Removal of ammonia and hydrogen sulfide from livestock farm by copper modified activated carbon

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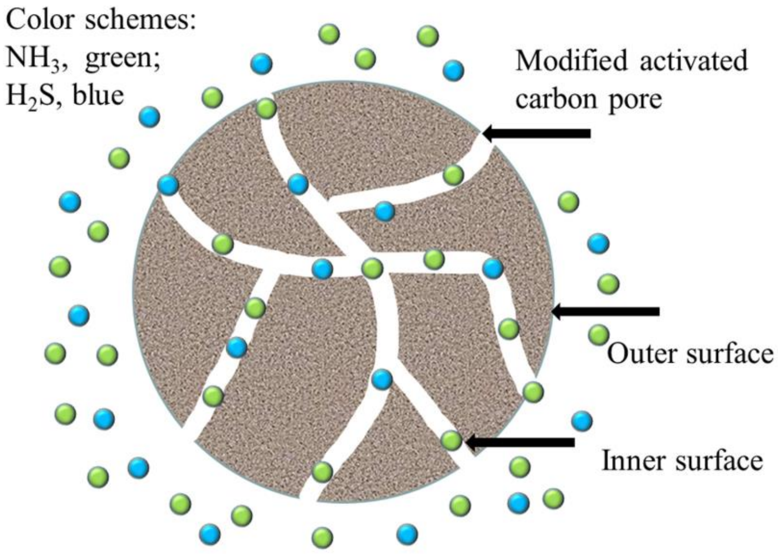
Graphical abstract



ABSTRACT

Ammonia (NH_3) and hydrogen sulfide (H_2S), as the main odorous substances in waste gas from livestock farm, have attracted more attentions rescently since their adverse effects. To remove NH_3 and H_2S efficiently, high-pressure hydrothermal modification (HPHM), metal salt solution impregnation modification (MSIM), and HPHM combined with MSIM are used to modify the activated carbon (AC). Meanwhile, the pore structure and surface functional groups of AC and MAC absorbents are characterized by BET, FTIR and Boehm titration method. The adsorption performance of activated carbon (AC) and modified activated carbon (MAC) are compared. The effects of modification and operation conditions on the adsorption performance of MAC for NH_3 and H_2S are studied in detail. It was found that the optimal adsorption performance of MAC can be achieved by high-pressure hydrothermal modification (HPHM) followed by the metal salt solution impregnation modification (MSIM). With gas space velocity of 900 h^{-1} and total inlet concentration of 550-650 mg m^{-3} at 50 ^{o}C, the adsorption capacities of NH_3 and H_2S of GS270CuCl6010 are 24.17 mg g^{-1} and 26.20 mg g^{-1}, respectively. The adsorption of NH_3 and H_2S by MAC is the result of both physical adsorption and chemical adsorption.

Keywords: Copper chloride, Modified Activated Carbon, Adsorption, NH_3 and H_2S

1. Introduction

With the development of intensive livestock production in our country in recent years, the effluent pollution has attracted more increasing attentions (Li *et al*., 2016; Chen *et al*., 2014). Emission of different pollutant gases from livestock and poultry breeding, including methane (CH_4), nitric oxide(NOx), hydrogen sulfide (H_2S), ammonia (NH_3), carbon monoxide (CO), carbon dioxide (CO_2) and so on (Matulaitis, 2015); can cause one or more of the following adverse effects: threats to human health (Schiffman *et al*., 2016; Nicell, 2009); Injury to livestock (Osorio *et al*.,2009); deterioration of equipment in the livestock farm (Kim *et al*.,2008); serious complaints from neighbors (Kim *et al*.,2008); and the damage to ecosystems due to soil acidification and photochemical smog (Heber *et al*.,2006; Petit *et al*.,2007). NH_3 and H_2S, as the main odorous substances in waste gas from livestock farm, have attracted more attentions (Kim *et al*.,2008; Liao and Chen, 2008). The State Environmental Protection Administration of China approved and implemented Emission Standards for Odor Pollutants (GB14554-93),which sets relevant regulations for the emissions of NH_3 and H_2S (Zheng *et al*.,2014).

Odor gas has features of dispersive emission source, low concentration of gases, large areas of production, and complex composition (Gao *et al*.,2004). Since 1960s, many researches have been reported on the odor gas of livestock and poultry in the world (Liu *et al*.,2017). The traditional treatment of odor gas, through physical, chemical, and biological means, has gradually developed from simple washing elimination to biological degradation and activated carbon adsorption removal. The removal rate of chemical cleaning is high, but the installation and operation cost increases because of the need of grade absorption treatment by several kinds of chemicals for the composition of pollutants in actual operation (Xu,2007).Water washing elimination is not a very economical option because of amount of water requirements (Rene *et al*.,2012). Biological removal is easy to block the bed during the biofilm development because the moisture and pH value are difficult to control (Datta and Allen,2005; Mudliar *et al*.,2010; Arellano-García *et al*.,2015).

