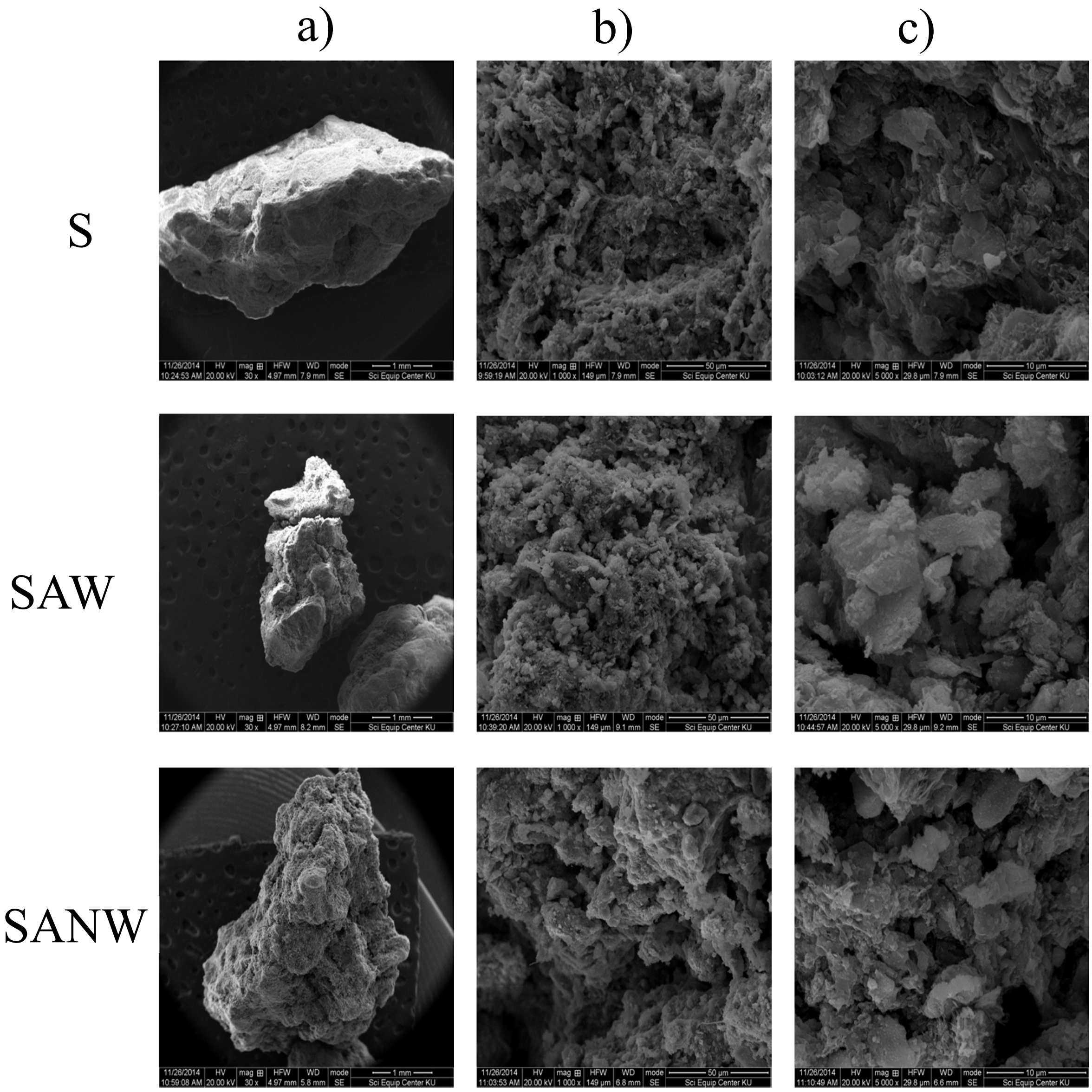


Figure 4. Scanning Electron Microscope (SEM) images of adsorptive materials S, SAW and SANW with magnification of a) 30, b) 1,000 and c) 5,000

