Comparative Study of the Effects of Various Activation Methods on the Desulfurization Performance of Petroleum Coke

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ABSTRACT

In this study, we activated different samples of petroleum coke, an economical carbonaceous substance with great potential as an activated carbon material for the removal of SO₂, via six common methods, viz., hydrothermal, high-temperature, acid-based, alkali-based, H₂O₂-based and Cu²⁺-based treatment, and evaluated the desulfurization efficiency of each sample by investigating the dynamic SO₂ adsorption along with various relevant factors. We found that high-temperature activation modified the structure and chemical properties of the petroleum coke, leading to an initial desulfurization efficiency of 76.4%, with a specific surface area of 59.0 m² g⁻¹, whereas acid-based treatment increased the SO₂ removal rate to above 82%, producing a specific surface area as high as 247.7 m² g⁻¹. However, alkali-based treatment applied at a KOH/coke ratio of 4:1 achieved the best performance, with a desulfurization efficiency of 96.3% under the optimal conditions. Further comparison of the activated samples' physicochemical properties revealed that both an optimized texture (due to the change in pore structure) and an increased number of active sites contributed to the enhanced desulfurization. Thus, our results demonstrate that activated petroleum coke exhibits several favorable properties that make it a promising sorbent for acidic SO₂ in industrial flue gas desulfurization.

Keywords: Petroleum coke, Activation, SO₂, Adsorption, Desulfurization

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1 INTRODUCTION

Sulfur dioxide (SO₂), as major air pollutant, released from coal-fired power plants, oil refining and gas processing, and smelting is not only a great threat to human health, but also regarded as one of major contributor for acid rain and haze formation (McInden *et al.*, 2016; Oberschelp *et al.*, 2019; Pi *et al.*, 2020). Although global sulfur emissions have been in decline over many decades, more than 100 million tons of SO₂ are still emitted globally every year (Aas *et al.*, 2019). On the other hand, a new emission standard has been adopted in China, which puts forward stricter requirements for the threshold of SO₂ emission. Thus, SO₂ emission control has always been an urgent problem to be solved and it is still necessary to develop new and efficient desulfurization technologies.

Various flue gas desulfurization (FGD) techniques have been developed so far, among which the lime/limestone process is the most commonly used because of its good high efficiency and stability (Liu *et al.*, 2010; Yan *et al.*, 2013). However, high capital costs, large consumption of H₂O, and formation of secondary pollutants restricted its wider applications (Chen *et al.*, 2015; Hao *et al.*, 2017). Sorption of SO₂ on carbonaceous materials provides an alternative in FGD with several advantages such as low capital cost, high operation flexibility and low maintenance cost (Karatepe *et al.*, 2008; Yan *et al.*, 2013; Xu *et al.*, 2016). Many carbonaceous materials have been explored, including biochar, activated carbon, coke, semicoke, and activated carbon fibers, as effective desulfurizer for FGD (Gaur *et al.*, 2006; Li *et al.*, 2008; Zhou *et al.*, 2012; Ding *et al.*, 2015; Nieto-Márquez *et al.*, 2016; Shao *et al.*, 2018; Yuan *et al.*, 2018). The previous studies have indicated

