Removal of H_2S and Mercaptan from Outlet Gases of Kermanshah Refinery Using Modified Adsorbents (Bentonite and Sludge)

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Abstract

In this work, adsorbents, namely bentonite and sludge, modified by iron and copper were used to remove the H_2S and mercaptan from Kermanshah refinery. The used adsorbents are inexpensive materials, which substantially decrease the operational costs. The structure of the adsorbents was analyzed using scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX). The effects of gas and flow rate on the H_2S and mercaptan removal were also studied. The results indicated that the bentonite modified by iron has a high capacity for removing H_2S (32.256 mg/g) and mercaptan (0.98 mg/g). Moreover, the adsorption capacity of the sludge modified by copper for removing H_2S and mercaptan was 11.18 and 0.81 mg/g respectively. Furthermore, by increasing the flow rate and concentration of H_2S and mercaptan, H_2S and mercaptan concentrations in the sludge output gas increased, but no considerable change was observed in the bentonite output gas.

Keywords: Gas Sweetening, Bentonite, Sludge, Adsorption, H_2, and Mercaptan

1. Introduction

One of the most important problems faced by natural gases is the presence of hydrogen sulfide and mercaptans in such gases, which decreases their commercial value. The common methods used for removing hydrogen sulfide have been adsorption, separation, and biological removal (Barea et al., 2014); all these methods have certain advantages and disadvantages. In the conventional methods, catalysts used require high-cost, high-technology, and special equipment, and they usually work in high pressure and temperature conditions, which increases the expenses of repairing, maintaining, and reviving (Gates et al., 1979). Among the disadvantages of catalysts is their high sensitivity and toxicity, if not kept in a suitable condition. If a catalyst becomes permanently toxic, it could not be revived by common methods and must be replaced.

Activated carbon is an ideal adsorbent with a high degree of porosity and surface area. Different

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characteristics of the activated carbon such as specific area, pore size, moisture, pH, and surface chemistry affect the adsorption of H_2S (Sasanipour et al., 2017). Furthermore, it has been observed that at lower pH values, a proper condition is provided for the oxidation of H_2S (Bagreev and Bandosz, 2001). Unfortunately, because of the weak catalytic properties of natural activated carbon, only a small portion of H_2S can be removed using this method. In order to improve the catalytic properties of activated carbon, the surface needs to be modified by methods such as oxidation, linking components containing nitrogen to the surface, and saturation with oxidants, bases, or metals (Bandosz, 2006). Saturating activated carbon using materials such as KOH and NaOH improves the adsorption capacity up to five times (Tsai et al., 2001).

Other weaker materials such as Na_2CO_3 can also improve the adsorption efficiency. Adding the aforementioned materials to activated carbon can influence the surface properties and increase the reaction between activated carbon and hydrogen sulfide (Xiao et al., 2008). Sludge-derived adsorbents have recently been considered; they have a smaller surface area compared to activated carbon, but, due to the presence of heavy metals in the sludge, it has more activated chemical sites than activated carbon to remove hydrogen sulfides. In a study, metal and urban sludge were combined at different mass ratios so that an adsorbent would be produced at different pyrolysis temperatures. The adsorption capacity of this adsorbent was reportedly around 1200 gr H_2S/m^3. They showed that the capacity of the metal adsorbent decreased as the pyrolysis temperature increased. However, by raising the pyrolysis temperature, the solid capacity of the urban sludge adsorbent also increased (Yuan and Bandosz 2007). In another study, the sludge obtained from wastes, fish waste, and similar compounds were carbonized at 650 and 950 ℃. The carbonized compound contained 26 to 45% carbon. These compounds, in a non-organic phase, contain oxides and metals such as silica, calcium, aluminum, and iron (Nielsen et al., 2015). To improve the amount of hydrogen sulfide adsorption, the dried sludge (obtained from wastes) was combined with polystyrene and sulfuric acid at different ratios, and the obtained compound was then carbonized at 950 ℃. Next, it was washed with water so that the additional salts would be removed, and the considered adsorbent was produced. They showed the adsorbent combined with polymer was able to remove a higher amount of hydrogen sulfide than the pure adsorbent (Ansari et al., 2005).

Alzouir et al. tested metal oxides such as zinc, tungsten, copper, cobalt, iron, molybdenum, tin, and nickel to remove hydrogen sulfide. They showed that molybdenum and tungsten oxides had high desulfurization properties, but their temperature range was limited because they formed carbides (Elseviers, Verelst, 1999). It has been shown that copper oxide adsorbent drastically reduces the concentration of hydrogen sulfide. However, copper oxide is reduced to copper in the presence of materials such as hydrogen and carbon monoxide, which then drops the desulfurization efficiency (Lee et al., 2001). Sulfatreat 400 HP, which is a commercial adsorbent, has been used for removing hydrogen sulfide from biogases. This adsorbent is a combination of metal oxides (Fe_2O_3 and Fe_3O_4) and an activating oxide containing one or multiple catalytic metals such as platinum, gold, silver, copper, cadmium, and nickel. The results showed that the capacity of this adsorbent is 0.11 gr H_2S for each gram of the adsorbent (Truong and Abatzoglou, 2005). Silica gel substances have been empirically used as a hydrogen sulfide adsorbent; some researchers put silica gel in a column and passed gas through it; they observed that hydrogen sulfide was selectively adsorbed by silica gel, while only about 2% of the CO_2 was removed (Chou et al., 1986). Zeolite is one of the most well-known hydrogen sulfide adsorbents, and it has three-dimensional pores in its crystalline structure, which enables it to adsorb hydrogen sulfide. To improve the adsorption capacity of zeolite, it has been modified by metals or metal oxides (Ozekmekci et al., 2015; Mohamadi et al., 2017; Salimi et al., 2017). Alonso et al. (2010) produced 13X and 5A zeolites for improving the properties of natural zeolite (Alonso-Vicario et al., 2010).