In contrast, owing to advantages of simple process, high purification efficiency, good regeneration property and low price (Guo *et al.*,2005; Liu *et al.*,2005), adsorption removal by Activated carbon (AC) has been widely used in the treatment of odor gas from livestock farm. Activated carbon can be usually used as adsorbent, catalyst or catalyst carrier because of the large specific area, developed pore structure and unique surface chemical properties. The adsorption removal rate of NH_3 and H_2S on activated carbon by simple raw activated carbon adsorption is limited and the adsorption capacity of NH_3 is weaker than that of H_2S (Harihastuti *et al.*,2015). The size of NH_3 molecules with a width of about 3Å is small, and NH_3 molecules can be strongly adsorbed only in pores similar in size to its diameter at ambient conditions rather than in the majority of an average activated carbon pore in the range of 10-20 Å, resulting in the use of only the small fraction of adsorbent surface (Petit *et al.*,2007). Modifications by some physical or chemical methods on surface physical structure and chemical properties of activated carbon seemed to be effective for improving the adsorption performance of activated carbon (Petit *et al.*,2007; Liu *et al.*,2005; Guo *et al.*,2007). Acid or alkali modifications are widely used. AC modified by acid can decrease the surface area and volume of micropores and increases the amount of acidic oxygen functional groups. While alkali modification increases the micropore volume of activated carbon and the amount of alkaline functional groups (Liu *et al.*,2005; Guo *et al.*,2007). It is reported that the increase of micropore volume and alkaline functional groups is beneficial to the adsorption of H_2S on AC (Guo *et al.*,2007; Zeng *et al.*,2007). And the adsorption of H_2S at low temperature is dominated by physisorption for micropore (Mochizuki *et al.*,2016). Meanwhile the chemical interaction between NH_3 molecule and surface acidic functional groups plays a leading role in the adsorption of ammonia by activated carbon (Guo *et al.*,2005; Mochizuki *et al.*,2016). The adsorption behavior of NH_3 and H_2S on AC prepared from petcoke with KOH chemical activation has been studied by Mochizuki et al (Mochizuki *et al.*,2016). They found that the amount of acidic functionalities interfering with the H_2S adsorption on basic centers by giving electrostatic repulsion with H_2S molecules was much more than that of basic groups on activated carbon surface, which was the reason of the fact that adsorption of H_2S proceeded very slowly at the same adsorption condition than that of NH_3.

Also it was reported that AC impregnated with Zn^{2+} and Cu^{2+} showed high pore volumes, surface areas, oxygen-containing groups, and the sorption capacities for the tested adsorbate in the study about AC using first-row transition metals (Co, Ni, Cu and Zn) as activating agents (Thue *et al.*,2017). Yi et al. have studied the simultaneous removal of SO_2, NO, and CO_2 onto coconut shell activated carbon impregnated with metal nitrates (Cu, Ca, Mg, Zn) and found that Cu-SAC showed the best adsorption (Yi *et al.*,2014). Petit et al. revealed that the carbon impregnated with chloride of copper is an efficient ammonia adsorbent and the strong adsorption is based on formation of complexes with metal chlorides (Petit *et al.*,2007). Many researches confirmed wood-based activated carbon ground and mixed with 10 % bentonite binders containing copper cations increased the capacity of carbon for hydrogen sulfide (Nguyen-Thanh and Bandosz,2005). The results indicated that copper present in the small pores acts as a catalyst for oxygen activation, which oxidizes hydrogen sulfide to sulfur and sulfur dioxide. However, it takes too long to prepare the modified materials by this method and the pore structure of activated carbon is not well developed. Liang et al. revealed that the combinatory method of HPHM followed by $CuSO_4$ impregnation modification, which increased the specific surface area, micropore area, micropore volume and average pore size of AC, obviously improved sulfur capacity of AC (Liang *et al.*,2014). It is reported that the treatment of AC produced from kernel with water vapour at 250 °C results in increase of the specific surface area due to development of microporosity (Skubiszewska-Zięba *et al.*,2011).

Both H_2S and NH_3 are present in waste gas from livestock farm waste gas, there is relatively little attention to simultaneous removal of NH_3 and H_2S by AC adsorption. In this paper, the adsorption behavior of AC modified by high-pressure hydrothermal modification (HPHM) and metal salt solution impregnation modification (MSIM)，under the simulated environmental conditions of hydrogen sulfide and ammonia gas in the livestock farm, is studied. Meanwhile, the pore structure and surface functional groups of AC samples were characterized by BET, FTIR and Boehm titration method.

The mechanism of the both NH_3 and H_2S adsorption performance on MAC is explored further.

2. Materials and methods

2.1. Sample preparation Activity tests

Activated carbon (diameter: 3 mm) from the Xinhua Chemical Plant are selected as raw materials. The high- pressure hydrothermal modification (HPHM) method is defined as the method that AC samples are maintained in autoclave with distilled water according to the volume ratio (the volume of AC in the natural accumulation state include the pore volume inside the activated carbon particles and the pore volume between the particles. All the activated carbon volume is defined in the same way in this paper) of 2:3 at a constant temperature for 3 h, and then dried at 85 ^oC for 3 h. The metal salt solution impregnation modification (MSIM) is defined as the method that AC samples impregnated with metal salt solution according to the volume ratio of 4:3 in a water bath at constant temperature for 2 h. The prepared AC samples are thoroughly washed with distilled water until the pH value of filtrate became neutral, and then dried at 85 ^oC for 3 h. The preparation of modified activated carbon is shown in Table 1.

Table 1. List of modified activated carbon

Activated carbon type	modification conditions
RAC	activated carbon (diameter: 3 mm) from the Xinhua Chemical Plant
GS270	AC by HPHM under 270 ^oC
MBC	AC by MSIM with different concentration of metal salt solution under the condition of adsorption temperature. M($Cu(NO_3)_2$,$Fe(NO_3)_3$,$Zn(NO_3)_2$,$ZnSO_4$,$ZnCl_2$,$CuSO_4$ or $CuCl_2$) stands for metal salt solution. B

	(30 °C, 60 °C or 90 °C) stands for adsorption temperature. C (5 %, 10 % or 15 %) stands for concentration.
MBCGS270	AC by MSIM firstly then by HPHM.
GS270MBC	AC by HPHM firstly then by MSIM.

2.2 Activity tests

The fixed bed reactor system used for H_2S and NH_3 adsorption and the flow chart of adsorption removal of H_2S and NH_3 are same as Ref (Liang *et al*., 2014). The 99.99 % H_2S and NH_3 gas, diluted with N_2 separately to simulate the livestock farm atmosphere, went through a fixed bed reactor of 20 ml AC. The effects of modification conditions are investigated at 50 °C, with gas space velocity of 900 h^{-1} and inlet concentration of 750-850 mg m^{-3}. Meanwhile, the effect of operation conditions are investigated on GS270CuCl6010. The H_2S and NH_3 concentration in gas phase is separately determined by means of Iodometric method and Nessler's Reagents spectrophotometer (China, 2010; China, 2009).