that microporous structure and surface chemical property of carbon materials are mainly responsible for the effective SO₂ removal, especially in the presence of H₂O and O₂ (Raymundo-Piñero *et al.*, 2000; Andrey *et al.*, 2002). Therefore, in addition to developing new carbon materials for enhancing SO₂ removal performance, great efforts have been devoted to improve its pore structure and modify surface chemical property. Atanes *et al.* (2012) applied two activations to improve the characteristics of activated biochar, and the specific surface area increased from 7 to 76 m² g⁻¹ after CO₂ activation and reached 584 m² g⁻¹ after KOH activation. The activated biochar with high surface area (> 1000 m² g⁻¹) were prepared by varying the activation temperature, retention time and flow rates of CO₂ and N₂ (Sumathi *et al.*, 2009). Moreover, surface basicity and nitrogen-containing functional groups play an important role in SO₂ adsorption since SO₂ is an acidic gas. Common alkaline substances, such as KOH, NaOH, and CaO were highly favored in the activation of carbon materials (Macías-Pérez *et al.*, 2007). Dou *et al.* (2020) demonstrated that the KOH/char sorbents completely removed SO₂ at desulfurization temperatures range of 40–150°C. Metal (V, Fe and Cu)-doped activated carbons samples showed the better SO₂ removal performance due to their catalytic properties (Gao *et al.*, 2011). Guo *et al.* (2008) prepared V₂O₅/AC by impregnation and found that the sulfur capacity reduced from 60 to 11 mg g⁻¹ after eight adsorption-regeneration cycles. Nitrogen-containing functional groups on the surfaces of carbon materials could be introduced via activation with ammonia water (Li *et al.*, 2001; Xu *et al.*, 2006). A generally accepted mechanism for the desulfurization of activated carbon materials is that SO₂ can be adsorbed and oxidized to SO₃ and hydrated to H₂SO₄ deposited in the pores of activated carbon. Under the condition of heating, the active sites are empty for the next adsorption cycle after the H₂SO₄ is evaporated (Begoña and María, 1998; Raymundo-Piñero *et al.*, 2000, 2003).

Petroleum coke, the industrial by-product, has great potential in using as activated carbon materials owing to its high carbon content and low price. To our best knowledge, there are few reports on petroleum coke for SO₂ adsorption in FGD. Thus, in this work, petroleum coke was used as a raw material to prepared activated carbon materials processed by a combination of hydrothermal activation, acid-base modification, high-temperature calcination, H₂O₂ oxidation and loading metal (Cu²⁺) activation. Moreover, their SO₂ adsorption performances were evaluated in the simulated fixed-bed reactor, along with various relevant factors (reaction temperature, time, space velocity, SO₂ concentration, H₂O and O₂ content). We aimed to investigate the effect of different activation methods on the SO₂ adsorption performance of materials, and further obtain the main factors that affect the adsorption performance.

2 EXPERIMENTAL SECTION

2.1 Materials

All chemicals were of analytical reagent grade and used without further purification. Petroleum coke from Jinan Coking Plant, China, was used as precursor in this study and the proximate and elemental analyses results are given in Table 1. Before activation, the raw petroleum coke was ground and sieved into granules ranging 10–20 mesh (0.85–2 mm), denoted as PC.

2.2 Preparation of Activated Petroleum Coke

2.2.1 Hydrothermal activation

In the experiment, 10 g raw petroleum coke (denoted as R-PC) were dissolved in 80 mL deionized water under magnetic stirring. Subsequently, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 170°C for 6 h. The precipitate was thoroughly washed by deionized water and dried at 100°C overnight to obtain the modified petroleum coke (denoted as Hy-PC).

2.2.2 High-temperature activation

The Hy-PC sample was carbonized at 400°C for 4 h and at 700°C for 2 h in a quartz tube furnace under N₂ atmosphere with a flow rate of 100 mL min⁻¹. The obtain sample denoted as Ht-PC. For comparison, the R-PC only activated by high temperature was also prepared (denoted as H-PC).

Table 1. Results of proximate and elemental analyses of petroleum coke (PC).

Sample	Proximate analyses (wt%)			Elemental analyses (wt%)				
	Fixed carbon	Volatile	Ash	C	H	N	S	O
PC	89.75	9.83	0.42	91.01	4.01	2.28	0.81	1.89

2.2.3 Acid activation

The Hy-PC sample was added in a beaker containing 250 mL acid solution (HNO_3 or HCl) with continuous stirring and heated at 80°C for 4 h in a constant temperature water bath. Then, the sample were thoroughly washed by deionized water until $\text{pH} = 7$ and dried at 100°C overnight. The dried modified petroleum coke was carbonized at 400°C for 4 h and at 700°C for 2 h in a quartz tube furnace under N_2 atmosphere with a flow rate of 100 mL min^{-1} . The obtain sample denoted as $\text{HNO}_3\text{-PC}$ and HCl-PC .