To improve the adsorption capacity of MSU-S adsorbent in desulfurization, it was modified by metals or metal oxides (Mohammadian et al., 2017; Rashidi et al., 2015). The results proved that the copper-modified MSU-S showed the highest capacity to adsorb sulfur compounds compared to other adsorbents. Melo et al. used 13X zeolite for removing hydrogen sulfide at 25 °C. They showed that the maximum adsorption capacity in this method can be equal to 53 mg H_2S per gram of the adsorbent (Melo et al., 2006).

In the present study, an adsorption method was utilized to remove hydrogen sulfide and mercaptan. At first, the adsorbents were modified by iron and copper, and the surface morphology was studied using SEM images. The existence of iron and copper in the adsorbent structure was proved by using the EDX spectrum. Next, the effects of the type and flow rate of the gas on the efficiency of the adsorbent was reviewed, and the adsorption capacity of the adsorbents was finally measured.

2. Materials and methods

2.1. Materials and instruments

Laboratory materials used in this research are as follows: copper (II) chloride dehydrate ($CuCl_2.2H_2O$) and iron chloride (III) ($FeCl_3.6H_2O$) purchased from MERCK Company. All the solutions were prepared with double-distilled deionized water. The SEM images were obtained using a HITACHI S-4160 field emission scanning electron microscope, and the amount of H_2S in the gas was measured by the gas chromatography device (Varian, model Fast RGA CP 3800). To measure the mercaptans in the gas, the detector tubes were made by the GAsTec Company (Japan).

2.2. Preparation of the bentonite as an adsorbent

Bentonite clay is placed in an oven for 48 hours at 104 °C so that their moisture is reduced to zero. The dried bentonite was manually turned into fine particles, and it was then ground into powder by an electric grinder. The obtained powder was passed through a 0.3 mm sieve, and a mixture with an average diameter of 0.3 mm was obtained.

2.3. Preparation of the sludge as an adsorbent

The sludge used in this research was obtained from the sludge drying unit of the wastewater treatment of Kermanshah Oil Refinery Company. To make sure that the sludge is uniform, about 20 kg of the aforementioned sludge was collected over two months. The collected samples were placed in an oven at a temperature of 104 °C for 48 hours so that they completely dry. Then, the dried sludge was manually turned into finer particles and passed through a 0.3 mm sieve so that only the finest particles would remain; finally, a mixture with an average diameter of 0.3 mm was obtained.

2.4. Preparation of modified nanozeolite

To prepare the adsorbents modified by Cu or Fe, 50 grams of the adsorbent were poured to one beaker and 28 ml of $FeCl_3$ (200 g/l) plus 12 ml of $CuCl_2$ (600g/l,) was added to it. Then, it was stirred for 4 hours at room temperature so that a uniform solution was formed. This solution was placed in an oven at 104 °C for 24 hours and cooled down to room temperature. Afterwards, the dried adsorbent was manually turned into fine particles and ground into powder by an electric grinder. The obtained powder was passed through a 0.3 mm sieve.

2.5. Methods for analyzing physical properties and surface area of the adsorbent

To calculate the bulk density of the adsorbent, a 100 ml beaker was filled with the adsorbent. The difference between the weight of beaker before and after the filling was recorded as W, and the density of the powder was calculated to be W/100 ml.

To calculate the density of the particles, a 50 ml beaker was filled with 10 grams of the adsorbent. Then, a certain amount of water was added to the adsorbent, and it rested for 24 hours so that the sedimentation process occurred at room temperature. After the sedimentation, the beaker was filled again with water, and the amount of added water was recorded as V_1. After discharging and drying the container, it was filled with water and the volume was recorded as V_2. The density of the particles was calculated using $10/(V_1-V_2)$.

a. Moisture content

To measure the humidity content of the adsorbent, a beaker, completely dried in an oven at a temperature of 105 ℃ for 4 hours, was weighed as C. Then, the beaker was filled with 10 grams of the adsorbent and weighted as A; afterwards, it was put in an oven for 8 hours at a temperature of 105 ℃. Finally, the beaker was left to cool down to room temperature and weighed again. The moisture content was calculated using the following formula:

$$\text{Percent humidity}\left(\%\right) = \frac{\left(A+C\right)_{before\ drying} - \left(A+C\right)_{after\ drying}}{\left(A+C\right)_{before\ drying} - C} \times 100 \tag{1}$$

b. pH measurement

2 grams of the adsorbent was dissolved in 100 ml of distilled water and stirred for 24 hours; it was then filtered using a paper filter; the pH of the resulting solution was calculated using a pH meter.

c. Analysis of the gas

Flame photometric detector gas chromatography (GC) was used to detect H_2S, and gas detector tubes were used in the feed gas for mercaptans; the detection ranges were 1 to 10 ppm for mercaptans. Each measurement was performed by inserting a detection tube through a gas outlet.

