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Alum sludge as an efficient sorbent for hydrogen sulfide removal: Experimental, mechanisms and modeling studies

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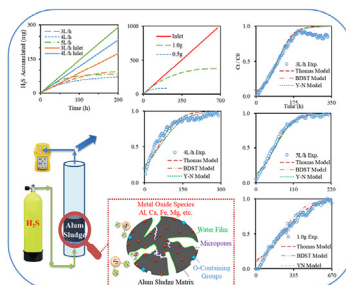
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H I G H L I G H T S

- First study of reusing alum sludge for H₂S adsorption.
- The effect of flow rate and bed depth were investigated.
- The adsorption mechanisms were proposed.
- Three kinetic adsorption models were applied for breakthrough behavior simulation.
- Mass transfer coefficients of the sorbent were determined.

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This paper firstly reported a systematic study of using alum sludge (waterworks residue) for H₂S adsorption. Various trials were performed at ambient temperature in a fixed bed column to study the effects of H₂S flow rate, sorbent bed depth on the alum sludge adsorption efficiency of H₂S. The Breakthrough Curves were simulated by the Thomas model, Bed Depth Service Time model and Yoon-Nelson models. The mechanisms of H₂S adsorption onto alum sludge was examined by different physiochemical characterizations of exhausted and raw alum sludge. Moreover, the mass transfer coefficients were determined from mathematical descriptions of breakthrough curves. The alum sludge adsorption capacity was determined to be 374.2 mg of H₂S/g, slightly decreasing with the increasing flow rate and increasing with the increasing bed depth. All the three models successfully predict breakthrough curves which could be used for scaling-up purposes. The microporous structure, alkaline pH and the inherent metal species of the alum sludge promoted the formation of metal sulphate species. This study demonstrated that alum sludge could be used as cost-effective, largely available, and efficient sorbent for H₂S removal.

1. Introduction

There is generally increasing public concern for and intolerance of odors and other air contaminants from sewerage facilities.

Management of air/odor emissions has become a significant activity in wastewater treatment plants (WWTPs). Furthermore, national and local regulations require a number of air pollutants to be controlled (de Oliveira, 2011). Hydrogen sulfide (H₂S) is one of several odorous gases from industrial effluents such as WWTPs, landfill sites and petrochemical industries (Bamdad et al., 2018). It is a poisonous, flammable, colorless gas with a characteristic odor of rotten eggs. The average odor threshold of H₂S is reported at 7 to

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9 part per billion (ppb) (Wu et al., 2018).

Generally, treatment technologies of H₂S in WWTPs include physical/chemical (such as adsorption, chemical scrubbing) and biological methods (biofiltration, biotrickling, activated sludge diffusion etc.) (Ren et al., 2019). Adsorption, a process based on the transfer of pollutants from gas phase to solid phase, has been broadly implemented. It is one of the most suitable methods for H₂S removal from a gas stream, as it allows for H₂S removal to less than 1 ppmv (Patel, 2019). For instance, in recent studies, Singh et al. (2019) used zinc oxide-decorated multi-wall carbon nanotubes (ZnO-MWCNTs), which was a synthesis of the carbon nanotube and zinc oxide, for a high values (98%) of H₂S removal in a bench-scale fixed bed reactor at the ambient temperature and atmospheric. Sánchez-González et al. (2018) investigated Mg-based metal-organic frameworks (MOFs) as a highly reversible sorbent for H₂S removal. The dynamic adsorption experiments were performed at 303 K using a quartz-tube filled with Mg-MOF. Results showed that the H₂S adsorption capacity of Mg-MOF was 3.1 mmol H₂S/g, under the 15 vol % H₂S feed concentration. Hervy et al. (2018) reported the H₂S removal by chars obtained from pyrolysis of wastes under ambient temperature in various dry gas matrices (N₂, Air, Syngas). It concluded that the most efficient material was the steam activated char from food waste and coagulation-flocculation sludge, with a removal capacity of 65 mg H₂S/g under dry syngas.

Other materials have been reported as sorbents for H₂S removal, including fly ash, activated carbon, polymers, carbon-coated polymers, ceramics, and synthetic zeolites. The H₂S removal efficiency of these materials ranged from 8.63 to 210 mg H₂S/g (Sharma and Verma, 2013; Sitthikhankaew et al., 2014; Wang et al., 2017). Activated carbon was applied in most of the studies dealing with H₂S removal (based on moist air) at room temperature. During the sorption process, H₂S could have interactions with O-containing groups and/or mineral species in the sorbent (in the presence of oxygen and humidity). This also results in several retention mechanisms including adsorption, dissociation and oxidation (Hervy et al., 2018; Chanaka Udayanga et al., 2019a). However, the removal capacity of H₂S by adsorptive materials depends on physicochemical properties (e.g., elemental composition, pore structure, surface O-containing groups, mineral species and pH) of the materials and varies with experimental conditions (e.g., temperature, water and/or oxygen) (Bamdad et al., 2018, Chanaka Udayanga et al., 2018; 2019b). Indeed, adsorption has the common shortcoming including material cost and the complexity of sorbent preparation. Therefore, direct utilization of low-cost raw materials from industrial by-product for H₂S removal has attracted intensive research interests.

Alum sludge (or Al-waterworks residue) is a kind of by-product during drinking water treatment process in waterworks where aluminum based coagulant is applied (Zhao et al., 2018a). It is a locally, easily and largely available “resources” in towns, cities and metropolis and free of charge for the moment. Unfortunately, it is treated as a “waste” for landfilling in most of the places in the world. Therefore, identifying novel, sustainable alum sludge reuse methods may provide significant social and environmental benefits. Actually, alum sludge has been intensively studied in recent years as a low-cost sorbent for phosphorous and other pollutants (Shen et al., 2019; Liu et al., 2018; Wang et al., 2018; Zhao et al., 2018b) and has been advocated to be a valuable reuse product, offering huge potential for a number of pollutants immobilization with unique feature of using “waste” for waste treatment (Yang et al., 2018; Zhao et al., 2016). However, to the best of our knowledge, no studies have used alum sludge for H₂S adsorption even it has been intensively studied and demonstrated to be a good material for impurities adsorption in wastewater treatment, i.e. pollutants in aquatic phase (Ahmad et al., 2016; Hidalgo et al., 2017;

Odimegwu et al., 2018).

Fixed-bed column is commonly employed for adsorption studies as it can be relatively easy to scaling up, but a fixed-bed column does not always run under equilibrium conditions, the performance depends on the flow conditions and mass-transfer phenomena (Gutiérrez Ortiz et al. 2014; Long and Loc, 2016). The breakthrough curve (e.g., the dynamic behavior of adsorption process) describes the effluent concentration with time profile, which is vital in the evaluation of the material efficacy. The shape of the breakthrough curve is also affected by both inter- and intra-particle transfer phenomenon in the column and sorbent (Kubonova et al., 2011). Therefore, breakthrough curves measuring and mass transfer phenomena are fundamental for understandings and predicting sorption phenomenon. Mathematical models are useful for describing and predicting the behavior of fixed-bed reactors and help to optimize as well as to design a system. The most commonly used models in literature are Thomas, Bed Depth Service Time, and Yoon-Nelson models, which are all used in this study.

Accordingly, this paper firstly systematically reported the experimental adsorption behavior modeling and mechanisms of using alum sludge for H₂S adsorption in a fixed-bed column at room temperature. The effects of reaction/adsorption conditions were trialed while three modeling approaches (Thomas, Bed Depth Services Time, Yoon-Nelson model) were examined and compared. Moreover, the adsorption mechanisms were proposed and the mass transfer coefficient was determined, which could be used to design and evaluate the alum sludge reactor on a larger scale. This study intends to pave a novel reusing route of alum sludge as H₂S abatement media.

2. Materials and methods

2.1. Sorbent and characterization

Dewatered raw alum sludge cakes were obtained from the Carmaux drinking water treatment plant located in Tarn, France. The plant produces 3014 m³/day of drinking water by treating raw water using aluminum sulphate as a coagulant. After collection, the sludge was dried, mechanically ground by a blender and sieved to pass a 250 μm mesh. Alum sludge moisture content was determined by drying at 105 °C for 24 h and measuring the mass difference before and after drying.