2.3 Activity tests

The specific surface area, pore volume and pore structure of activated carbon samples were measured by Nitrogen isothermal adsorption method using Micromeritics ASAP2020 (Micrometrics, USA). The adsorption and desorption isotherms of N_2 in the relative pressure of 0-0.99 were measured by static volumetric method at the liquid nitrogen temperature of 77 K. The total specific surface area was calculated by BET model from the adsorption isotherms when the relative pressure $P \cdot P_0^{-1}$ was less than 0.3. The total pore volume was converted from the adsorption value of liquid nitrogen at relative pressure of 0.99. The micropore volume and specific surface area are calculated by the t-diagram method. The mesoporous volume is the total pore volume minus the micropore volume.

The content of acidic and basic surface groups is determined according to Boehm titration method improved by researchers. 1 g AC sample and 20mL hydrochloric acid (sodium hydroxide) solution is placed in 250 mL iodine bottle (Lisovskii *et al*., 1997). After shaking, the bottle remains static for 48 h. 10 mL of the filtrate is pipetted to the conical bottle and then titrated by standard sodium hydroxide (hydrochloric acid) solution.

The functional groups on the surface of the AC samples were studied using VERTEX70 Fourier transform infrared spectrometer (Bruker Co.) in the scanning range of 500-4000 cm^{-1} with a scanning speed of 0.2 cm s^{-1}.The AC samples are of 200 mesh mixed with potassium bromide(KBr) at the ratio of 300: 1. The mixtures are ground into powder under infrared lamp, and tableted for FTIR tested.

3. Results and Discussion

3.1. Effect of modification methods on H_2S and NH_3 adsorption performance

The adsorptions of H_2S and NH_3 by MAC are shown in Figure 1a and b. The NH_3 capacity of RAC, GS270, CuNO3010, GS270CuNO3010 and CuNO3010GS270 is 4.84, 5.98, 7.23, 16.41 and 9.13 $mg \cdot g^{-1}$, respectively. The H_2S capacity of RAC, GS270, CuNO3010, GS270CuNO3010 and CuNO3010GS270 is 5.48, 6.84, 8.51, 18.32 and 10.11 $mg \cdot g^{-1}$ separately. The results demonstrate that the combinatory method of HPHM and MSIM is the combining of the advantages of both approaches, and the adsorption performance of MAC improved. The effect of HPHM followed by MSIM is much better than that of MSIM followed by HPHM, and the removal rate of the former is relative high. The impregnant is more easily loaded in the developed AC pores by HPHM. MSIM followed by HPHM cannot increase the loading amount further, and may cause desorption of the originally loaded impregnant. Thus, modifying AC by MSIM on the basis of HPHM could improve the H_2S and NH_3 adsorption performance.

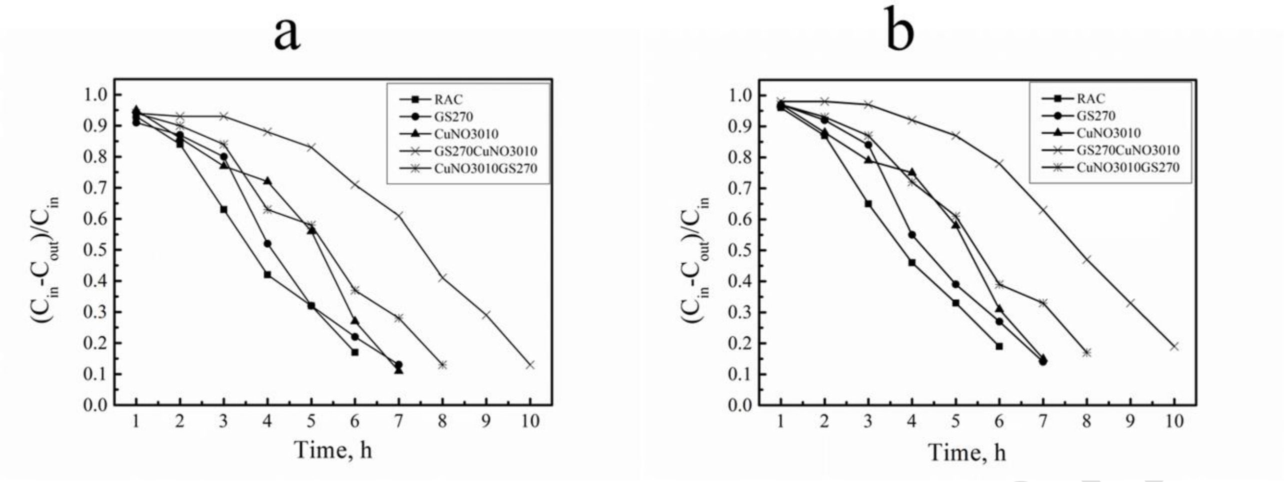


Figure 1. NH_3 and H_2S adsorption curves of modification methods

The H_2S and NH_3adsorption performance on MAC by combinatory method with different metal salt solution is shown in Figure 2. Figure 2a shows that the total adsorption capacity of GS270ZnNO3010 and GS270CuNO3010 is respectively more than 70 % higher than that of GS270FeNO3010. Copper salt and zinc salt solution are ideal impregnating solution. Figure 2b shows that the total adsorption capacity of GS270CuCl3010 and GS270CuSO3010 is better than that of GS270ZnCl3010 and GS270ZnSO3010 and the total adsorption capacity of GS270CuCl3010, which reaches the best adsorption performance, is 2.8 times that of GS270. It is concluded that the adsorption effect of MAC by copper salt solution is better under the condition of the same anion in metal salt solution, due to the fact that copper is easier to chemically adsorb with H_2S and NH_3; the adsorption efficiency of the anions in the impregnation solution is the best under the condition of the same cation in the metal salt solution, which may be because the smallest ion radius of the Cl^- is easier to load on the activated carbon micropores. So, AC modified by HPHM at 270 ^oC followed by MSIM with $CuCl_2$ solution has good H_2S and NH_3 adsorption performance.