2.6. Dynamic experiments for removal of H_2S and mercaptan

A schematic diagram of the adsorption system is illustrated in Figure 1. A continuous flow column reactor (glass column), packed with prepared material, was used to measure the adsorption capacities of the synthesized materials for the feed gases at ambient temperature. The feed gases were generated from a vessel (12.7 kg) at ambient temperature. The pressure and gas flows were controlled by pressure regulator and mass flow controller (MFC) respectively. Before the experiments, the concentration of the feed gas was confirmed by gas chromatograph with a flame photometric detector GC (Varian, model Fast RGA CP 3800) through a by-pass line of the sorption column. Also, in different time intervals, the GC was used to monitor the concentrations of H_2S and mercaptan at the outlet of the sorption column. In this study, an equal amount of sample particles was packed into the column for each experiment. The packing length occupied by the sorbent particles was also kept equal in every experiment to maintain the same packing density. Each of the experiments was performed twice, and the measurement error was about 4%.
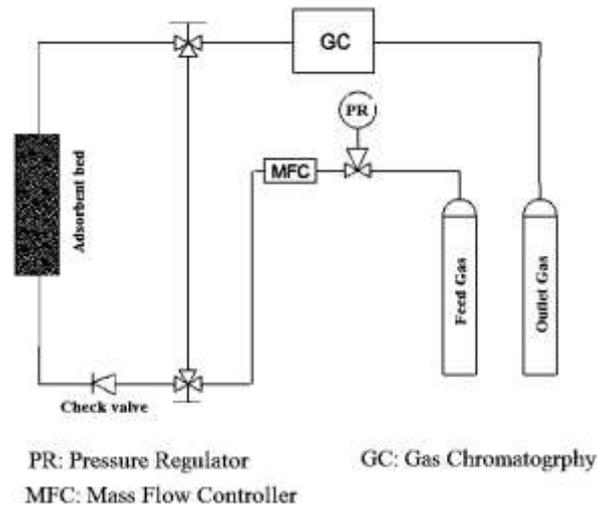
Figure 1
A schematic diagram of the adsorption apparatus.

2.7. Sample gases

To evaluate the efficiency of the adsorbent, two types of refinery gases containing different compounds were used as tabulated in Table 1.

Table 1
Analysis of feed gases.

Feed	NC_5	IC_5	NC_4	IC_4	C_3	C_2	C	H	H_2S	Mercaptan
F1	0.1	0.1	0.7	0.7	5.9	16.2	29	44.8	2.5	0
F2	0.1	1.6	50.4	14.6	26.6	5.6	0.7	0	0.4	2000 ppm

The mercaptan compounds consist of methyl and ethyl mercaptans having almost the same concentration.

2.8. Calculation of the adsorption capacity

In this method, after measuring the amount of H₂S and mercaptan in the gas, a specific amount of gas was passed through an adsorbent bed until it was saturated. The amount of H₂S in the output gas was measured, and, by using Equation 2, the adsorption capacity (AC) was calculated in mg of H₂S or mercaptan for each gram of the adsorbent.

$$Adsorbent\, Capacity = \frac{\left(C_f - C_0\right) \times V \times M_V}{V_M \times W}$$

(2)

where, W is the adsorbent weight of bed, and C_0 and C_f are the H₂S concentration in the inside and outside of the bed respectively. V, M_W, and V_M are the gas volume (ml), molecular weight of H₂S (34 mg/mmol) or mercaptan, and molar volume (22.4 ml/mmol) respectively.

3. Results and discussion

3.1. Physical properties and properties of the adsorbent surface

Different properties of the modified and unmodified adsorbents, including density, pH, and moisture content are listed in Table 2.