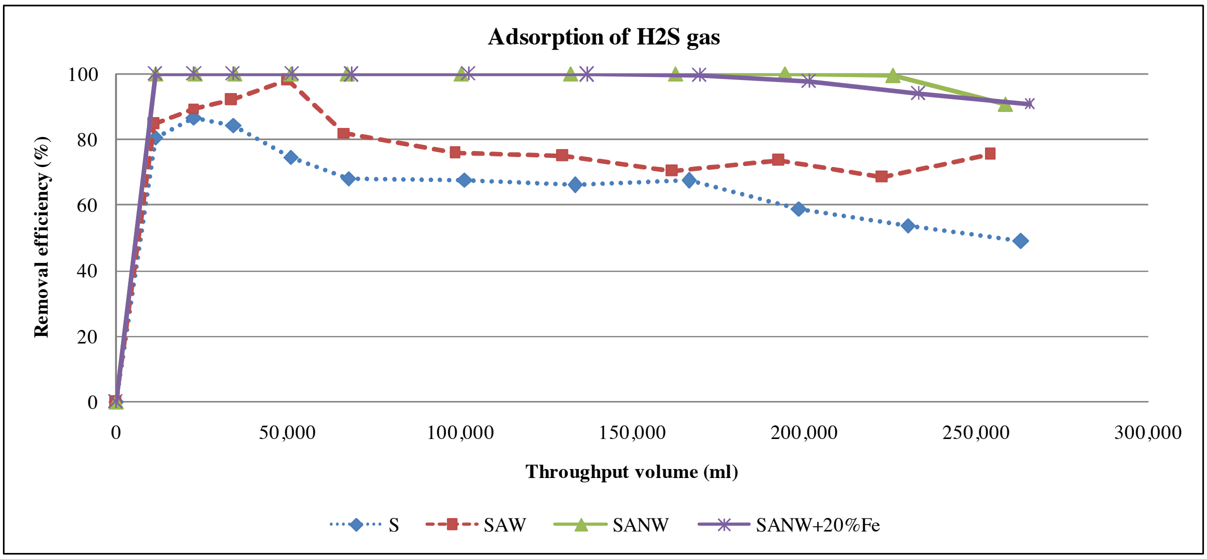


Figure 5. Removal efficiency of S, SAW, SANW, and SANW+20%Fe

The reason for high adsorption capacity of SANW was the remaining of strong base, i.e. NaOH, in the material, which can react with H_2S and immobilize it. H_2S adsorbed on the surface of the alkaline adsorptive material and generated two products and a water film. The chemical reactions are as followed (Chiang *et al*., 2000):

$$H_2S + NaOH \rightarrow HSNa + H_2O \tag{3}$$

and

$$H_2S + 2NaOH \rightarrow Na_2S + 2H_2O \tag{4}$$

Fig. 6 shows the elemental analysis of S, SAW and SANW after the adsorption process. About 1-2 wt% of sulfer was found in every used sludge samples (no sulfur was found in unused raw sludge). Conformed to the highest q_e value of SANW there was also the highest amount of sulfur (2.02 wt%) found in used SANW, compared with those in S (1.16 wt%) and SAW (1.54 wt%).

For SANW, drinking water sludge acted more as a passive support for NaOH rather than actively participating in the H_2S removal. This is in a similar manner to activated carbon impregnated with alkaline. The alkaline addition has a catalytic effect by oxidizing sulfide ions to elemental sulfur until there is no alkaline left to react (Siefers, 2010). The typical adsorption capacity for alkaline impregnated activated carbon compared with unimpregnated one were 150 and 20 mg H_2S/ g of activated carbon, respectively (Abatzoglou and Boivin, 2008). For this reason, SANW was used for the next following study.

Iron filing was then added into SANW by the amount of 20 wt%. Same as previous experiments, the total amount of the adsorptive materials was 10 g. The result showed the removal efficiency of SANW + 20 wt% iron filing (named as SANW+20% Fe in Fig. 5) was above 99 % for throughput volume up to ca. 170,000 ml. For throughput volume from ca. 200,000 to 265,000 ml, the removal efficiency dropped from 97.8 to 90.7 %, respectively, see Fig. 5. By considering the adsorption capacity (q_e) from the beginning to the end of the experiment, SANW+20% Fe had the highest q_e of 105.22 mg H_2S/g adsorptive material. In this case, SANW was, as previously described, used as a passive support for NaOH and iron filing reacted with H_2S according to the following reaction (Ryckebosch *et al*., 2011):