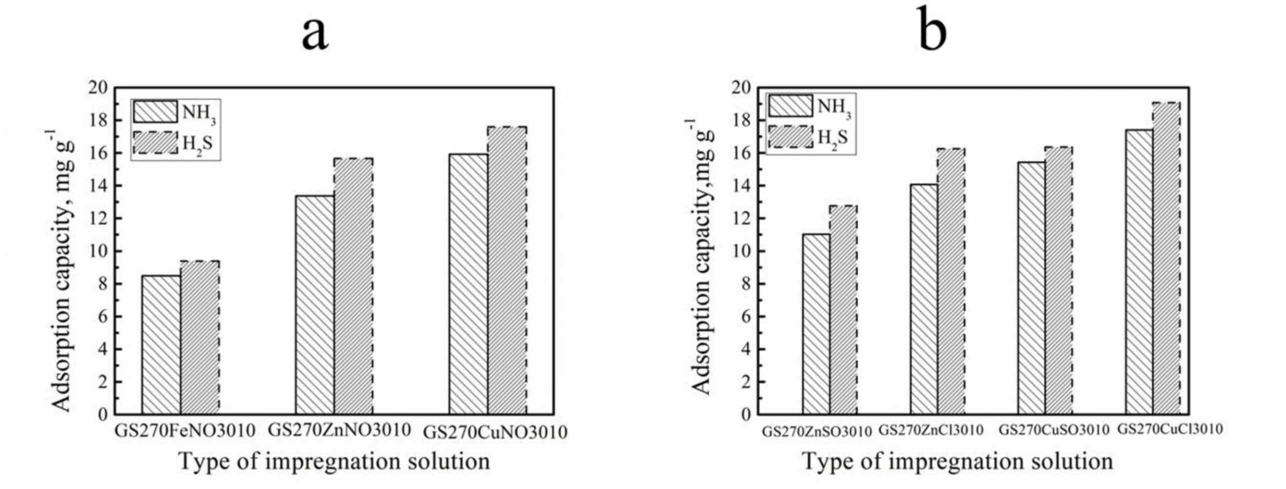


Figure 2. Adsorption capacity of different metallic salt solutions and different copper and zinc salt solutions

Figure 3 shows the effect of impregnation solution concentration and impregnation temperature on the H_2S and NH_3 adsorption properties of MAC by the combined method. The H_2S and NH_3 adsorption properties of MAC are obviously increased with the increase of impregnation solution concentration. It is found that the total adsorption capacity reached 36.4 mg g^{-1}, 3.5 times as much as that of raw activated carbon, when the concentration of impregnation solution was increased to 10%; the total adsorption capacity of MAC almost does not increase, due to the saturated adsorption of modified activated carbon on impregnating solution, when the concentration of impregnation solution continued to increase to 15 %. In addition, the distribution and uniformity of ions on AC affect the catalytic activity of ions (Klinik and Grzybek, 1992; Liu *et al*., 2000).Figure 3b shows that the total adsorption capacities of GS270CuCl3010, GS270CuCl6010 and GS270CuCl9010 are 3.6 times, 4.4 times and 3.7 times as much as those of RAC respectively and those of GS270CuCl6010 reaches the maximum. With the increase of impregnation temperature, the activity of solute ions increases and the diffusion rate is accelerated due to the accelerated speed of irregular movement, which makes it easier to load on the activated carbon. But too high activity of solute ions by further heating may cause adversely effect of solute ion loading on MAC. GS270 modified by HPHM by MSIM with 10% $CuCl_2$ solution at 60 ^{o}C achieves the optimal adsorption performance.

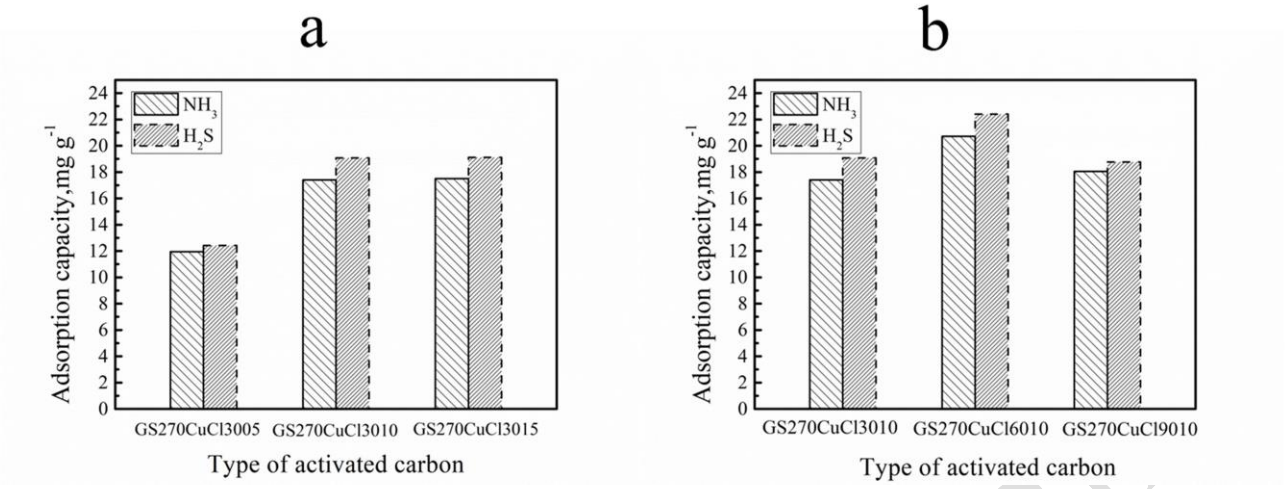


Figure 3. Adsorption capacity of different impregnation solution concentrations and different impregnation temperature

3.2. Effect of different operation conditions on H_2S and NH_3 adsorption performance

Figure 4 shows the H_2S and NH_3 adsorption performance on MAC (GS270CuCl6010) at adsorption temperature of 30 °C, 50 °C, 70 °C and 90 °C respectively. The NH_3 adsorption capacity of MAC reaches its maximum at 50 °C and then decreases sharply, which indicates that Physical adsorption plays a major role in NH_3 adsorption; the H_2S adsorption capacity of MAC reaches its maximum at 70 °C and decreases obviously at 90 °C. This is because that the degree of enhancement of H_2S chemical adsorption on MAC is greater than that of weakening of physical adsorption at 70 °C. It is concluded that temperature is a very important factor in the NH_3 and H_2S adsorption on MAC which contains both physical adsorption and chemical adsorption. The optimum operating temperature for adsorption of NH_3 and H_2S on MAC is considered at 50 °C.