Table 2
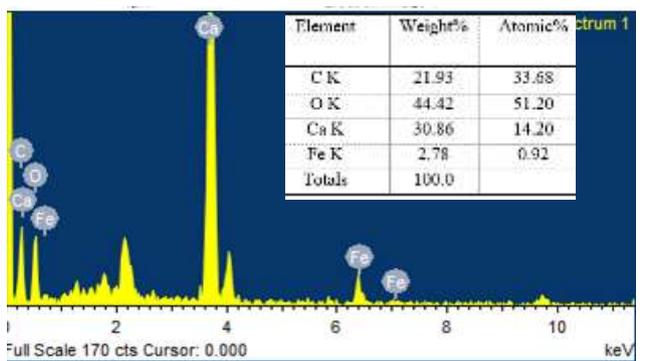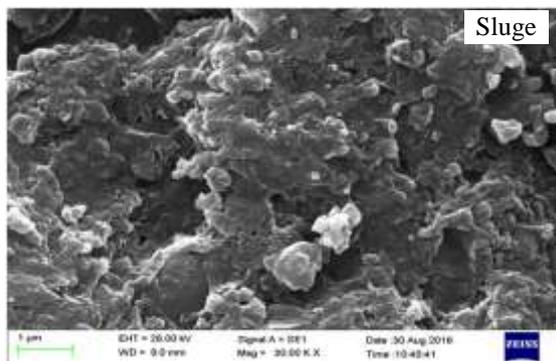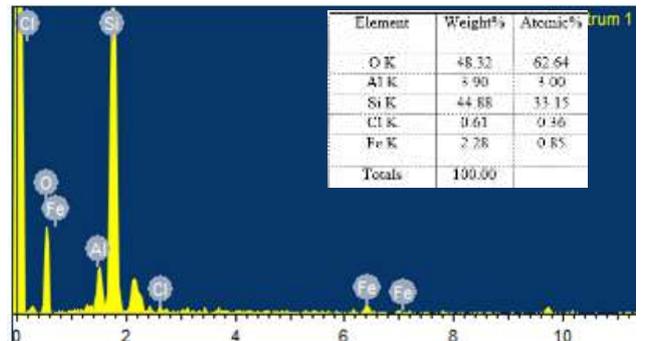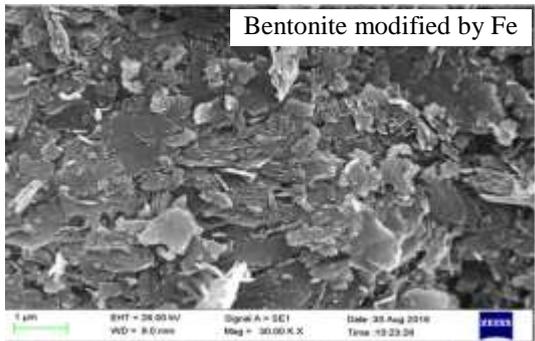Properties of the adsorbents.

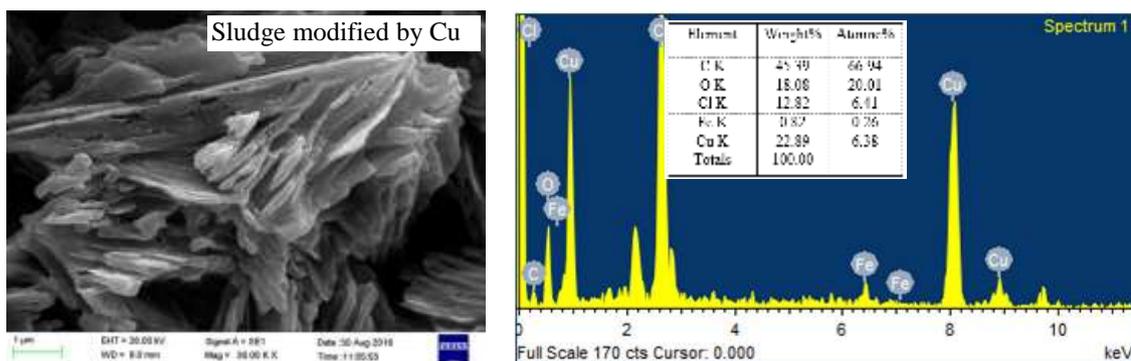|	Humidity (%)	pH	Bulk density (g/ml)	Particle density (g/ml)
Bentonite	5.4586	7.7	0.71647	2.0
Cu- Bentonite	3.4503	5.0	0.57637	1.82
Fe- Bentonite	4.0845	3.6	0.57741	1.18
Sludge	3.655	7.8	0.9887	1.43
Cu-Sludge	4.281	6.3	0.9996	1.54

3.2. Investigating the structure of the adsorbents using SEM

The SEM and SEM/EDS images of the adsorbents, before and after modification, are shown in Figure 2. The structure of bentonite is leafy like and very porous. After modifying, the previous structure is retained, indicating that the mechanical structure of bentonite clay is preserved.

Since the surface of bentonite clay is less dense than the surface of the modified bentonite, deposition of metals on bentonite surfaces after contacting Fe and Cu is possible. These results indicate that, after the modification of bentonite with Fe and Cu, the surface area is increased (Masindi et al., 2015), and the cluster-like structural properties are formed.

The spectrum of bentonite clay by elemental analysis using SEM–EDS is shown in Figure 2. The SEM micrographs confirm the presence of spherical agglomerates on the bentonite matrices. The analysis indicates that Al and Si are the main elements since the material under study is an aluminosilicate; high levels of base cation (Ca) are also present. O is available on the clay matrices too, which may have been introduced into the clay surface through atmosphere by the hydrolysis or decomposition of organic compounds. By comparing the EDX images associated with the Fe-bentonite (Cu-bentonite) and the bentonite adsorbent, it becomes clear that the surface of the adsorbents is covered with iron and copper. In the case of raw sludge, as the results of the EDS indicate, carbon, oxygen, calcium, and iron are the main compounds. Carbon is due to oil in the wastewater, and calcium is available as a salt in the water that precipitates in the sludge. The iron in the sludge is due to $FeCl_3$ injected into the wastewater for coagulation. However, in addition to the mentioned elements, copper and chlorine are also found in the modified sludge, which is due to the modification of the adsorbent with $CuCl_3$.