Different physicochemical characteristics were determined before and after H₂S sorption. The alum sludge pH was measured by adding 0.5 g of alum sludge to 20 ml of distilled water. Particle size distribution was determined by a laser particle sizer MALVERN Laser Mastersizer Hydro 2000 at size interval of 0.01–1000 μm. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed by using HORIBA Jobin-Yvon Ultima 2. Scanning electron microscopy (SEM) was employed (Philips XL30 ESEM apparatus, FEI Company), it was coupled with an energy-dispersive X-ray spectroscopy (EDX analysis). The transmission electron microscopy (TEM) was used on the JEOL JEM-ARM200F and the elemental mapping of chemical species in the sample was performed by using an EDX module in the same microscope. Specific surface area and pore structure were determined by the BET method (Micromeritics Gemini Vacprep 061). The pore structure of alum sludge was determined by nitrogen adsorption at 77 K using a Micromeritics 3 Flex high-resolution analyzer.

To investigate the various resultant sulfur products, a thermogravimetric analysis (ATG STA409PC, Netzsch) coupled with a mass spectrometer (OMNISTAR, Pfeiffer) was applied. Heating rate of 20 °C/min up to 800 °C at a nitrogen flow rate of 3 L/h was used. For each measurement, a sample of 200–300 mg of alum sludge was analyzed.

2.2. Sorption trials

The H₂S removal trials were carried out at ambient temperature (20 °C) by using a glass fixed-bed column. Fixed bed columns test can be easily scaled up from a laboratory to an industrial application (de Franco et al., 2018). Fig. 1 shows the photographic description of the column setup. The column (length 60 mm, internal diameter 11 mm) is equipped with a porous glass disc at the bottom which could hold alum sludge and allow H₂S to pass through. The height of alum sludge layer varied from about 5 to 11 mm, corresponding to the amount of alum sludge used for each trial (0.5–1.0 g). A synthetic gas containing 200 ppmv of H₂S (based on dry air) passed through alum sludge at different flow rates of 3, 4, 5 L/h, respectively, as controlled by a flow meter. The outlet H₂S concentration was monitored every 2 min using a gas analyzer (BW Technologies, Gas Alert QUATTRO). The effluent gas was treated by a CaO solution before it was released to the atmosphere. Sorption experiments were ended when the H₂S sorption rate significantly decreased. During the various trials, material fluidization was not observed under three flow rates (3, 4 and 5 L/h) and the space velocity of 3, 4 and 5 L/h are 526 h⁻¹, 702 h⁻¹ and 877 h⁻¹, respectively. In this study, the following Eqs. (1) and (2) are used in order to calculate the accumulation of H₂S: 1) H₂S_{input} (mg) represents the total quantity of H₂S put into the bed at a given time; 2) Accumulated_{sorbent} (mg) refers to the H₂S accumulated quantity on alum sludge at a given time.

$$H_2S_{input} = \frac{PQM}{10^6 RT} C_0 t \quad (1)$$

$$Accumulated_{sorbent} = \frac{PQM}{10^6 RT} \left[C_0 t \int_0^t C_t dt \right] \quad (2)$$

where, P represents the pressure of gas (1 atm), Q is the inlet flow rate (L min⁻¹), M is the molecular weight of H₂S (34.06 g mol⁻¹), C_0 is the inlet concentration of H₂S (200 ppmv), while C_t is the outlet concentration of H₂S (ppmv), t is the reaction time (min), R is the standard ideal gas constant (8.31 J/mol·K), and T is the temperature (K).

2.3. Modeling

The three most commonly used models to describe the experiment data in breakthrough curves are the Thomas, Bed Depth Service Time, and Yoon-Nelson models, all used in this study (de Franco et al., 2018; Long and Loc, 2016; Rout et al., 2017).

The Thomas model (Thomas, 1944) is applied to evaluate sorbent adsorption capacity in a fixed bed column, and is useful in practical applications. It is based on two hypotheses: (i) the adsorption follows Langmuir isotherms and second-order sorption–desorption kinetics with no axial dispersion; and (ii) the adsorption is controlled by the mass transfer at the interface. The linearized form of the model is given as:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{Th}q_0m}{F} - K_{Th}C_0t \quad (3)$$

where, K_{Th} refers to Thomas rate constant (L mg⁻¹ min⁻¹), q_0 represents adsorption capacity (mg g⁻¹), m is the mass of sorbent in the column (g), while F is the volumetric flow rate (L min⁻¹). The kinetic coefficient K_{Th} and the adsorption capacity of the sorbent q_0 can be determined from a plot of $\ln[(C_0/C_t)-1]$ against t at a given flow rate.

The BDST model (Hutchins, 1973) was used to describe the relationship between the service time and the column packed-bed depth. It mainly focuses on predicting the time taken by the sorbent to remove a specific amount of adsorbate from bulk phase before exhaustion. This model is based on the assumption that the surface reaction step is rate-controlling. The model is given as:

$$t = \frac{N_0h}{uC_0} - \frac{1}{KC_0} \ln\left(\frac{C_0}{C_t} - 1\right) \quad (4)$$

where, K is the constant (L mg⁻¹ min⁻¹), N_0 is the adsorption capacity (mg L⁻¹), h is the bed depth (cm), u refers to the linear flow rate (cm min⁻¹), and t is breakthrough times (min). BDST curves can be plotted using adsorption data, while estimation of the characteristic parameters K and N_0 can be computed from the slope and intercept of the plots.

To evaluate a fixed bed adsorption kinetics, the Yoon-Nelson model (Yoon and Nelson, 1984) is often used, which is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the

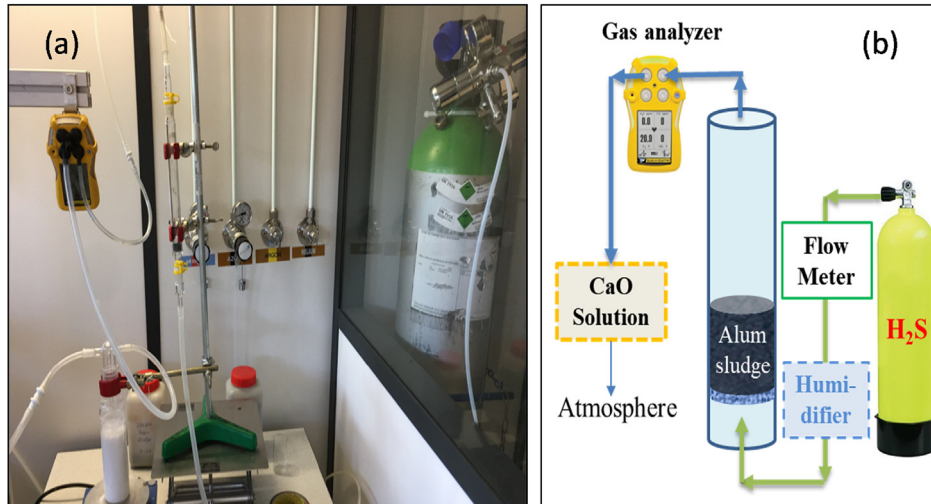


Fig. 1. Photographic description (a), and the schematic description (b) of the fixed-bed adsorption system.

probability of adsorbate adsorption and the probability of adsorbate breakthrough on the sorbent. The model provides information about the breakthrough rate in a fixed-bed column and the time realized to achieve 50% breakthrough. The linearized model for a single component system is expressed as:

$$\ln \frac{C_t}{C_0 - C_t} = K_{YN}t - \tau K_{YN} \quad (5)$$

where, K_{YN} is the rate constant (min^{-1}) and τ is the special time required for 50% adsorbate breakthrough (min). The calculation of theoretical breakthrough curves for a single-component system requires the determination of the parameters K_{YN} and τ for the adsorbate from the plot of $\ln[C_t/(C_0 - C_t)]$ versus sampling time (t).

2.4. Determination of mass transfer coefficient

Mass transfer was described as a lumped overall resistance. Ideal homogeneous phase was the original thought of sorbent particle, diffusion occurs with a constant effective diffusivity, mass transport is slower than reaction kinetics (Gutiérrez Ortiz et al. 2014). Thus, the mass transfer is described as:

$$\frac{\partial q}{\partial t} = K_a(q_e - q) \quad (6)$$

where, K_a represents overall effective mass transfer coefficient, q_e is the value of q in equilibrium with C , q is the concentration of H_2S (or load) in solid phase.