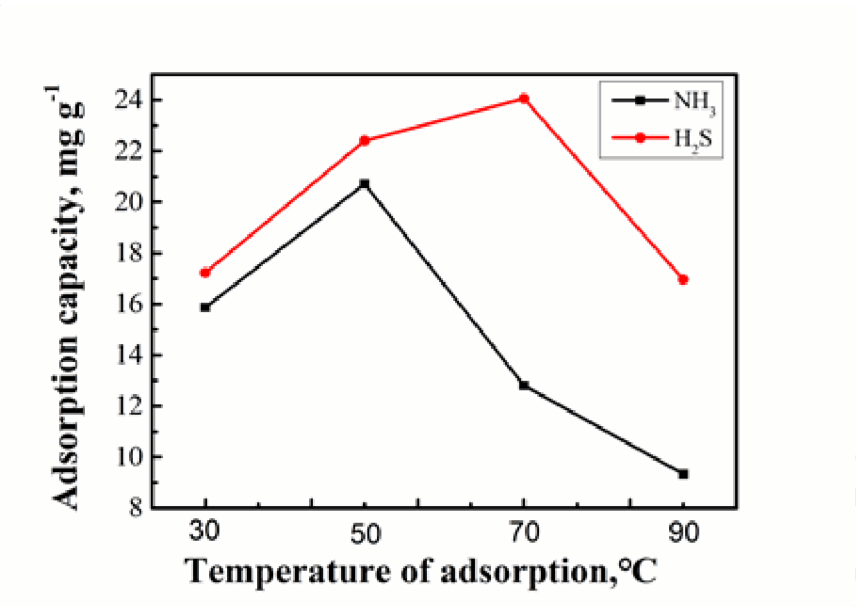


Figure 4. Adsorption capacity of GS270CuCl6010 at different adsorption temperature

Figures 5 show the adsorption properties of NH_3 and H_2S on MAC at different gas space velocity. The NH_3 capacity of 300, 600, 900 and 1,200 h^{-1} is 14.15, 18.41, 20.47 and 11.66 mg g^{-1} separately. The H_2S capacity of 300, 600, 900 and 1,200 h^{-1} is 14.61, 18.85, 22.23 and 12.17 mg g^{-1} separately. The total adsorption capacity reaches the maximum at 900 h^{-1}. Obviously, the retention time of high removal rate and breakthrough time at 300 h^{-1} are much longer than that at 1200 h^{-1}. But the NH_3 and H_2S adsorption capacity of AC would not increase with the decrease of gas space velocity, due to less NH_3 and H_2S entering the fixed bed in unit time and the serious effect of external diffusion. Meanwhile high gas space velocity makes retention time not enough for H_2S and NH_3 to be adsorbed before it overflows. So MAC has good H_2S and NH_3 adsorption performance under the condition of gas space velocity of 900 h^{-1}.

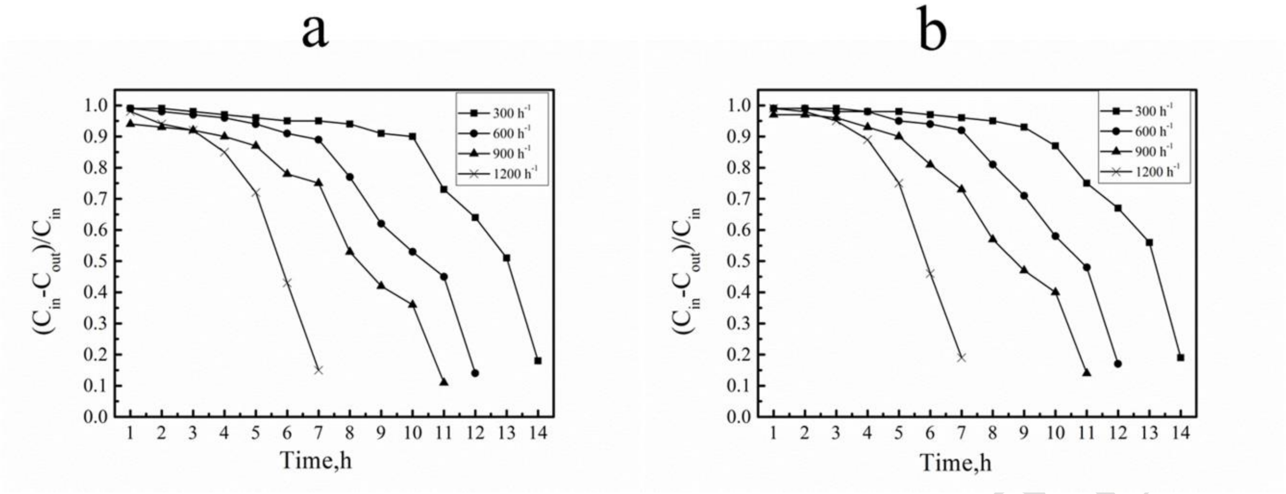


Figure 5. NH_3 and H_2S adsorption curves of different space velocity

Figures 6 show the effect of NH_3 and H_2S adsorption properties on MAC at different inlet concentrations of NH_3 and H_2S. The NH_3 capacity of 150–250, 350–450, 550–650 and 750–850 mg m^{-3} is 13.87, 19.35, 24.17 and 20.71 mg g^{-1} separately. The H_2S capacity of 150–250, 350–450, 550–650 and 750–850 mg m^{-3} is 14.85, 21.34, 26.20 and 22.40 mg g^{-1} separately. With the increase of the total inlet concentration, the breakthrough time of GS270CuCl6010 to NH_3 and H_2S and the retention time of high removal rate are both shortened, but the NH_3 and H_2S capacity generally increases except at 750–850 mg m^{-3}.The condition of total inlet concentration of 550-650 mg m^{-3} is beneficial to NH_3 and H_2S adsorption properties on MAC.