SEM images and EDX spectra/tables for Bentonite, Bentonite modified by Cu, Bentonite modified by Fe, and Sluge.

Bentonite

Element	Weight%	Atomic%
O K	44.28	58.40
Al K	5.93	4.41
Si K	48.14	36.17
Ca K	1.94	1.02
Totals	100.00	

Bentonite modified by Cu

Element	Weight%	Atomic%
O K	49.00	63.23
Al K	13.92	10.65
Si K	33.73	24.80
Cl K	0.93	0.54
Cu K	2.43	0.79
Totals	100.00	

Bentonite modified by Fe

Element	Weight%	Atomic%
O K	48.32	62.64
Al K	3.90	3.00
Si K	44.88	33.15
Cl K	0.61	0.36
Fe K	2.28	0.85
Totals	100.00	

Sluge

| Element	Weight%	Atomic%
C K	21.93	33.68
O K	44.42	51.20
Ca K	30.86	14.20
Fe K	2.78	0.92
Totals	100.0	

Full Scale 170 cts Cursor: 0.000   keV

Figure 2
SEM images and EDS spectrum of the adsorbents.

3.3. H₂S adsorption efficiency

Figure 3 illustrates the effect of the adsorbent and gas flow rate on H_2S adsorption. To this end, F2 at various flow rates was passed through the adsorbent bed, and the amount of H_2S was measured at different times.

Figure 3 indicates that bentonite is highly capable of removing H_2S. The results suggest that there is no considerable difference between the modified and unmodified bentonite for H_2S adsorption, and the output H_2S is the same. The important thing after the modification of the adsorbent is that the emission of hydrogen sulfide gas from the bed is negligible.

Figure 4 displays the effect of the modified and unmodified sludge on the amount of adsorbed H_2S. The adsorption results are similar to the results obtained for bentonite, and the modification of sludge reduces the amount of H_2S output. For example, the modified sludge has decreased the amount of H_2S from approximately 200 ppm to 100 ppm at a 1000 ml/min flow rate. Moreover, by raising the gas flow, the amount of H_2S output rises, which seems to be due to the reduction of the gas retention time in the bed; the AC of the sludge is also less than that of bentonite.
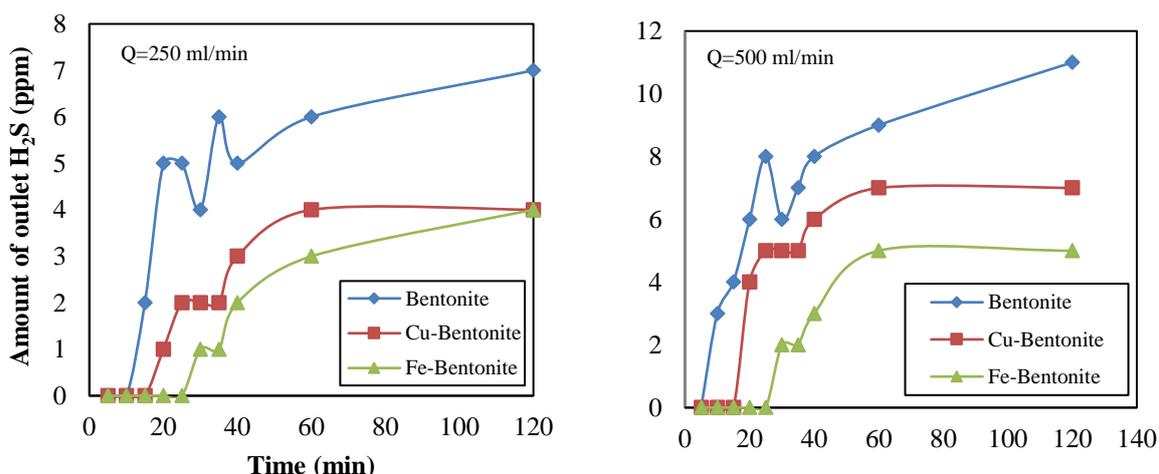
Figure 3
The effect of gas flow rate and bentonite modification on the amount of outlet H_2S (F2).

To study the type of gas, F1 gas, which is one of the most polluted refinery gases (containing about 2.5% H_2S), was used for evaluating the adsorbents. This gas was tested using bentonite at a flow rate