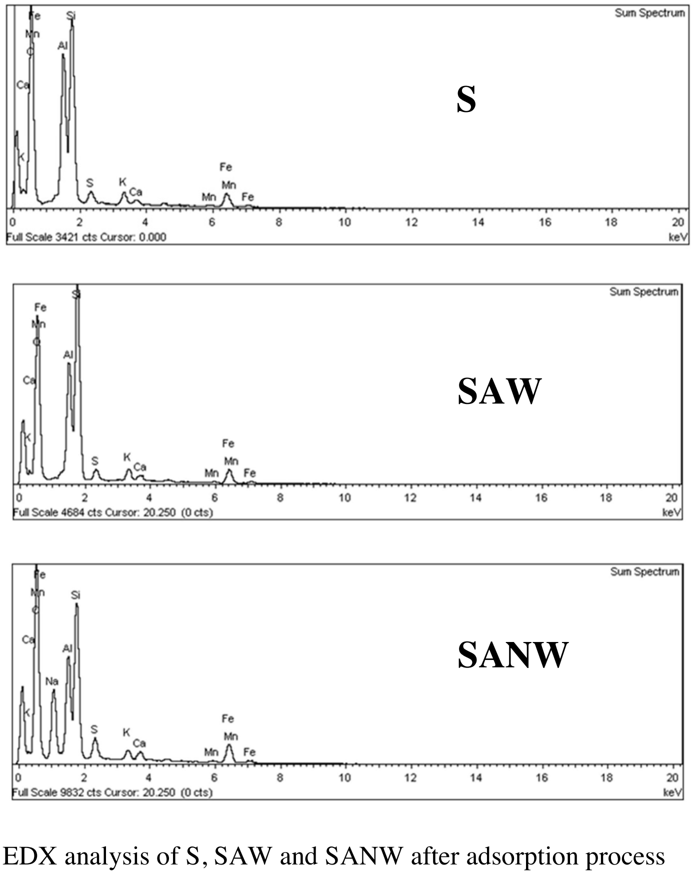


Figure 6. The spectrum EDX analysis of S, SAW and SANW after adsorption process

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \quad (5)$$

Whereas Fe_2S_3 can react to (Sharma, 1991)

$$Fe_2S_3 \rightarrow 2FeS + S \quad (6)$$

Moreover, it should be noticed that iron and other metals that were present in drinking water sludge itself can also react with H_2S (Ting *et al.*, 2008).

$$MO_x(s) + xH_2S \leftrightarrow MS_x(s) + xH_2O\ (g) \quad (7)$$

Where, M represents metals, and thus MO_x refers to metal oxides in drinking water sludge.

Table 2 shows the adsorption capacity (q_e), comparison with previous studies on different materials used by other researchers. The direct comparison with activated carbon and sewage sludge impregnated with NaOH is difficult. However, it must be pinpointed that the activation methods used in this study were simple and the temperature used in the material preparation process was quite low (105°C) compared with those of activated carbon (730°C, Lillo-Ródenas *et al.*, 2001) and sewage sludge (700°C, Ros *et al.*, 2007). Therefore, drinking water sludge activated with NaOH with addition of iron filing can be considered as a high potential energy saving and low cost adsorbent for removal of H_2S.

4. Conclusion

The H_2S-adsorption capacity, and thus H_2S removal efficiency of drinking water sludge were affected by both chemical treatment and the addition of iron filing. Drinking water sludge itself had a low surface area of 70.8 m^2/g. Furthermore, it also contained about 4 wt% iron and traces of other metals, which can react with H_2S. After chemical treatment with NaOH, the total surface area of drinking water sludge was increased to 90.51 m^2/g. The experimental results showed that the remaining NaOH in the adsorptive materials improved the adsorption capacity q_e of the adsorbents. In this case drinking water sludge will act as a support material for NaOH. The chemical reactions between H_2S and NaOH were described in equations (3) and (4). By adding iron filing, the adsorption capacity, q_e, was the highest (105.22 mg H_2S/g adsorbent). Iron filing also contributed to the adsorption of H_2S as shown in equation (5). To regenerate or reuse drinking water sludge and iron filing, using air flow or oxidation with oxygen are interested for further study, due to following reaction:

$$Fe_2S_3 + O_2 \rightarrow 2Fe_2O_3 + 3S_2 \quad (8)$$

Though, compared with commercial adsorptive materials, the adsorption capacity, q_e, of drinking water sludge with addition of iron filing was moderate, but it can be considered as a high potential energy saving and low cost adsorbent for removal of H_2S.

Table 2. Adsorption capacity (q_e) of some alternative adsorptive materials

Adsorptive material	Adsorption capacity q_e (mg H_2S/g adsorbent)	Reference
Activated carbon mixed with NaOH	300 - 330	Lillo-Ródenas *et al.*, 2001
Lateritic soils	14.4	Manajit, 2008
Redmud	21	Sahu *et al.*, 2011
S	72.64	this study
SAW	81.38	this study
SANW	87.93	this study
SANW+20% Fe	105.22	this study
Sewage sludge impregnated with $FeCl_3$	104.5	Bagreev *et al.*, 2001
Sewage sludge impregnated with NaOH	456	Ros *et al.*, 2007

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References

Abatzoglou N, Boivin S. A review of biogas purification processes. Biofuels, Bioproducts and Biorefining 2008; 3(1): 42-71.