2.2.4 Alkali activation

A suitable KOH was first dissolved in deionized water. Then the Hy-PC sample with various mass ratio ($\text{KOH:coke} = 1:1\text{--}5:1$) was soaked in the solution for 6 h at room temperature and heated at 100°C to evaporate water. The impregnated sample was carbonized at 400°C for 4 h and at 700°C for 2 h in a quartz tube furnace under N_2 atmosphere with a flow rate of 100 mL min^{-1} . The residual KOH was washed by deionized water $\text{pH} = 7$ and the sample was dried at 100°C overnight. The obtain sample with KOH-to-coke ratio of 4:1 denoted as K-PC . For comparison, the sample activated by NaOH with the same method ($\text{NaOH:coke} = 4:1$) was prepared (denoted as Na-PC).

2.2.5 H_2O_2 activation

The Hy-PC is soaked in H_2O_2 with different concentrations (10%, 20% and 30%). Then the sample was washed with water until $\text{pH} = 7$ and dried at 100°C overnight. The modified sample was obtained after at 400°C for 4 h and at 700°C for 2 h in a quartz tube furnace under N_2 atmosphere with a flow rate of 100 mL min^{-1} (denoted as $\text{H}_2\text{O}_2\text{-PC}$).

2.2.6 Cu^{2+} activation

The above petroleum coke activated by HNO_3 was soaked in the $\text{Cu}(\text{NO}_3)_2$ solution for 10 h at room temperature to obtain the samples with different Cu loadings (5%, 8% and 10%). Then the sample was obtained after dried at 100°C overnight (denoted as xCu-PC).

2.3 Structural Characterizations

X-ray diffraction (XRD) measurements were determined using a Rigaku D/MAX RAPID diffractometer employing $\text{Cu K}\alpha$ radiation. The morphology of the samples was observed by using a FEI Quanta 200 scanning electron microscope (SEM). The N_2 adsorption-desorption experiments were performed at -196°C on a QUADRASORB SI sorptometer.

2.4 Desulfurization Activity

The desulfurization activity test was conducted in a fixed-bed quartz tube reactor of 10 mm internal diameter. 1.5 g sample was first pretreated in the middle of the reactor between two quartz wool plugs with highly purified N_2 stream at 300°C for 1 h to eliminate the adsorbed gases. Subsequently, when the temperature in the reaction zone reached the desired value and kept a steady state, the feed gas containing SO_2 , O_2 , H_2O and balance N_2 was introduced into the reactor with a flow rate of 300 mL min^{-1} . The inlet and outlet SO_2 concentration were continually monitored by a Wuhan Tianhong TH-990S SO_2 gas analyzer. The SO_2 removal efficiency was calculated as follows:

$$\text{SO}_2 \text{ conversion (\%)} = \left(1 - \frac{[\text{SO}_2]_{\text{out}}}{[\text{SO}_2]_{\text{in}}}\right) \times 100\% \quad (1)$$

where $[\text{SO}_2]_{\text{in}}$ and $[\text{SO}_2]_{\text{out}}$ is the inlet and outlet SO_2 concentration (ppm).

3 RESULTS AND DISCUSSION

3.1 Characterizations

The chemical composition and phase structure of the samples were determined by XRD patterns. As shown in Fig. 1, an obvious main broad peak can be found at 25° over raw petroleum coke, indicating that the raw petroleum coke still retained a partially graphitized structure (Liu *et al.*, 2011; Zhan *et al.*, 2011). The high crystallinity and the tight structure may decrease the adsorption performance of petroleum coke. Compared with the raw petroleum coke, the characteristic peak of the sample with a KOH/coke ratio of 2:1 showed new absorption peaks at 29° and 44° , which are the characteristic peaks of graphite-like. With the increase of KOH/coke, the intensity of the peaks at 29° and 44° gradually decreased, which means that the degree of crystallization is reduced and the degree of activation is further increased.