of 250 ml/min and using sludge at a flow rate of 150 ml/min; the results are shown in Figures 5 and 6; it is clear that an increase in H₂S concentration does not affect the H₂S output, indicating that bentonite is highly capable of adsorbing H₂S. However, as the concentration of H₂S increases, the amount of H₂S output also rises, which is because of the low adsorption capacity of the bed for adsorbing H₂S.
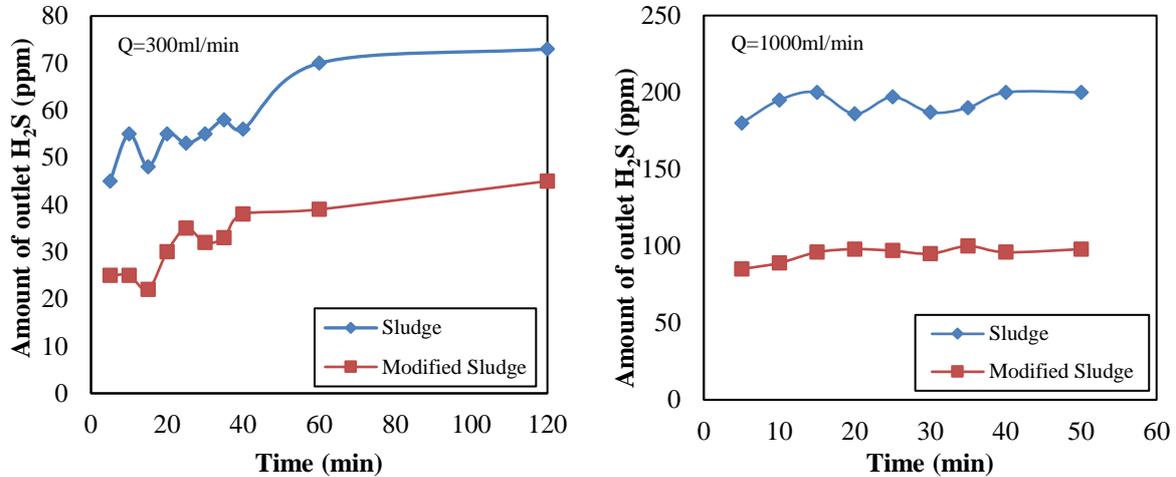
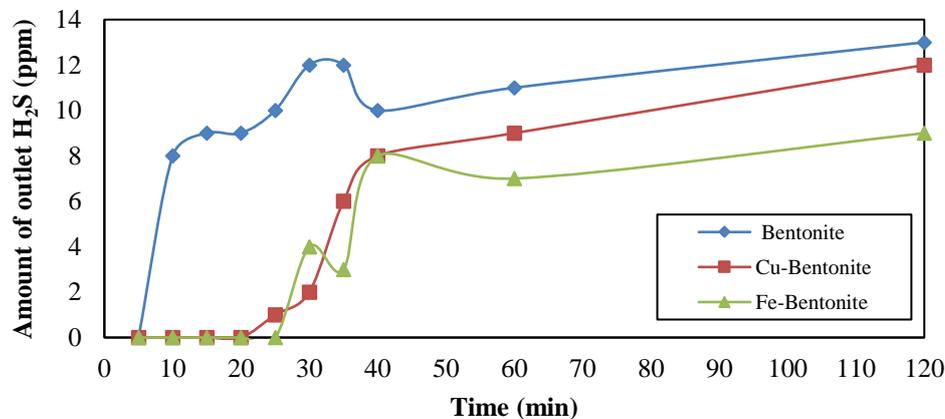**Figure 4**

The effect of gas flow rate and sludge modification on the amount of outlet H₂S (F2).

3.4. Mercaptan adsorption efficiency

To evaluate the adsorption efficiency of mercaptan, F2 was passed though the bed at two different flow rates. Results similar to that of H₂S removal were obtained for mercaptans, and the modification of bentonite reduced the mercaptan in the output (Figure 5). Furthermore, the results associated with the flow rate state that increasing the gas flow rate does not influence the amount of mercaptan in the outlet. Seemingly, it is due to the high capacity of bentonite for adsorbing mercaptans. Regarding the adsorption of mercaptan by the sludge, the results are similar to those of the adsorption of H₂S; as the gas flow rate rises, the amount of mercaptan in the output also increases, and the modification of the sludge by Cu has a substantial impact on the amount of the adsorption of the mercaptan in the output; for example, at a gas flow rate of 500ml/min, modification has reduced the amount of the mercaptan in the output from approximately 400 ppm to 100 ppm, which indicates that the copper in the structure of the sludge impacts on the removal of mercaptans from the gas.
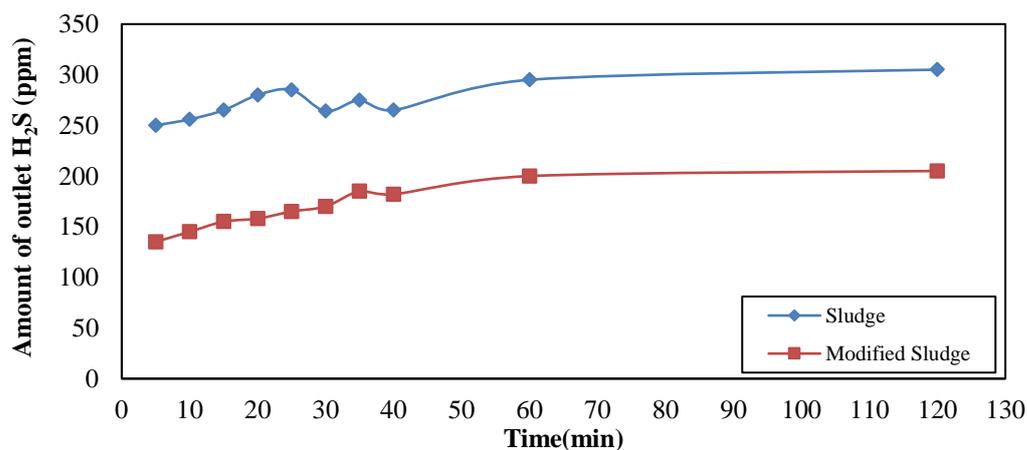
Figure 5