If the equilibrium isotherm is linear ($q_e = K_e C$), an analytic expression can be derived, such as Klinkenberg performed (Klinkenberg, 1948) using dimensionless equations as follows:

Mass balance in the bed:

$$\frac{\partial \varphi}{\partial \xi} + \frac{\partial \phi}{\partial \tau} = 0 \quad (7)$$

Adsorption velocity:

$$\frac{\partial \phi}{\partial \tau} = \varphi - \phi \quad (8)$$

where: $\varphi = \frac{C}{C_0}$; $\phi = \frac{q}{q_s}$; $\xi = \frac{K_e K_a Z}{u} \left(\frac{1-\varepsilon}{\varepsilon} \right)$; $\tau = K_a \left(t - \frac{z}{u} \right)$ q_s is the exhausted value of q , K_e is the equilibrium constant, z is the distance from the bed entrance, u is the gas interstitial velocity, ε is the bed void fraction, and t is the time. Therefore, by considering the initial and boundary conditions, the analytical solution is as follows:

$$\frac{C}{C_0} \approx \frac{1}{2} \left(1 + \operatorname{erf} \left(\sqrt{\tau} - \sqrt{\xi} + \frac{1}{8\sqrt{\tau}} + \frac{1}{8\sqrt{\xi}} \right) \right) \quad (9)$$

where, $\operatorname{erf}(x)$ is the Gauss error function, defined by Eq. (10).

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad (10)$$

The overall mass transfer coefficient (e.g., external and internal mass transfer) was given as:

$$\frac{1}{K_e K_a} = \frac{d_p}{6K_{ext}} + \frac{d_p^2}{60D_e} \quad (11)$$

d_p is the mean particle diameter, D_e is the effective diffusivity.

The external mass transfer coefficient (K_{ext}) was determined by

the Ranz–Marshall correlation (Ranz and Marshall, 1952):

$$Sh = 2 + 1.58Re^{0.4}Sc^{1/3}; \quad 10^{-3} \leq Re \leq 5.8 \quad (12)$$

where: $Sh = \frac{K_{ext} d_p}{D_m}$; $Re = \frac{u_e d_p \rho}{\mu}$; $Sc = \frac{\mu}{\rho D_m}$ D_m is the molecular diffusivity, d_p is particle diameter, ρ is gas density, μ is gas viscosity. The Fuller-Schettler-Gridding correlation was used to calculate D_m (Fuller et al., 1966):

$$D_m = \frac{10^{-3} T^{1.75} \left(\frac{1}{M_{gas}} + \frac{1}{M_{H_2S}} \right)^{0.5}}{\left(V_{gas}^{1/3} + V_{H_2S}^{1/3} \right)^2} \quad (13)$$

where, T in K, M is molecular weight, V is the diffusion volume, D_m in cm^2/s . D_e is effective diffusivity, which could be calculated by the Bosanquet equation (Gutiérrez Ortiz et al. 2014):

$$D_e = \frac{\varepsilon_p}{f_{tor}} \left[\frac{1}{D_m} + \frac{1}{D_K} \right]^{-1} \quad (14)$$

where, ε_p is particle porosity, f_{tor} is tortuosity factor, D_K is the Knudsen diffusivity, which is given by Eq. (15).

$$D_k = 4850 d_{pore} \left(\frac{T}{M_{H_2S}} \right)^{1/2} \quad (15)$$

where, d_{pore} is the mean pore diameter.

3. Results and discussion

3.1. Sorbent characterization

The moisture content of alum sludge cake was 63 wt%, while the mean particle diameter (d_{50}) of the alum sludge was 16.5 μm . Aluminum and calcium were the most abundant elements. Other elements were also present, including various metals, silicon and phosphorus. The pH of the alum sludge is 10, indicating the basicity. The total carbon is 30.6 wt% which is composed of 3.6 wt% inorganic carbon and 27.0 wt% organic carbon (in Table S1). Important to note, alum sludge shows a high specific surface area of 257.1 m^2/g , greater than “normal” sorbents such as used wood pellets chars (78.8 m^2/g) (Hervy et al., 2018); municipal solid waste incineration (MSWI) fly ash (17.7 m^2/g) (Wu et al., 2018); and rice husk activated carbon (168 m^2/g) (Nam et al., 2018). The relatively high specific surface area was due to the addition of activated carbon before the raw water purification processes in Carmaux (France) waterworks, in order to remove the odor and tastes of raw water.

The microstructures of the alum sludge were obtained by SEM and a representative EDS analysis which showed the chemical composition of its surface. Analysis result by EDX indicated a relatively large amount of C on the alum sludge. From the physical texture, the alum sludge presents a porous and rigid structure with many irregular particles being observed (Fig. S1). In particular, as shown in the EDX analysis, there are various metal elements on the surface of alum sludge, such as Al, Fe, Mg, Ca, and it has been demonstrated that adsorption of H_2S largely depends on the metal species contained in the materials and reacted with H_2S to produce metal sulfides (Hervy et al., 2018).

3.2. Sorption trials

Fig. 2 shows the sorption results obtained with 0.5 g alum sludge under different flow rate of 3, 4, 5 L/h, respectively. The inlet curve describes the quantity of introduced H_2S into the bed. Other

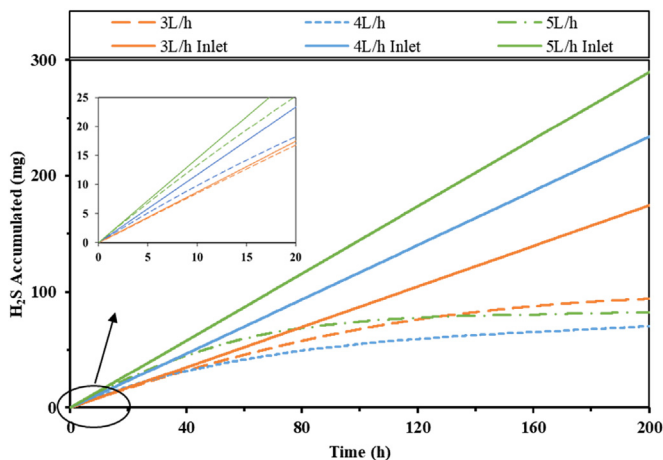


Fig. 2. Quantity of the H₂S fed into the reactor (Inlet curve) and fixed on 0.5 g alum sludge under different flow rate.

curves represent the H₂S accumulated in alum sludge. In general, sorption performance showed that in the initial test period, sorption occurred rapidly, and then slowed to gradually reach a flat stage with time under all three flow rates. The minimum flow rate (3 L/h) obtained the largest fixed quantity of 95.9 mg for 0.5 g of alum sludge, which is 191.8 mg H₂S/g alum sludge at 200 h. In particular, the flow rate of 3 L/h showed the best performance from the beginning of sorption. However, after about 133 h, the quantity of 3 L/h accumulated H₂S was over that of 5 L/h accumulated H₂S. The adsorption capacity revealed no significant dependence on the flow rate, for example, at 200 h, the accumulated H₂S on 0.5 g alum sludge under 3, 4, 5 L/h was 95.7, 72.2, 82.9 mg, respectively. In addition, for the 0.5 g alum sludge trials under 5 L/h, it has been repeated three times to check repeatability. This is an expected outcome as the adsorption capacity does not depend on the flow rate. Indeed, it is an intrinsic characteristic of the sorbent.

To test the effect of the sorbent quantity on the sorption performance, the amount of alum sludge was increased while the gas flow rate remained unchanged. Fig. 3 shows the results obtained with 0.5 g and 1.0 g alum sludge, which corresponded to the 0.5 and 1.1 cm bed height under 5 L/h flow rate. It was observed that the accumulated H₂S on 0.5 g and 1.0 g alum sludge at 215 h are 82.9 mg (165.8 mg H₂S/g alum sludge) and 235.4 mg H₂S/g alum sludge, respectively. The increase of alum sludge quantity improved

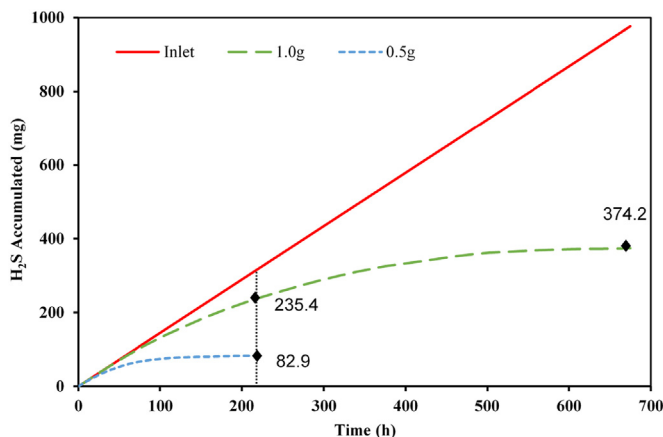


Fig. 3. Quantity of the H₂S fed into the reactor (Inlet curve) and fixed on different mass of alum sludge under 5 L/h flow rate.