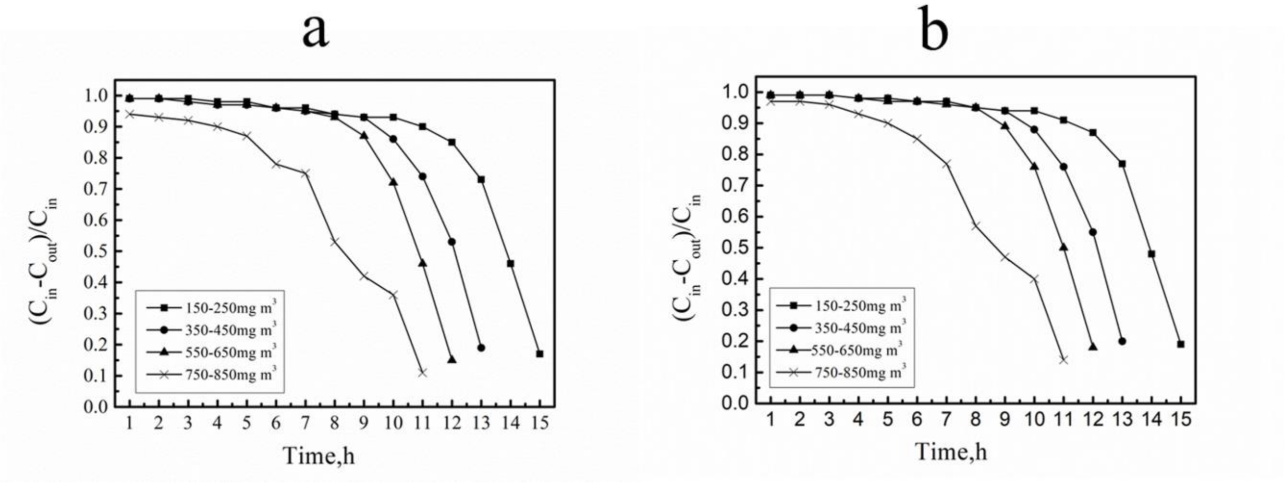


Figure 6. NH_3 and H_2S adsorption curves of different total inlet concentration

3.3. Characterization and analysis for MAC

Table 2. Pore structure measure of modified activated carbon

Type of AC	Surface area (m^2 g^{-1})	Average pore size (nm)	Total pore volume (cm^3 g^{-1})	Mesopore volume (cm^3 g^{-1})	Micropore volume (cm^3 g^{-1})	Micropore area (m^2 g^{-1})
RAC	196.3352	2.6787	0.131482	0.053322	0.078160	169.3630
GS270	347.4687	3.4786	0.236651	0.084519	0.152132	252.9031
CuCl6010GS270	347.3212	3.4692	0.234332	0.083307	0.151025	252.6828
GS270CuCl6010	346.1785	3.3455	0.221049	0.072755	0.148294	251.9526
GS270CuCl6010 (Adsorbed)	278.9070	2.7401	0.159708	0.067702	0.092006	197.1655

The BET characterization for AC samples is summarized in Table 2. The surface area, average pore size, total pore volume, mesopore volume, micropore volume and micropore area increase by 151.1335 m^2 g^{-1}(77 %), 0.7999 nm(30 %), 0.105169 cm^3 g^{-1}(80 %), 0.031197 cm^3 g^{-1}(58 %), 0.073972 cm^3 g^{-1}(95 %) and 83.5401 m^2 g^{-1}(49 %) separately after modification by HPHM at 270 ℃. Among them, total pore volume, surface area and micropore volume increased significantly, which is the result of the opening of the originally closed or incomplete activated carbon pores by internal and external pressure difference. Increase in the quantity of mesopores and micropores make the surface area increase. Similar results to the present study have been reported by other researchers (Skubiszewska-Zięba *et al.*, 2011). In addition, the pore structure of GS270 is more developed than that of CuCl6010GS270 which is more developed than that of GS270CuCl6010. It indicates that HPHM followed by MSIM can increase the amount of modifiers loaded in the pore. The surface area, average pore size, total pore volume, mesopore volume, micropore volume and micropore area of adsorbed GS270CuCl6010 reduce by 19 %, 18 %, 28 %, 7 %, 38 % and 22 % compared with GS270CuCl6010.The obvious decrease of micropore volume indicates that the adsorption of NH_3 and H_2S by MAC is mainly carried out in micropores, which play a important role in the adsorption process. Meanwhile, the slightly decrease of mesopore volume indicates that mesopore acts as the channel in the adsorption process.

Table 3. Content of surface acidic and alkaline groups on activated carbon

Type of AC	Content of acidic Group(mmol g^{-1})	Content of acidic Group(mmol g^{-1})
RAC	0.8065	0.7712
GS270	1.2946	1.2017
CuCl6010	1.3078	1.2282
CuCl6010GS270	1.2894	1.2603
GS270CuCl6010	1.3669	1.2895
GS270FeCl6010	1.3078	1.2439
GS270ZnCl6010	1.3326	1.2504

The content of surface acidic and alkaline groups on activated carbon on AC samples by Boehm titration is collected in Table 3. It can be seen the content of acid and base functional groups on the surface of MAC by HPHM both increase by more than 40 % than that of RAC due to the greatly increase of specific surface area. It is one of the reasons that the adsorption property of GS270 is better than that of RAC. While the content of surface acidic and alkaline groups of GS270, CuCl6010, CuCl6010GS270, GS270CuCl6010, GS270ZnCl6010 and GS270FeCl6010 is almost unchanged. In this experiment, the difference of adsorption properties of various AC samples is not determined by the content of surface acidic and alkaline groups.