Fig. 2 presents the SEM image of R-PC, HNO_3 -PC and K-PC. From Figs. 2(a) and 2(b), the surface of raw petroleum coke appeared wrinkled, relatively rough, and basically without gaps, which indicates that its crystallinity and ordering degree is high. In other word, raw petroleum coke was partially graphitized with tight structure, which is in agreement with the results of XRD analysis. A lamellar surface of petroleum coke activated by HNO_3 can be seen in Figs. 2(c) and 2(d) and a certain amount of micropores and larger pores appeared on the surface. This may be due to HNO_3 as a strong corrosive agent, which can remove the ash from the raw petroleum coke and react with its carbon skeleton through the strong oxidation, thereby forming many micropores. As shown in Figs. 2(e) and (f), the petroleum coke activated by KOH also had prominent porous structure, indicating the selective activation of KOH could consume carbon atoms of petroleum coke to produces a developed porous structure. The highly developed pore structure could provide reactive sites for SO_2 , promoting SO_2 removal activity.

3.2 The Effect of Hydrothermal and High-temperature Treatment on Desulfurization Performance

The efficiency curve will decay and reach zero with time. For an excellent adsorbent, it must show a high efficiency close to 100% at the beginning. In order to better compare and avoid errors caused by gas delay, the data within 0.5–4 h was monitored for all samples.

Petroleum coke is rich in volatiles and ash. The volatiles can be removed by dehydration. Thus, the desulfurization effect of petroleum coke activated by high-pressure hydrothermal and high temperature has been studied, as shown in Fig. 3. It can be seen that the desulfurization efficiency of R-PC was very low, basically maintaining between 35–45%. The desulfurization efficiency of sample processed by hydrothermal or high-temperature activation improved. Furthermore, with two combined activations, the Ht-PC sample showed the remarkably improved

Fig. 1. XRD spectra of raw petroleum coke and petroleum coke treated with different KOH/coke ratio.

Fig. 2. SEM image of (a–b) R-PC, (c–d) HNO₃-PC and (e–f) K-P.

Fig. 3. Desulfurization curve of different samples after hydrothermal activation and high-temperature activation. Reaction conditions: 1000 ppm SO₂, 5% O₂, 8% H₂O, SV = 5732 h⁻¹, T = 120°C.

desulfurization efficiency compared with the raw material. The initial desulfurization efficiency can reach 76.4%, and can basically maintain more than 60% with the extension of time. The raw petroleum coke had high crystallinity with compact structure. The specific surface area of raw petroleum coke was only 2.67 m² g⁻¹ and there were a few basic active groups on the surface.

The specific surface area of Ht-PC reached $59.0 \text{ m}^2 \text{ g}^{-1}$. The tar and hydrocarbons on the surface of the activated petroleum coke are removed, so that the micropores covered or blocked by these substances are opened and exposed, which contribute to SO_2 removal.

3.3 The Effect of Acid Activation on Desulfurization Performance

Strong acid with super acidity can modify the surface structure of materials by etching particles and ash on the surface of materials. The desulfurization performances of petroleum coke activated by two common strong acids (HCl, HNO_3) were studied. As shown in Fig. 4, comparison with the sample without acid treatment (Ht-PC), the desulfurization performance of HCl-PC improved slightly. Moreover, the HNO_3 -treated sample exhibited an obviously increased desulfurization performance with the SO_2 removal rate above 82%. It should be noted that the specific surface area of HNO_3 -PC was up to $247.7 \text{ m}^2 \text{ g}^{-1}$ compared to that of Ht-PC ($59.0 \text{ m}^2 \text{ g}^{-1}$). Thus, well-developed pores resulted from the consumption of ash and carbon skeleton were formed on HNO_3 -PC (Lizzio and Debarr, 1996; Lisovskii *et al.*, 1997), which could provide more reactive sites for SO_2 . Moreover, strong acid can oxidize functional groups on the surface of activated carbon to improve the content of oxygen-containing acidic groups on the surface and enhance the surface polarity, enhancing the adsorption capacity of activated carbon to polar substances.