H₂S removal, contact time was a crucial parameter for H₂S removal. At about 667 h, the accumulated H₂S was 374.2 mg H₂S/g of alum sludge. The capacity of the alum sludge-based sorbent is much higher than the majority sorbents, e.g., pyrolysis char = 57.6 mg H₂S/g (Hervy et al., 2018), Fe₂O₃-based sorbent = 17.1 mg H₂S/g (Long and Loc, 2016), and sewerage sludge-based sorbents = 8.63 mg H₂S/g (Gutiérrez Ortiz et al. 2014). This may be due to alum sludge specific surface area and pore structural differences. The alum sludge presents microporous structure, with sorption occurring in these pore sites (Yan et al., 2004). Furthermore, the various metals (e.g., Al, Ca, Mg, Fe) contained in the alum sludge could possibly facilitate H₂S adsorption (Hervy et al., 2018).

3.3. Breakthrough through curves modeling

3.3.1. Model parameters

Breakthrough curve and breakthrough time are vital factors for operation and dynamic description of an adsorption process (Dong and Zhao, 2018). In order to explain the dynamic adsorption behavior and to scale it up for industrial application, Thomas, BDST and Yoon-Nelson models were utilized. The determined relative constants and correlation coefficients for all three models are shown in Table 1. All the model constants (K_{Th} , K , K_{YN}) increased with the decreasing of sorbent height, which likely due to the increase in mass transfer resistance (Gutiérrez Ortiz et al. 2014; Rout et al., 2017). By increasing the flow rate, the value of K_{Th} increased and q_0 decreased, which attributed to the lower empty bed contact time (EBCT) resulting in insufficient contact between the adsorbate with the available active sites on the sorbent.

The correlation coefficients R^2 of Thomas, BDST, and Y–N models were 0.90, 0.93, 0.91, respectively, under 1 g alum sludge and 5 L/h flow rate, while Thomas model has the highest R^2 of 0.93 under the 0.5 g alum sludge and 5 L/h. However, the R^2 the three models were not satisfied under the 0.5 g alum sludge 4 L/h condition. This is due to the experiment data turbulence and could not fit well with the models. As shown in Fig. 4 (b), the experimental data slightly deviate from a model line, suggesting the complex nature of the H₂S adsorption process by alum sludge, which might be due to more than one rate limiting step (Rout et al., 2017). Additionally, the Thomas, BDST, and Y–N models' R^2 under the 0.5 g alum sludge and 3 L/h condition were 0.9, 0.93, 0.92, respectively, indicating that all three models accurately predicate H₂S breakthrough.

The simulated breakthrough curves as well as experimental data are presented in Fig. 4. The capacity of the sorbent determined the general position of breakthrough curve, with respect to sorbent height and flow rate. Apart from the breakthrough part of Fig. 4 (a) and initial part of (d), and compared with correlation coefficients, all Thomas, BDST and Y–N models can better describe the adsorption behavior. The 50% ($C_t/C_0 = 0.5$) experimental breakthrough time and their corresponding simulated time by the three models were calculated and presented (Table S2). The Thomas, BDST and Y–N models could predict the breakthrough time of 0.5 g alum sludge under 3 L/h with the same 2.0% deviation. However, the deviation was 28.3, 33.3, 34.5% when those models were applied to 0.5 g alum sludge under 4 L/h condition. This may be due to the turbulence of experimental time data around 50% breakthrough capacity. As shown in Fig. 4 (b), the turbulence of the data makes the three simulation curves behind of the experimental time. Regarding the 0.5 g alum sludge under 5 L/h flow rate, the prediction of Thomas model was the best (deviation of 1.9%), compared to the BDST model (3.6%) and Y–N model (5.4%). In addition, among the three models, the BDST model could well predicate the 1.0 g alum sludge under 5 L/h, with the lowest deviation of 3.1%.

Table 1
Model parameters calculation.

C_0 (mg/kg)	m (kg)	Q (L/min)	K_{Th} (m ³ /kg-min)	q_0 (kg/L)	R^2	K (L/kg-min)	N_0 (kg/L)	R^2	K_{YN} (min ⁻¹)	τ (min)	R^2
200	0.001	0.083	0.4612	0.235	0.90	0.5	0.222	0.93	0.0001	14477.9412	0.91
200	0.0005	0.083	1.9765	0.107	0.93	2.3	0.108	0.89	0.0006	3301.3600	0.85
200	0.0005	0.067	1.3835	0.083	0.78	1.1	0.090	0.75	0.0004	3537.1429	0.70
200	0.0005	0.050	1.4165	0.124	0.90	1.4	0.118	0.93	0.0004	5930.2326	0.92

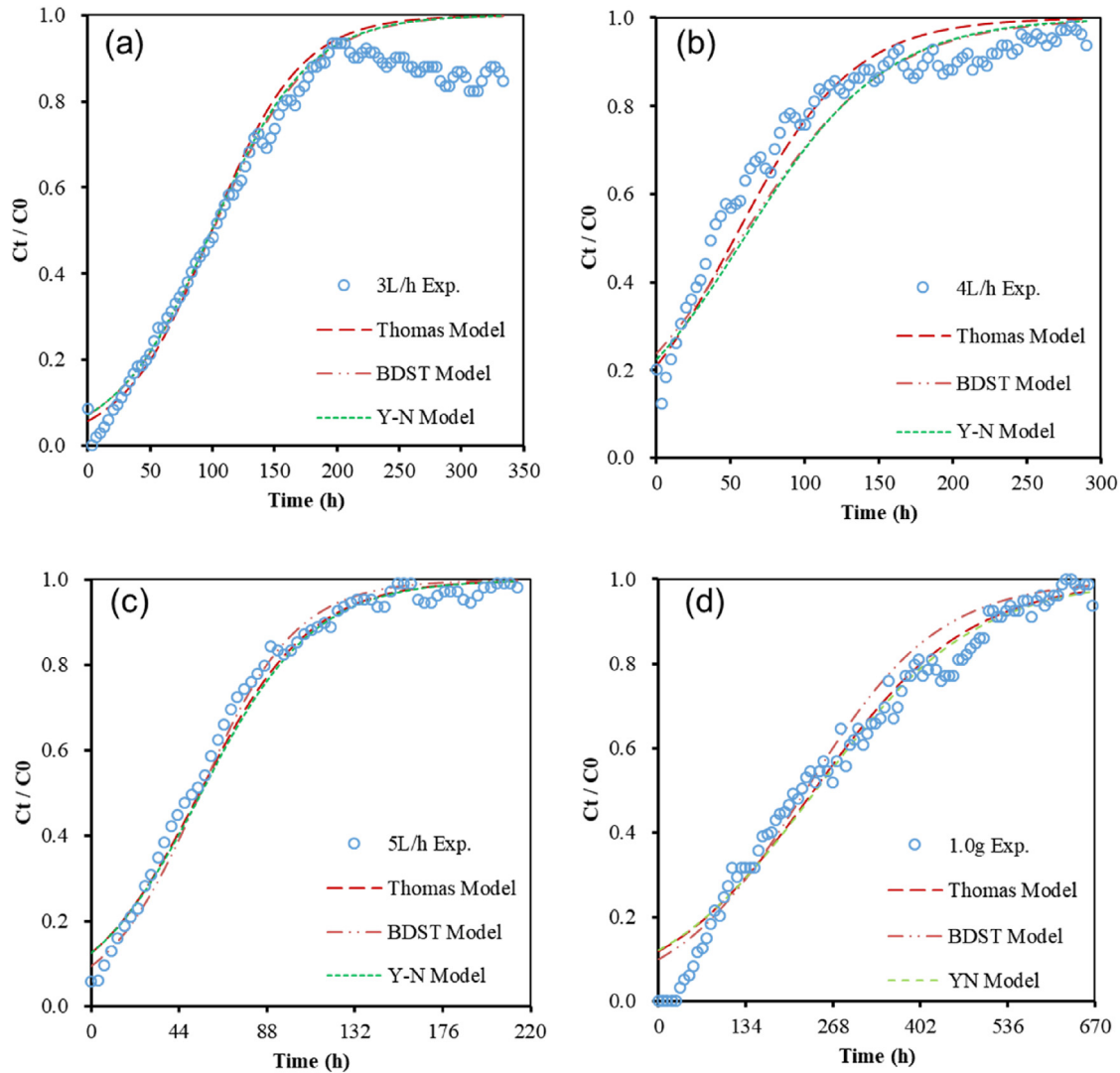


Fig. 4. The simulative curves and experiment data under three different model, (a), (b), (c) 0.5 g alum sludge under the flow rate of 3, 4, 5 L/h, (d) 1 g alum sludge under the flow rate of 5 L/h.