The effect of gas feed type (F1) on the amount of the outlet H₂S (Q= 250 ml/min)

3.5. Calculation of adsorption capacity of H2S

To calculate the adsorption capacity of the adsorbents, the feed gas was passed through the bed until the bed was saturated. Finally, the adsorption capacity was calculated by measuring the H2S concentration in the input and output containers. To calculate the adsorption capacity, 50 grams of the adsorbent and 30 liters of F1 gas, containing the highest amount of H2S, were passed through the bed at a gas flow rate of 300 ml/min. After specific periods of time, the H2S in the output was measured, and the experiment was continued until full saturation. The entire gas passed through the bed was collected in another container. The difference between the amounts of H2S in both conditions as well as the adsorption capacity of the adsorbent was calculated. Table 3 tabulates the properties of the bed, type of gas, and the data obtained. The results show that the adsorbent modified by iron (32.256 mg(H2S)/g) was more efficient in removing the gas. A similar procedure was observed for the sludge, and modifying the sludge with copper increased the adsorption capacity from 5.46 to 11.18 mg(H2S)/g. Adding divalent metals to the structure of the adsorbent caused the following reaction in the adsorbent and drastically improved the adsorption capacity.

$$Me^{2+} + H_2S + 2H_2O \rightleftharpoons MeS^- + 2\,H_3O^+ \tag{3}$$

The values of the maximum adsorption capacity of H2S obtained in this work are compared with those of other adsorbents and summarized in Table 4.

Figure 6
The effect of gas feed type (F1) on the amount of outlet H2S (Q=150 ml/min).

Table 3
Data on adsorbent capacity (F1).

	Bed volume (ml)	Adsorbent amount (gr)	Gas volume of injection (ml)	Amount of inlet H2S (ppm)	Amount of outlet H2S (ppm)	Adsorbent capacity (mgr. H2S/gr)
Bentonite	511	30	30000	25000	15319	14.693
Cu-bentonite	511	30	30000	25000	10915	16.568
Fe-bentonite	511	30	30000	25000	3749	32.256
Sludge	511	100	30000	25000	13000	5.46
Cu-sludge	511	100	30000	25000	450	11.18

Table 4

Comparison of H$_2$S adsorption capacity of different adsorbents.

Authors	Yuan and Bandosz, 2007	Truong and Abatzoglou, 2005	Melo et al.	This work	This work
Adsorbent	Sludge	Sulfatreat 400 HP	13X Zeolite	Fe-bentonite	Cu-sludge
Adsorption capacity	1200 gr H$_2$S/m^3	0.11 gr H$_2$S/gr	53 mg H$_2$S/gr	32.256 mg H$_2$S/gr	11.18 mg H$_2$S/gr