Aylmore LAG. Gas sorption in clay mineral systems. Clays and Clay Minerals 1974; 22: 175-83.

Bagreev A, Bashkova S, Locke DC, Bandosz TJ. Sewage sludge-derived materials as efficient adsorbents for removal of hydrogen sulfide. Environmental Science and Technology 2001; 35(7): 1537-43.

Cheerawit R, Thunwadee T, Duangporn K, Tanawat R, Wichuda K. Biogas production from Co-digestion of domestic wastewater and food waste. Health and the Environment Journal 2012; 3(2): 1-9.

Chiang HL, Tsai JH, Tsai CL, Hsu YC. Adsorption characteristics of alkaline activated carbon exemplified by water vapour, H_2S, and CH_3SH gas. Separation Science and Technology 2000; 35(6): 903-18.

Deublein D, Steinhauser A. Biogas from waste and renewable resources: an introduction. Wiley VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. 2008. 85-95.

Jam SL, Xiujin L. Removal of H_2S during anaerobic bioconversion of dairy manure. Chinese Journal of Chemical Engineering 2009; 17(2): 273-77.

Jonge HD, Mittelmeijer-Hazeleger MC. Adsorption of CO_2 and N_2 on soil organic matter: nature of porosity, surface area, and diffusion mechanisms. Environmental Science and Technology 1996; 30(2): 408-13.

Khanto A, Banjerdkij P. Biogas production from batch anaerobic Co-digestion of night soil with food waste. EnvironmentAsia 2016; 9(1): 77-83.

Lillo-Ródenas MA, Lozano-Castelló D, Cazorla-Amorós D, Linares-Solano A. Preparation of activated carbons from Spanish anthracite: II. Activation by NaOH. Carbon 2001; 39(5): 751-59.

Manajit A. Hydrogen sulfide removal by iron containing media (Master Thesis). Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand, 2008.

Pires J, Pinto ML. Pillared interlayered clays as adsorbents of gases and vapours. *In*: Pillared clays and related catalysts (*Eds*: Gil A, Korili SA, Trujillano R, Vicente MA). Springer New York, New York, USA. 2010; 23-42.

Pomeroy RD. Biological treatment of odorous air. Journal of Water Pollution Control Federation 1982; 54(12): 1541-45.

Ros A, Lillo- Ródenas MA, Fuente E, Montes-Morán MA, Martin MJ, Linares-Solano, A. High surface area materials prepared from sewage sludge-based precursors. Chemosphere 2006; 65(1): 132-40.

Ros A, Lillo- Ródenas MA, Canals-Batlle C, Fuente E, Montes-Morán MA, Martin MJ, Linares-Solano A. A new generation of sludge-based adsorbents for H_2S abatement at room temperature. Environmental Science and Technology 2007; 41(12): 4375-81.

Ryckebosch E, Drouillon M, Vervaeren H. Techniques for transformation of biogas to biomethane. Biomass and Bioenergy 2011; 35(5): 1633-45.

Sahu RC, Patel R, Ray BC. Removal of hydrogen sulfide using red mud at ambient conditions. Fuel Processing Technology 2011; 92(8): 1587-92.

Sharma BK. Industrial chemistry: including chemical engineering. Krishna Prakashan Media (P) Ltd., Uttar Pradesh, India.1991; 814.

Siefers AM. A novel and cost-effective hydrogen sulfide removal technology using tire derived rubber particles (Master Thesis). Iowa State University, Ames, USA, 2010.

Suriyachart D, Wichitamornpan P, Ruangsamred W. The application of water supply sludge (Report). The Department of Primary Industry and Mines, Bangkok, Thailand, 2004. (In Thai)

Ting KT, Han CC, Hsin, C, Hung TC. Hydrogen sulfide removal from coal gas by the metal-ferrite sorbents made from the heavy metal wastewater sludge. Journal of Hazardous Materials 2008; 160(2-3): 482-88.

van Lith C, Leson G, Michelsen R. Evaluating design options for biofilters. Journal of the Air and Waste Management Association 1997; 47(1): 37-48.

Zicari MS. Removal of hydrogen sulfide from biogas using cow manure compost (Master Thesis). Graduate School, Cornell University, Ithaca, USA, 2003.

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