3.3.2. Effect of flow rate

Fig. 4 (a), (b), (c) show the effects of flow rate (3, 4 and 5 L/h, respectively) on the sorption, keeping constant the inlet H₂S concentration (200 ppmv) and the alum sludge mass (0.5 g). The flow rate represents the major influence in the shape of the breakthrough curve. By increasing the flow rate from 3 to 5 L/h, a decrease in both breakthrough and exhaustion times occurred from 350 to 220 h. The lower flow rate presented a longer breakthrough time, reflecting a wider mass transfer zone. Moreover, the results also indicated that by increasing the flow rate at a constant bed height (mass), the breakthrough time tend to become lower. For example, for $m = 0.5$ g, H₂S adsorption saturation time varied from 200 to 151.7 h with the flow rate increasing from 3 to 5 L/h.

Increasing flow rates result in a lower residence time. It also weakens the H₂S interaction with alum sludge and disturbs the intraparticle mass transfer between the H₂S and the alum sludge (Zheng et al., 2017). Intra-particle diffusion has been treated as the rate limiting step of adsorption process. Decreasing the flow rate could facilitate the intra-particle diffusion (Aguilera and Gutiérrez Ortiz, 2016; Arim et al., 2018). Furthermore, a more H₂S-alum sludge interaction and higher diffusion of H₂S onto alum sludge could make use of the maximal percentage of the bed, which improved the column performance. Similar trends have been reported by other researchers using different sorbents (e.g., Fe₂O₃-based sorbent and dolochar) (Long and Loc, 2016; Rout et al., 2017). Additionally, in Fig. 4 (a), the differences of experimental data and

three dynamic adsorption model curves observed near the breakthrough point can be attributed to lower concentration gradient between adsorbate in the sorbent surface and in the bulk phase. Similar phenomenon was reported by de Franco et al. (de Franco et al., 2018) by using activated carbon for diclofenac removal from water in a fixed-bed column. The lower flow rate showed flatter breakthrough profiles, with a more extended breakthrough zone.

3.3.3. Effect of bed height

Fig. 4 (c) and (d) present the effects of bed height (0.5 or 1.1 cm) on H₂S sorption. Increasing the bed height from 0.5 to 1.1 cm resulted in an increase in both breakthrough and exhaustion times from 220 to 670 h. However, contrary to the effect of the flow rate, as the bed depth increases, the breakthrough and the saturation time also increase, resulting in a greater operating time to take the column to the exhaustion point. By increasing bed height, the slope of the breakthrough curves became flatter, result in a longer mass transfer zone (MTZ). This is because the quantity of alum sludge was increased, more binding sites were available for sorption (Ahmed and Hameed, 2018). For a lower bed height, the mass transfer was controlled by the axial dispersion phenomena, result in a reduction of the diffusivity of H₂S. Thus, H₂S does not have enough time to diffuse into the alum sludge, allowing H₂S leaving the column earlier. On the other hand, the contact time between the H₂S and the alum sludge is higher when the bed depth increases (Rout et al., 2017). Similar types of results have already been reported in earlier researches (Aguilera and Gutiérrez Ortiz, 2016; de Franco et al., 2018; Long and Loc, 2016).

3.4. Adsorption mechanisms of H₂S onto alum sludge

3.4.1. Sorbent characteristics before and after the adsorption trials

As shown in Table 2, S increased from 0 to 34,981 mg/kg after sorption, suggesting that H₂S was sorbed onto alum sludge. During the H₂S removal trials, the alum sludge pH decreased from 10 to 7.5. The pH decreasing from 10 to neutral was likely due to the dissolution of H₂S in moist surface of the alum sludge and formation of sulfuric acid. It also suggested that the presence of air promoted the formation of acidic species, resulted in the acidification of sorbent (alum sludge) surface (Hervy et al., 2018). Nevertheless, the pH decrease seemed insignificant compared with the results in the literature. E.g., Bandosz (2002) reports that a pH decreasing from 9.7 to 2.8 when using the moist activated char for H₂S removal from. It suggested that the formation of sulfur oxide species is relatively low in the current study.

It has been pointed out by Yan et al. (2004) that pH has impact on the efficacy of H₂S dissociation and oxidation. The dissociation of H₂S prefers the basic pH. By accumulating of HS⁻ ions, they were oxidized to sulfur polymers (Bandosz, 2002). On the contrary, the moderately or acid sorbent is believed to inhibit the dissociation of H₂S and the creation of H₂S ions. After the sulfuric acid is formed, these ions are oxidized to sulfur oxides (in low concentration and small pores). In the literature, a threshold value of pH 4.5 was proposed (Yan et al., 2004). If pH is below 4.5, only physical adsorption could occur, and the concentration of dissociated H₂S

ions is negligible.

As such, the adsorption process of alum sludge was dominated by chemisorption as the pH value of alum sludge is 10. The H₂S first and second dissociation pK_a constants are 7.2 and 14, respectively. Thus, HS⁻ ions will be at high concentration, resulting in the formation of polysulfides. Along with the reaction progressed, pH will decrease and change from caustic to neutral.

It can be seen from Table 3 that alum sludge presents a greater micropore volume and surface area. The pore structural properties of alum sludge were significantly modified during the H₂S removal trials. The adsorption process reduces the micropore volume as well as the surface area (S_p) of alum sludge. The microporous volume of alum sludge was zero after the adsorption trials, which can be explained by the higher amount of H₂S adsorbed by alum sludge in these pores.

In addition, the average pore diameter of alum sludge also increases from 2.4 nm to 5.3 nm by H₂S adsorption process. This could suggest that adsorption takes place in most of the smaller diameter pores. As these pores are getting less and less, the number of pores with a greater diameter remains stable. The average overall pore diameter value measured is based on the nitrogen adsorption test, which was carried out on the exhausted alum sludge sorbent. Similar observations were also made by de Falco et al. (2018), Hervy et al. (2018), and Sigot et al. (2016). Yan et al. (2004) states that the physical conditions for H₂S adsorption and oxidation require the pores containing functional groups and small enough when at low humidity a water film could be created, and this seems in the range between the 0.5–1 nm region. In addition, by heating the exhausted alum sludge to 200 °C, the relevant S_p and the microporous volume were increase. It suggested that the H₂S is desorbed. The exhausted alum sludge could potentially be used again by thermal regeneration, further studies would be warranted.

The SEM-EDX image in Fig. 5 was obtained from the exhausted alum sludge. The EDX peaks clearly show adsorbed sulfur, confirming H₂S sorption onto alum sludge (Nam et al., 2018). Regarding the other element analysis, it was in accordance with the ICP results (Table S1), as well as the TEM-EDX image which is presented in Fig. 6.

It can be seen from Fig. 6, the exhausted alum sludge contained various metals such as Al, Ca, Fe, Mg. In addition, C, Si and O were also found on the surface of exhausted alum sludge, which was corresponding with the abovementioned ICP and SEM-EDX result. Apart from that, S was observed and it was homogeneously distributed throughout the alum sludge surface. Noteworthy, the S distribution appears to be correlated with Fe, Ca, Mg, and O distribution. This indicates that H₂S sorption was likely preferred on alum sludge metal oxide species. The reaction between various metal oxide species with H₂S could produce metal sulfides (de Falco et al., 2018). Additionally, alum sludge O-containing groups could have triggered an H₂S oxidation reaction and increased the H₂S removal capacity (Hervy et al., 2018).