3.6. Calculation of the removal capacity of mercaptan

To calculate the AC of mercaptan, a method similar to the one used for H$_2$S was employed. To this end, F2 gas containing 2000 ppm of mercaptan was passed through a bed containing 20 grams of adsorbent at a flow rate of 150 ml/min, and the concentration of mercaptan was measured after the full saturation of the bed. It is necessary to note that capacity was calculated in the presence of H$_2$S. As Table 5 indicates, modifying the adsorbent improves the mercaptan AC; moreover, the AC of the bentonite modified by iron is higher than that of the bentonite modified by copper. A comparison between the sludge and the sludge modified by copper clearly confirms that the amount of AC is increased by about 25%.
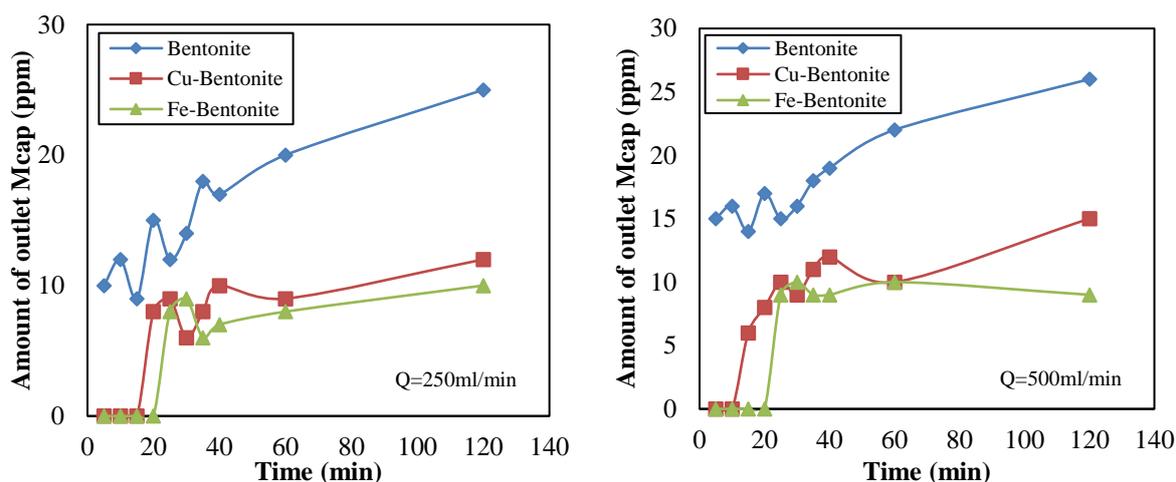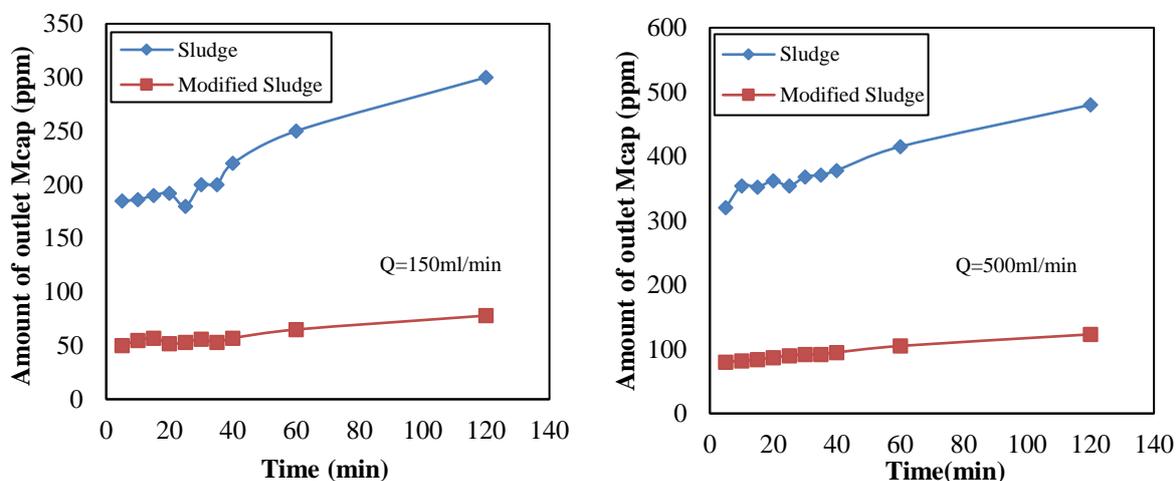

Figure 7
The effect of gas flow rate and bentonite modification on the amount of outlet mercaptan (F2).

3.7. Regeneration study

The experiment about the adsorption capacity of the recycled adsorbent was investigated by using three-time cycles. In this part, F1 gas at a flow rate of 250 ml/min was used, and a steam of 200 °C was passed through the adsorbent bed to regenerate the adsorbent. From Table 6, it is clear that the H$_2$S adsorption capacity of the adsorbent is declined from 99.73 to 93.27% for Fe-bentonite and from 97.35 to 89.30% for Cu-sludge after applying three-time cycles.

Table 5
Adsorbent capacity of mercaptan (Feed F2).

	Adsorbent amount (gr)	Gas volume of injection (ml)	Amount of Mercaptan inlet (ppm)	Mercaptan outlet (ppm)	Inlet H_2S (ppm)	Outlet H_2S (ppm)	Adsorbent capacity (mgr. H_2S/gr)	Adsorbent capacity (ml. Mercaptan/gr)	Adsorbent capacity (mgr. Mercaptan/gr)
Bentonite	20	5000	2000	860	4000	0	1.518	0.285	0.70
Fe-bentonite	20	5000	2000	400	4000	0	1.518	0.4	0.98
Cu-bentonite	20	5000	2000	560	4000	0	1.518	0.36	0.89
Sludge	20	5000	2000	950	4000	0	1.518	0.263	0.65
Cu-sludge	20	5000	2000	680	4000	0	1.518	0.33	0.81

Figure 8
The effect of gas flow rate and sludge modification on the amount of outlet mercaptan (F2).

Table 6
Effect of recycling the adsorbents on the adsorption capacity.

	Recycle times	1	2	3
Adsorbent capacity (mgr. H_2S/gr)	Fe-bentonite	99.73	95.22	93.27
	Cu-sludge	97.35	92.11	89.30

4. Conclusions

In the current study, in order to remove mercaptan and H_2S existing in the gases emitted from Kermanshah Oil Refinery Company, bentonite and sludge modified by Cu and Fe were used. The effects of various gas flow rates and gas types on the amount of adsorbed H_2S and mercaptan were investigated. The results showed that the modified bentonite was highly capable of removing H_2S and mercaptan. The adsorption capacity was equal to 32.256 mg H_2S/gr and 0.98 mg mercaptan/gr for the bentonite modified by iron. Furthermore, the adsorption capacity of the sludge modified by Cu is equal to 11.18 mg(H_2S)/g and 0.81 mg(mercaptan)/g. In conclusion, it can be stated that the adsorbents, whether modified or unmodified, is quite capable of removing H_2S and mercaptan. Moreover, since the data in

this work are obtained in a low-pressure and low-temperature condition, this adsorbent can be a suitable replacement for the current technology, which works in high-temperature and high-pressure condition. Finally, further work, especially for using this catalyst on a large scale, has been proposed.

Reference

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