3.4 The Effect of Alkali Activation on Desulfurization Performance

KOH as a strong oxidant can also activate petroleum coke and increase its surface alkalinity. It can be seen from Fig. 5(a) that the desulfurization performance of petroleum coke by KOH greatly improved and the amount of KOH played an important role in desulfurization performance. Among them, activated carbon with a KOH/coke ratio of 4:1 had the optimal desulfurization performance. The SO_2 removal rate of K-PC can reach up to 96.3%, and after 4 h of reaction, the SO_2 removal rate was still higher than 85%.

To further explore the effect of alkali amount for petroleum coke, the specific surface area of samples activated by different alkali/carbon ratios were measured. It can be seen from Table 2 that with the increase of KOH/coke ratio, the specific surface area of activated petroleum coke first increased and then decreased. When the KOH/coke ratio was 4:1, specific surface area of K-PC was up to $476.4 \text{ m}^2 \text{ g}^{-1}$. This indicated that the KOH amount is the crucial factor affecting the pore structure of activated coke. A proper amount of KOH can consume the active-site carbon, thereby forming pore structures consisted of micropores and mesopores (Lillo-Ródenas *et al.*, 2001; Lozano-Castelló *et al.*, 2001). Previous studies have demonstrated that the adsorption and oxidation of SO_2 mainly take place in the micropores (Moreno-Castilla *et al.*, 1993; Guo and Lua, 2002). The excessive KOH can further reacted with the carbon atom layer in the microporous

Fig. 4. Desulfurization curve of different samples after acid activation. Reaction conditions: 1000 ppm SO_2 , 5% O_2 , 8% H_2O , $\text{SV} = 5732 \text{ h}^{-1}$, $T = 120^\circ\text{C}$.

Fig. 5. Desulfurization curve of different samples activated by various mass ratio of (a) KOH and coke, (b) KOH and NaOH (alkali:carbon = 4:1). Reaction conditions: 1000 ppm SO₂, 5% O₂, 8% H₂O, SV = 5732 h⁻¹, T = 120°C.

Table 2. Specific surface area of samples activated by different KOH/coke ratios.

Samples	KOH/coke mass ratio				
	1:1	2:1	3:1	4:1	5:1
BET (m ² g ⁻¹)	312.5	378.3	421.6	476.4	443.2

structure and caused excessive ablation of carbon materials, which leads to the formation of more macropores, so that decreasing the specific surface area.

In view of the K-PC had the highest specific surface area, the texture played a major role for desulfurization performance. For comparison, NaOH-activated petroleum coke with an NaOH/coke ratio of 4:1 exhibited a slightly lower desulfurization performance than K-PC in Fig. 5(b). This may be due to the alkalinity of KOH was stronger than NaOH, and had a stronger destructive force on the internal structure of the sample. Under the same dosage condition, more KOH can penetrated into the basic crystallites of petroleum coke and chemically reacted with petroleum coke, thereby producing more pores for SO₂ adsorption.

3.5 The Effect of Concentration of H₂O₂ on Desulfurization Performance

The effect of concentration of H₂O₂ on desulfurization performance of petroleum coke was shown in Fig. 6. The H₂O₂ concentration of 10% can significantly improve the desulfurization performance. As the concentration of H₂O₂ further increased, the desulfurization performance of the prepared desulfurizer only slight enhanced. H₂O₂ is unstable, easy to be decomposed into OH and adsorbed on the surface of the adsorbent. The effect of H₂O₂ on desulfurization may be understood in the following two aspects: On the one hand, the generated OH may activate the adsorbent by reacting with the surface carbon sites; on the other hand, it provided surface oxygen-containing group and basic sites for adsorbent, which is conducive to SO₂ removal.