3.4.2. Identification of sulfur products

To go further in the identification of the gas removed during the thermal treatment, sulfur species coupled with MS analyses were performed with raw and used alum sludge. Fig. 7 shows the derivative thermogravimetric (DTG) curves and the releasing of the effluent. Based on literature data (Hervy et al., 2018; Nam et al., 2018; Yan et al., 2004; Zeng et al., 2018), there are two temperature ranges for sulfur compound desorption, while the corresponding releasing gas provides clues on the nature of these compounds: 1) In the first zone (highlighted in green in Fig. 7) between 200 and 350 °C, a SO₂ release suggested the desorption of physisorbed SO₂ or other sulfur oxides, while a H₂S release reveals the decomposition of metallic sulphides; 2) In the second zone

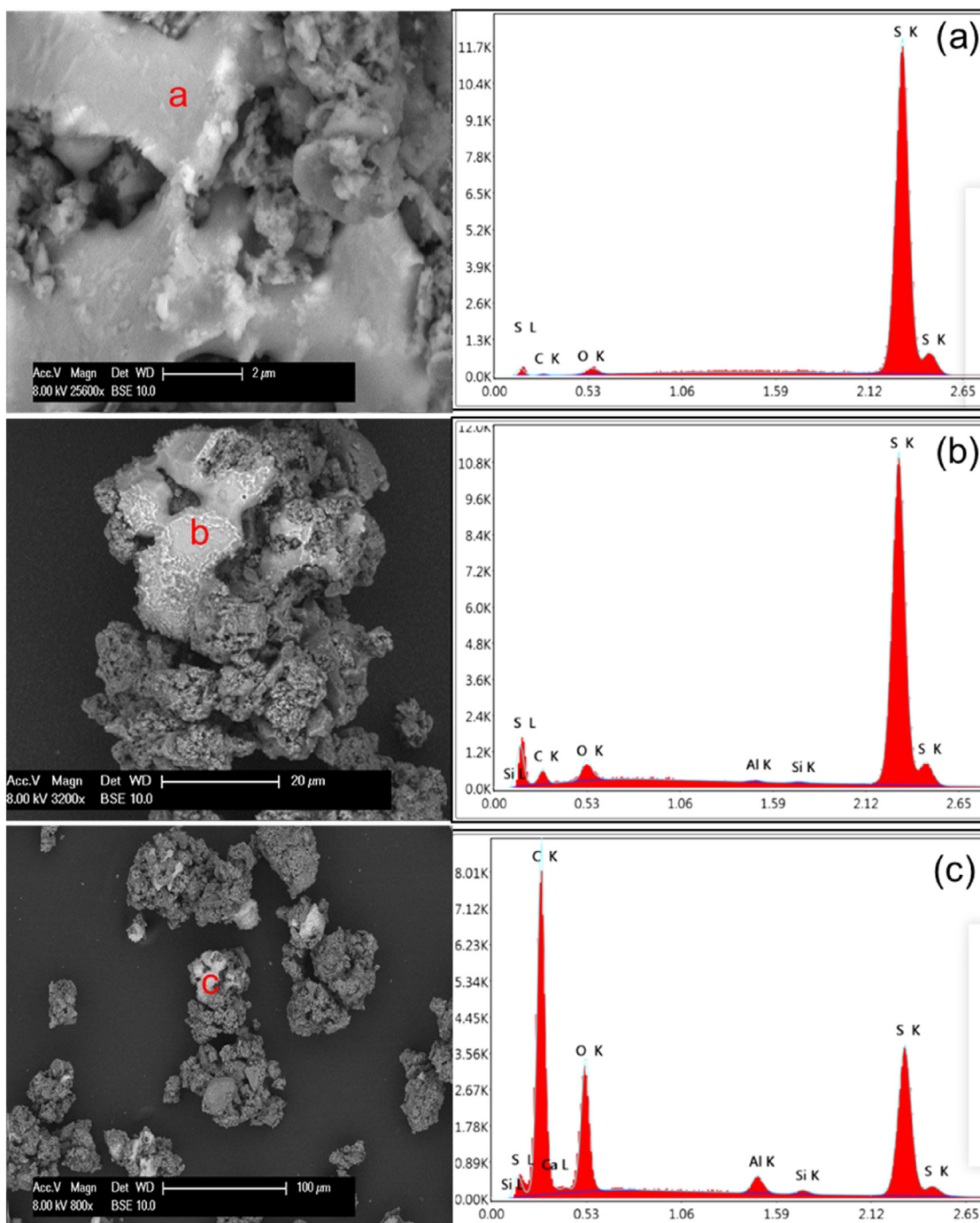
Table 2
Elemental analysis and pH of the sorbent.

Characteristics	Alum sludge	Exhausted alum sludge
pH	10.0	7.5
S (mg/kg)	0	34,981
C (%)	30.7	20.0
N (%)	0.5	0.5

Table 3

Structural properties of alum sludge.

Samples	S_p (BET) (m ² /g)	S_{mic} (m ² /g)	V_{mic} (cm ³ /g)	$V < 2$ nm (cm ³ /g)	$V < 25$ nm (cm ³ /g)	d_{pore} nm
Alum sludge	238 (105 °C)	119.56	0.05	0.082	0.237	2.4–3.2–5.0
Exhausted alum sludge	65 (105 °C)	1.74	0.00	0.015	0.136	3.3–5.3
	111 (150 °C)	29.13	0.01	0.033	0.154	2.4–3.2–5.0
	198 (200 °C)	93.45	0.04	0.069	0.195	2.4–3.2–5.0

**Fig. 5.** SEM-EDX of the exhausted alum sludge.

(highlighted in orange in Fig. 7) between 350 and 600 °C, a release of SO₂ reflects the decomposition of sulfur radicals and/or

elemental sulfur, while a release of H₂S indicates the decomposition of polysulfides.

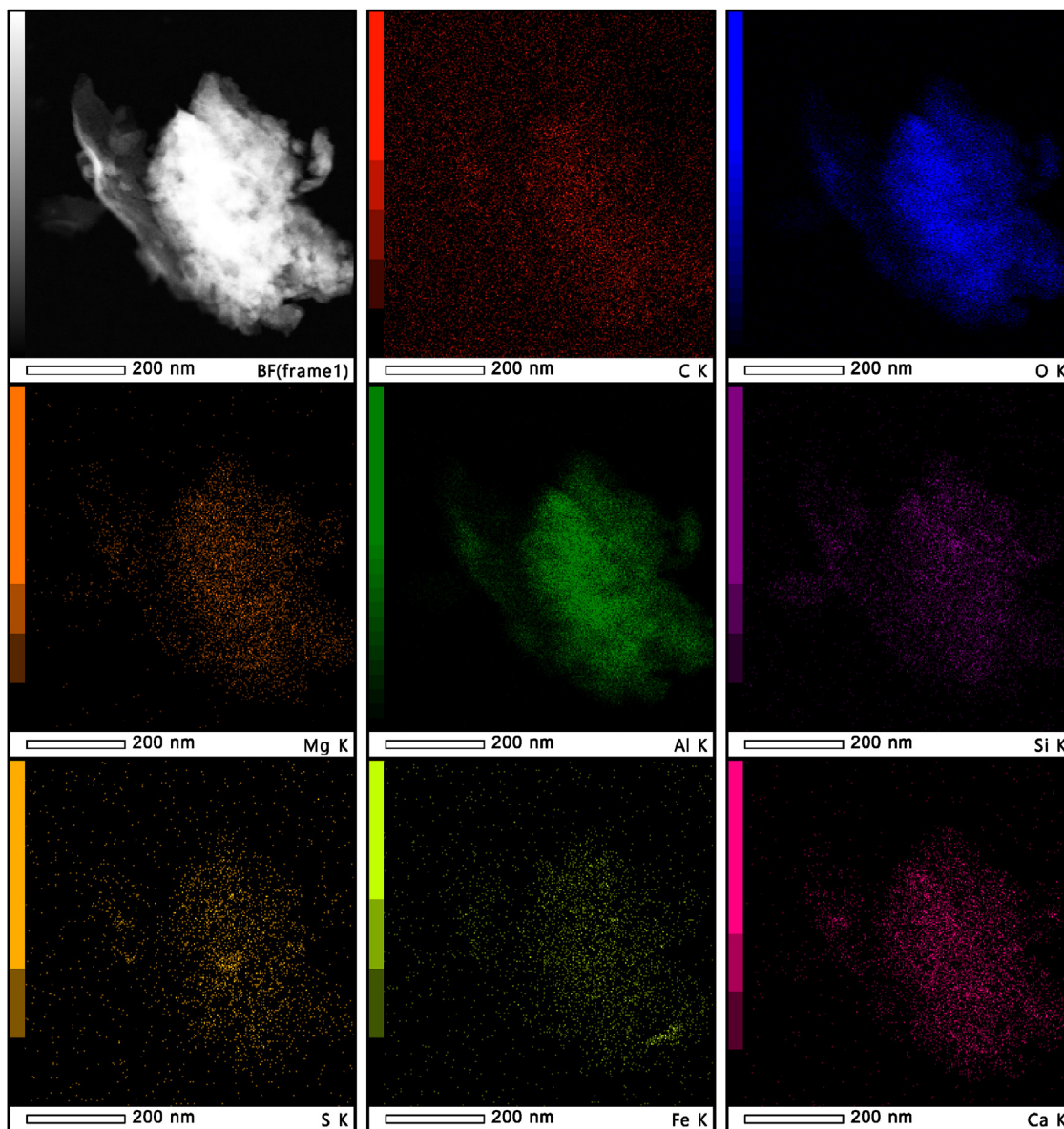


Fig. 6. TEM-EDX images of the exhausted alum sludge sorbent.