FTIR absorption spectra of AC samples are recorded as shown in Figure 7. The main absorption peaks at 1089, 1417, 1627, 2877, 2925 and 3444 cm^{-1} in the spectrum of AC samples are assigned to the stretching vibration characteristic peak of ether group (–C–O), carboxylate group (symmetric and asymmetric), carbonyl group (–C=O), aliphatic group(–CH_3), aliphatic group (–CH_2) and hydroxyl group (intermolecular association). Figure 7a shows that the characteristic peak intensity of RAC at 1089 cm^{-1} is obviously higher than that of MAC by combined method modification and single HPHM but is basically consistent with that of MAC by single MSIM; the characteristic peak intensity of AC at 1417 cm^{-1} almost disappeared by single HPHM, but increased slightly by combined method modification and single MSIM; At 2877 cm^{-1}, the characteristic peaks of all MAC samples belonging to aliphatic group disappeared basically; the quantity of carbonyl group, and hydroxyl group increases significantly by the combined method modification. So, carbonyl group and hydroxyl group are conducive to the removal of H_2S and NH_3. Ether group is not favorable for adsorption. That is one of the reasons why combinatory method is better than single HPHM or MSIM. Figure 7b shows that the quantity of carbonyl group and hydroxyl group of MAC impregnated with $CuCl_2$ and $ZnCl_2$ solution is larger than that of $FeCl_3$ solution. And the transformation and decomposition to ether group of impregnation modification by $CuCl_2$ and $ZnCl_2$ solution are stronger than that of $FeCl_3$. That is one of the reasons why MAC impregnated $CuCl_2$ or $ZnCl_2$ solution is better than that of $FeCl_3$. Figure 7c shows that the characteristic peak at 1627 cm^{-1} of MAC impregnated with 5 % $CuCl_2$ solution is slightly weaker than those of 10 % and 15 % $CuCl_2$ solutions. 10 % $CuCl_2$ solution is high enough for the modification of activated carbon sample. The following conclusions can be drawn: Modification of surface functional groups on AC by combined method achieves the best effect.

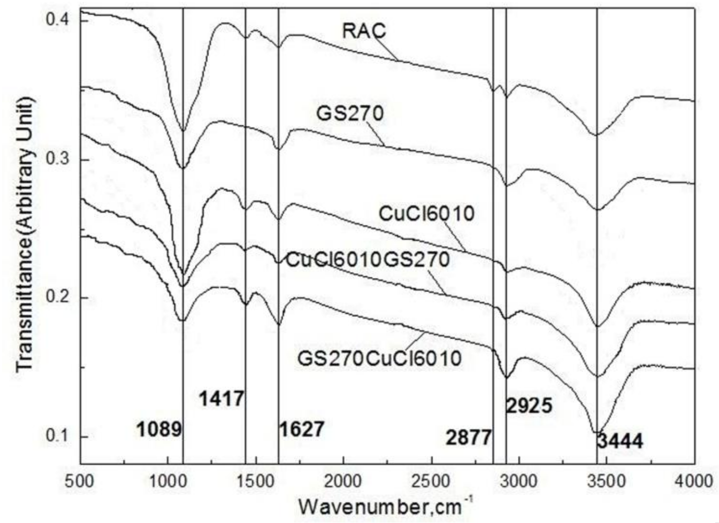


Figure 7a. FTIR spectra of activated carbon modified by different methods

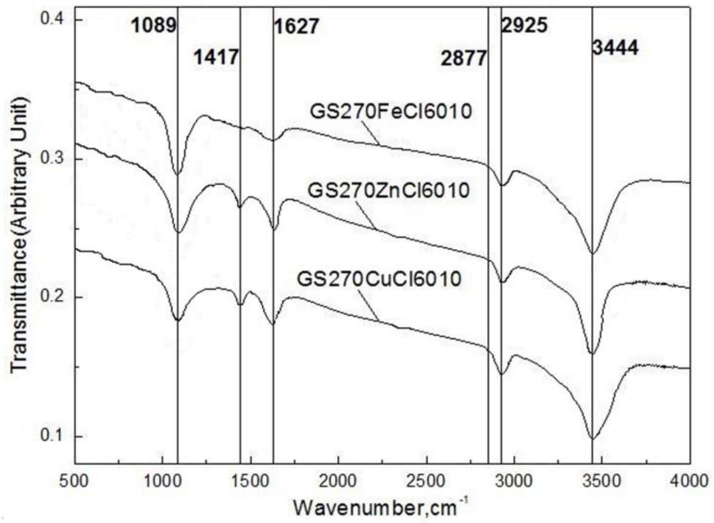


Figure 7b. FTIR spectra of activated carbon modified by different impregnation solution

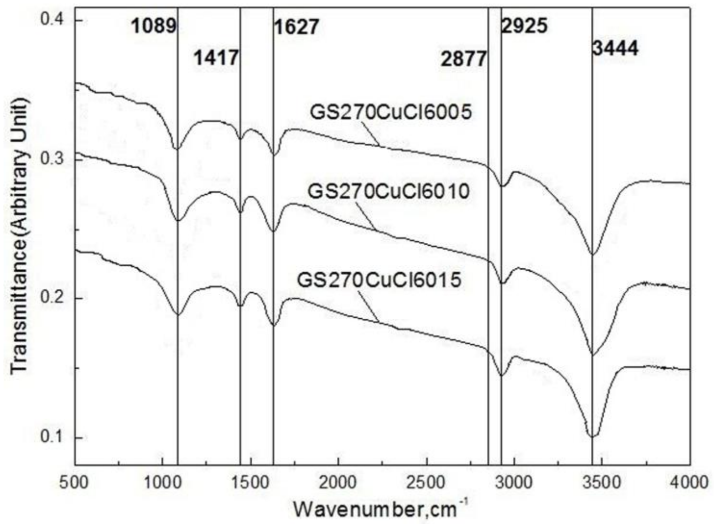


Figure 7c. FTIR spectra of activated carbon modified by different impregnation solution concentrations