As shown in Fig. 7, the DTG curves of both raw and exhausted alum sludge present two prominent peaks at around 110 and 300 °C. The peak at 110 °C, corresponds to dehydration processes as well as the desorption of weakly adsorbed H₂S (Zeng et al., 2018). The weight loss of exhausted and raw alum sludge in this stage was 20.8 and 6.7%, respectively. However, the second DTG peaks (around 300 °C) of exhausted alum sludge were wider than the DTG peak curve of raw alum sludge. The weight loss of exhausted and raw alum sludge in this stage was 21.7 and 3.1%, respectively. This was in agreement with the ICP results. Moreover, the mass lost between raw and exhausted sorbent was 31.7%. From the ICP analysis, the increased S in exhausted sorbent was 33.5%. This represents the removal of SO₂ from the decomposition of oxysulfur acids or H₂S from decomposition of alkali metal sulfides, while the peak at 350–600 °C is probably the result of the desorption of elemental sulfur and decomposition of the surface reaction products (Siriwardane et al., 2017).

The Mass Spectrometry analyses coupled with the thermal analyzes allows identification of the gas associated with a thermal

transformation of the solid. For exhausted alum sludge, the first mass loss occurred at 310 °C, while a release of H₂S (red curve) and SO₂ (orange curve) was observed. The second peak at 510 °C corresponding to a release of H₂S, SO₂ and CO₂, it indicates the resultant products are sulfur radicals, elemental sulfur, and/or metal sulfides (Bandosz, 2002; Hervy et al., 2018; Yan et al., 2002). This behavior (e.g., mass loss at 310 °C and a simultaneous release of H₂S and SO₂) also suggested that the resultant sulfur products formed on alum sludge were sulfur oxide species, alkali metal sulfides (310–350 °C), sulfur radicals, elemental sulfur (SO₂ release from 350 to 500 °C), polysulfides and/or metal sulfides (H₂S release from 350 to 500 °C). Previously published works have shown similar observations (Sigot et al., 2016; Siriwardane et al., 2017; Zeng et al., 2018), which established that the first peak in the range of 200–600 °C was likely the oxidized sulfur desorption, while the second peak was the elemental sulfur components.

The exact locations of the two DTG peaks vary in temperature from literature. The study carried out by Yan et al. (2002) showed the DTG peaks of the exhausted sorbent were at around 290 and

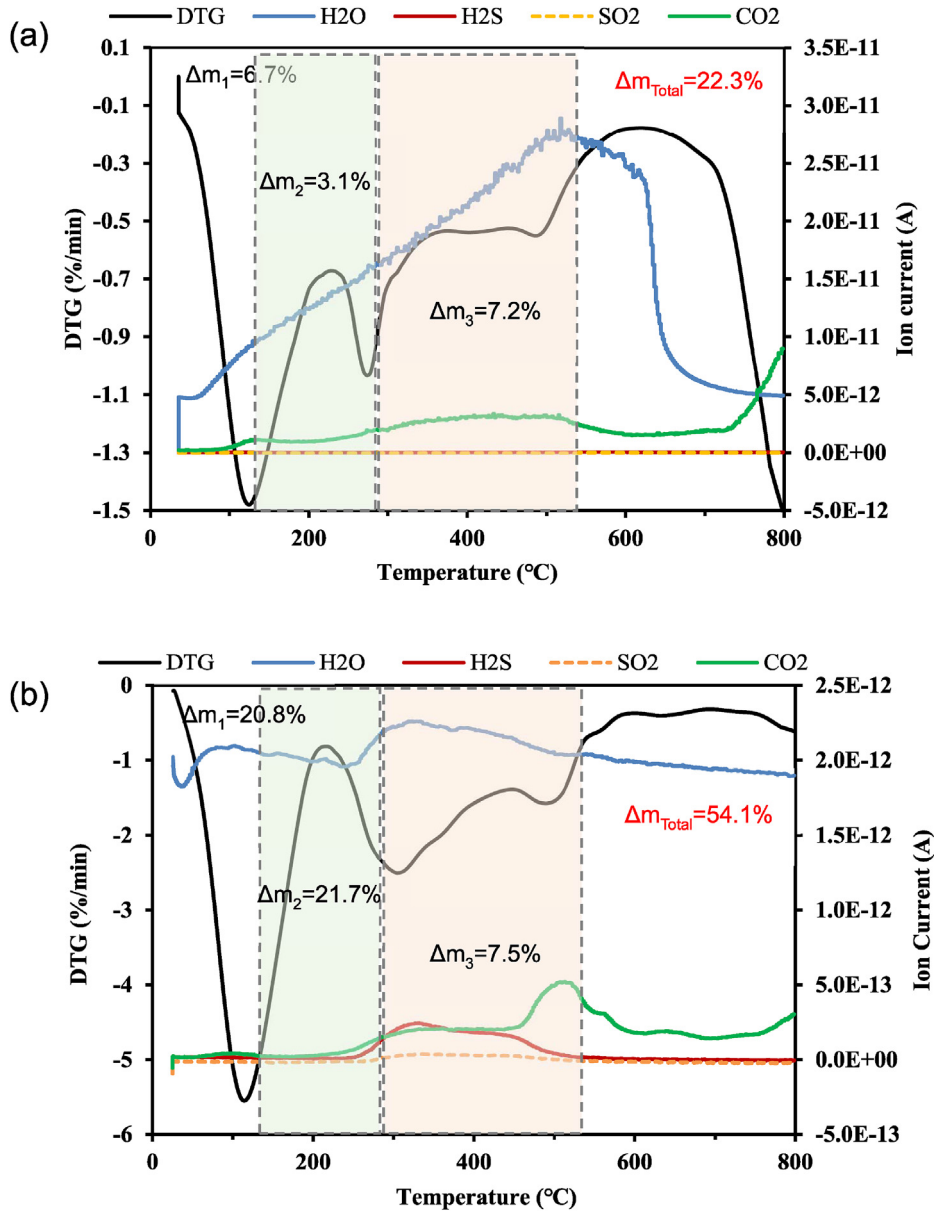


Fig. 7. TGA-MS analysis of raw alum sludge before (a) and after (b) the adsorption trials.

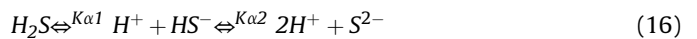
530 °C, while in the study of [Hervy et al. \(2018\)](#) the two DTG peaks were at 285 and 370 °C. Both studies agree that the peak relative to the elemental sulfur is behind sulfur oxides peak. The DTG peaks occur at different temperatures is due to the various physico-chemical characteristics of the sorbent. [Yan et al. \(2004\)](#) pointed out that the sulfur oxides were more soluble than elemental sulfur. Washing could be applied on the exhausted sorbents to check the differences in their thermal desorption pattern, and this could be the form about another study regarding H₂S adsorption onto alum sludge.

The presence of various forms of sulfur compounds in addition to the oxides of sulfur on the surface of alum sludge after H₂S adsorption indicates that chemical reactions are involved in H₂S retention. The alkaline and chemical promoter presence on the surface and water facilitated dissociation, dimerization and oxidation reactions.

3.4.3. Proposed mechanisms of H₂S removal by alum sludge

The various resultant sulfur compounds suggested that the sorption process of H₂S on alum sludge consists of a complex reaction. This is likely due to the presence of various reactive sites, such as carbon, metal oxides and carbonates ([Bamdad et al., 2018](#); [Hervy et al., 2018](#)). Based on these data, the following reactions ([Fig. 8](#)) proposed are expected to occur during alum sludge H₂S sorption.

When the sorption process begins and H₂S molecules are located on alum sludge active sites, alum sludge humidity/moisture can dissociate the H₂S ([Hervy et al., 2018](#)):



with $K_{\alpha 1} = 10^{-7}$ and $K_{\alpha 2} = 10^{-13}$. When the pH is basic, the HS⁻ concentration is relatively greater, which forces the created sulfur atoms to be close to each other, capable of creating polysulfides.