3.4. Mechanism discussion

The content of acid and base functional groups on the surface of MAC by HPHM both increase by more than 40 % than that of RAC due to the greatly increase of specific surface area. But the content of surface acidic and alkaline groups of AC samples by different modification methods is almost unchanged which indicates that the content of surface acidic and alkaline groups is not a deciding factor of the difference of adsorption properties on various AC samples. The surface area, average pore size, total pore volume, mesopore volume, micropore volume and micropore area of AC by HPHM at 270 ℃ increase by 77 %, 30 %,80 %, 58 %, 95 % and 49 % separately, which is the result of the opening of the originally closed or incomplete activated carbon pores by internal and external pressure difference. The adsorption capacity of GS270 and GS270CuCl6010 is separately 1.24 times and 4.4 times as high as that of RAC. While the micropore volume and mesopore volume of CuCl6010GS270 are slightly lower than that of GS270. It means that modifier doesn't take up too much of the pore volume of the activated carbon. Similar results to the present study have been reported (Nguyen-Thanh and Bandosz, 2005; Liang *et al*.; 2014; Zhang et al., 2016). And Copper is loaded in the inner space oft AC. In addition, the obvious decrease of micropore volume of adsorbed GS270CuCl6010, comparing with GS270CuCl6010, indicates that the adsorption of NH_3 and H_2S by MAC is mainly carried out in micropore, which is important in the adsorption process. Meanwhile, the slightly decrease of mesopore volume indicates that mesopore acts as the channel in the adsorption process. Mochizuki also thought micropores play an important role in the adsorption process of H_2S (Mochizuki *et al*., 2016; Wang *et al.*, 2019). It was reported that copper on the surface of activated carbon may be present mostly in the form of $CuCl_2$ (Kim and Yie, 2005). Copper in carbon micropores acts as an oxygen activator until the complete reduction to Cu^{1+} from Cu^{2+} occurs and then Cu_2S is deposited on the surface (Nguyen-Thanh and Bandosz,2005). Reaction of copper with NH_3 to form $Cu(NH_3)_2Cl_2$, involving series of associative and dissociative processes (Petit *et al.*, 2007). These lead to the more active adsorption of both H_2S and NH_3 on MAC by HPHM followed by MSIM. Furthermore, one of the main reasons why combinatory method is better than single method is the increase of useful groups and the reduction of harmful groups in quantity. Carbonyl group (–C=O) and hydroxyl group (intermolecular association) are conducive to the removal of H_2S and NH_3 and ether group (–C–O) is not favorable for adsorption. The reduction of ether group can promote the reduction of Cu^{2+} by weakening the interaction force between Cu^{2+} and carrier (Zhang *et al.*, 2016). And Hydrogen atoms of NH_3 and H_2S can interact with oxygen in the form of carbonyl groups (–C=O) and hydroxyl groups (intermolecular association) on MAC (Miyauchi and Ohba, 2019; Arellano-García *et al.*, 2015; Guo *et al.*, 2007; Lee and Reucroft, 1999). At low temperature, the adsorption of NH_3 and H_2S by activated carbon is mainly physical adsorption, and the chemisorption can be enhanced by increasing adsorption temperature, which makes NH_3 and H_2S more easily adsorbed by modified activated carbon to some extent. But the adsorption of modified activated carbon is the result of the interaction of physical adsorption and chemical adsorption. At 50 °C, the combined action of physical and chemical adsorption reaches the maximum.

The research team is currently conducting further research on the removal of ammonia and hydrogen sulfide from livestock farms. The copper modified catalyst life, easy regeneration method of catalyst, amplification experiments on catalytic reactor, energy issues of technology application - Solar Energy Utilization, and noise reduction methods were studied and investigated.

4. Conclusions

From the experimental studies of H_2S and NH_3 adsorption onto MAC, the following conclusions can be drawn:

(1) The optimal adsorption performance can be achieved by the combinatory method of high-pressure hydrothermal modification (HPHM) at 270 °C followed by the metal salt solution impregnation modification (MSIM) with 10 % $CuCl_2$ solution at 60 °C for 2 h under the simulated environmental conditions of hydrogen sulfide and ammonia gas in the livestock farm.

(2) The adsorption capacity of GS270 is 1.3 times that of the raw activated carbon. The adsorption capacity of GS270CuCl2 solution at 60℃ was 4.4 times that of the activated carbon. Modifying AC by the combinatory method of HPHM and MSIM could improve the H_2S and NH_3 adsorption performance.

(3) Adsorption of NH_3 and H_2S by AC is mainly carried out in micropore and mesopore which act as the adsorption channel. After impregnation modification with $CuCl_2$ solution of AC by HPHM, Cu^{2+} loaded in the micropores react with NH_3 and H_2S to achieve the adsorption of both NH_3 and H_2S. NH_3 and H_2S can therefore adsorb onto active adsorption sites (Carbonyl group and hydroxyl group) provided by oxygen functional groups via hydrogen boding. Ether group (–C–O) is not favorable for adsorption. The both NH_3 and H_2S adsorption of MAC is the result of the interaction of physical adsorption and chemical adsorption.

AC modified by the combinatory method of high- pressure hydrothermal modification and the metal salt solution impregnation modification can significantly improve the adsorption performance. After regeneration treatment, its adsorption performance to a large extent to recover. MAC, as a highly efficient and economical industrial adsorbent, is conducive to the radical treatment of waste gas pollution from livestock farm.

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