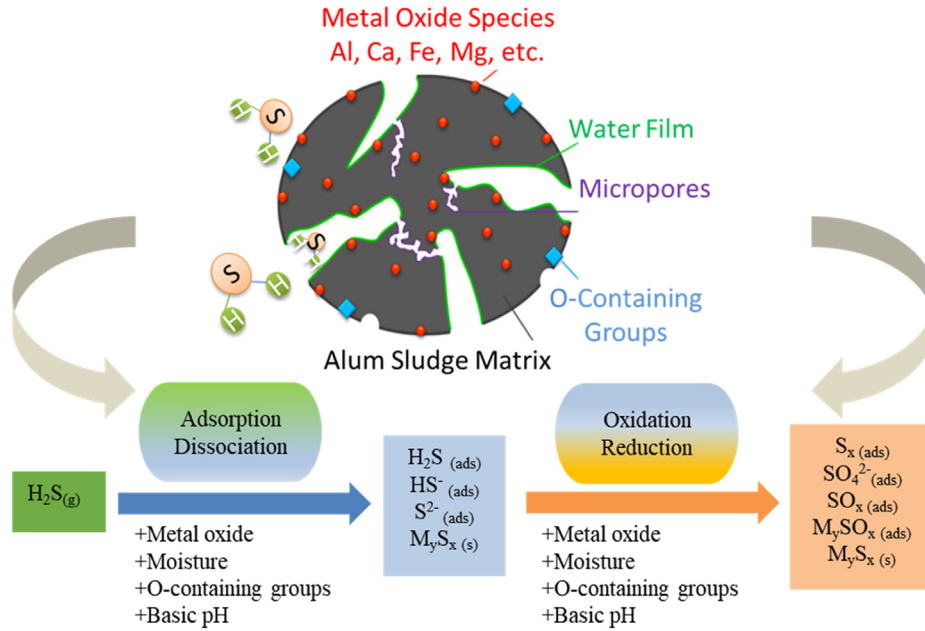
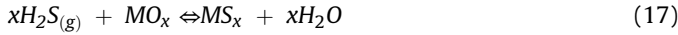


Fig. 8. Mechanisms of H₂S adsorption onto alum sludge.

Secondly, H₂S reacts with the alum sludge-containing metal oxide species (MO_x) to produce metal sulfides (MS_x) (Hervy et al., 2018; Wu et al., 2018). Thereafter, the metal sulfur oxidation with oxygenated organic and inorganic species leads to the formation of metal sulphate (Bandosz, 2002). The reaction could be as follows:



Lastly, O-containing groups in alum sludge also increase the H₂S removal capacity by the H₂S oxidation reaction (Yan et al., 2002). In the presence of air, alum sludge surface acidification can be explained by the oxidation of H₂S to H₂SO₄ (Bandosz, 2002).



3.5. Determination of the mass transfer coefficient

The H₂S sorption mechanism is governed by external and internal diffusion mass transfer coefficient. Thus, correctly estimating the various mass transfer coefficients is a vital step. To predict the dynamics of the H₂S sorption, mathematical models must include the mass-energy balance of the sorbent and the gas phase in the bed as well as an equation for the mass flux (de Franco et al., 2018). The axial dispersion, nonlinear equilibrium behavior, resistance to mass transfer and sorption kinetics are described in terms of partial differential equations, which generally involve a numerical solution (Arim et al., 2018).

Modeling and simulation of empirical models such as Thomas, BDST and the Yoon-Nelson models for H₂S adsorption have been investigated. However, these models are based on the assumption that the adsorption rate is limited by the surface reaction. Thus, the current study mainly focuses on the overall mass transfer coefficients determination from the mathematical description of breakthrough curves and their dependency on experimental conditions, which means that the external/internal diffusions are

included.

Regarding the adsorption process, H₂S molecules are located on the surface of alum sludge. Diffusion mechanisms govern the transport of H₂S molecules into the alum sludge pores. In porous materials, diffusion mechanisms are of several types: i) molecular diffusion caused by collisions between molecules, ii) Knudsen diffusion caused by collisions of the molecules with the walls of the pore, iii) surface diffusion caused by the electrostatic forces exerted by the walls on the molecules. Since the alum sludge has microporous structure (Table 3). It may be concluded that Knudsen diffusion was the main diffusion mechanism.

In this study, based on the selected parameters (Table S3), the value of tortuosity factor (Gutiérrez Ortiz et al. 2014), the equilibrium constants (K_e) calculated by fitting the experimental data, overall mass transfer coefficients are determined for H₂S surface diffusivity over interior surface of alum sludge. Results of the mass transfer coefficient from experimental breakthrough fronts at several conditions are shown in Table 4. External and overall mass transfer coefficients are slightly decreased along with flow rate. It should be noted that the external and overall mass transfer coefficients should be the same by using the same sorbent. However, an error of 35% under the flow rate of 3 L/h could be caused by the slow flow rate, leading to a very long saturation time (667 h). The Knudsen diffusion contributes to internal diffusion (Ahmed and Hameed, 2018); however, this contribution is very small compared to the contribution of external diffusion.

In addition, the Knudsen, Molecular, Effective and Pore diffusivity remained the same under different flow rate and mass of sorbent. This indicates that sorption mechanisms were the same regardless of the experimental conditions.

4. Perspectives

Alum sludge as an easily, largely available by-product of water purification processes was firstly reused for H₂S abatement. From this study, alum sludge H₂S adsorption capacity is relatively good compared to the majority of sorbents in the literature. Alum sludge could be directly reused as the “ready to use media” without any

Table 4
Determination of the various mass transfer coefficient.

Flow rate (L/h)	Mass (g)	Knudsen diffusivity D_k (m^2/s)	Molecular diffusivity D_m (m^2/s)	Effective diffusivity D_e (m^2/s)	Pore diffusion D_p (m^2/s)	Re	Sc	Sh	External mass transfer coefficient K_{ext} (m/s)	Overall mass transfer coefficient K_a (s^{-1})
5	1.0	4.98×10^{-5}	1.753×10^{-5}	2.5895×10^{-6}	1.2948×10^{-5}	0.0100	0.8490	2.2373	2.37	0.0017
5	0.5	4.98×10^{-5}	1.753×10^{-5}	2.5895×10^{-6}	1.2948×10^{-5}	0.0100	0.8490	2.2373	2.37	0.0017
4	0.5	4.98×10^{-5}	1.753×10^{-5}	2.5895×10^{-6}	1.2948×10^{-5}	0.0080	0.8490	2.2171	2.35	0.0017
3	0.5	4.98×10^{-5}	1.753×10^{-5}	2.5895×10^{-6}	1.2948×10^{-5}	0.0060	0.8490	2.1935	2.33	0.0011

extra treatment. Results demonstrated that alum sludge for H_2S control could be an emerging and promising approach for desulfurization. It will pave an avenue for odor control as well as the sustainable sludge management. Indeed, a necessary cost in adsorption technologies is the media replacement, i.e. the replacement of alum sludge in adsorption column in this study. No doubt, the choice of eco-friendly, sustainable, and low-cost alum sludge is in line with the need to develop the "Circular Economy". This is the first time and a small-scale alum sludge- H_2S sorption trial and more studies along with large-scale investigations are highly desirable. Moreover, the regeneration of exhausted alum sludge needs further investigation.

5. Conclusions

Alum sludge can be used for H_2S adsorption (adsorption capacity of 374.2 mg/g), this capacity is higher than that of several sorbent reported in literature. Application of Thomas, BDST and YN models suggested that the models can simulate the breakthrough curves, with R^2 values ranged from 0.7 to 0.93. The breakthrough behaviors were regulated by the bed depth and flow rate. The important alum sludge properties for H_2S removal are greater specific surface area, microporous volume, alkaline pH, metal species (especially Ca, Al, Fe) and O-containing groups. The mechanisms study highlighted various resultant sulfur compounds, resulting from a complex reaction mechanism. The overall mass transfer coefficients considering film resistance and pore resistance obtained by numerical modelling allowed to evaluating surface diffusivity of H_2S over the interior surface of alum sludge. Since the alum sludge has microporous structure, it can be concluded that Knudsen diffusion was the main diffusion mechanisms. Moreover, the Knudsen, Molecular, Effective and Pore diffusivity were remaining the same under different flow rate and mass of sorbent. It indicated that the adsorption mechanisms were the same regardless of the experimental conditions.

CRedit authorship contribution statement

Baiming Ren: Methodology, Data curation, Formal analysis, Writing - original draft. **Nathalie Lyczko:** Software, Investigation, Supervision. **Yaqian Zhao:** Supervision, Writing - review & editing. **Ange Nzihou:** Conceptualization, Methodology, Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.126010>.

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