3.6 The Effect of Concentration of Cu on Desulfurization Performance

The effect of concentration of Cu on desulfurization performance was investigated. As shown in Fig. 7, when Cu loading is 5%, the desulfurization performance of the desulfurizer is the best, and as the reaction time is extended to 2 h, the change of the desulfurization performance tends to be consistent compared with the sample without Cu activation. As previously reported (Gao *et al.*, 2011), the loaded metal ions eventually exist as oxides. The good desulfurization performance of 5%-Cu-activated petroleum coke may be due to the good redox property of CuO, which can promote the reaction SO₂ → SO₃. However, introducing too much Cu is easy to form large CuO particles, which had an inhibitory effect on desulfurization because of blocking the pore entrances into activated carbon.

Fig. 6. Desulfurization curve of different samples activated by various concentrations of H_2O_2 . Reaction conditions: 1000 ppm SO_2 , 5% O_2 , 8% H_2O , $\text{SV} = 5732 \text{ h}^{-1}$, $T = 120^\circ\text{C}$.

Fig. 7. Desulfurization curve of different samples activated by various concentrations of Cu^{2+} . Reaction conditions: 1000 ppm SO_2 , 5% O_2 , 8% H_2O , $\text{SV} = 5732 \text{ h}^{-1}$, $T = 120^\circ\text{C}$.

3.7 The Effect of Temperature on SO_2 Adsorption

It can be found from Fig. 8 the relationship between desulfurization rate and reaction temperature. When the reaction temperature was 120°C , the desulfurization performance was better than that under the conditions of 80°C and 160°C . Temperature is an important factor affecting desulfurization efficiency, and activated-carbon material removal of SO_2 is the main adsorption process. Furthermore, given the adsorption reaction ($\text{SO}_2 \rightarrow \text{SO}_3$) was an exothermic process (Lizzio and Debarr, 1996), high temperature had adverse effect on SO_2 adsorption. Conversely, further reacting with H_2O to generate H_2SO_4 was an endothermic process, which occurred more easily at high temperatures. However, water vapor could not be adsorbed on the surface of K-PC at high temperatures, and thus the active site could be occupied by the generated insoluble H_2SO_4 which in turn hinders the reaction to proceed. Thus, there was an optimal value in the experiment. The desulfurization temperature was optimal when the heat released by the adsorption reaction was approximately equal to the transfer required for the catalytic reaction. From the experiment, the best desulfurization temperature was 120°C .

3.8 The Effect of Space Velocity on SO_2 Adsorption

Fig. 9 shows the relationship between desulfurization rate and space velocity. It can be seen

Fig. 8. Desulfurization curve of K-PC under various temperatures. Reaction conditions: 1000 ppm SO₂, 5% O₂, 8% H₂O, SV = 5732 h⁻¹.

Fig. 9. Desulfurization curve of K-PC under different space velocity. Reaction conditions: 1000 ppm SO₂, 5% O₂, 8% H₂O, SV = 5732 h⁻¹, T = 120°C.

that as the space velocity increases, the desulfurization rate showed a downward trend. When the space velocity was 5732 h⁻¹, the change trend of the desulfurization rate of the sample was relatively stable. This may be because as the velocity increased, the external diffusion resistance decreased, which facilitated the SO₂ adsorption. However, meanwhile, the residence time of the flue gas on the surface of the desulfurizer became shorter, and the gas adsorption and SO₂ oxidation reaction time was shortened, so that the SO₂ cannot be fully absorbed and oxidized, resulting in a lower desulfurization rate.

3.9 The Effect of SO₂ Concentrations on SO₂ Adsorption

As shown in Fig. 10, the SO₂ concentration had slight effect on the desulfurization rate. With the increase of the SO₂ intake concentration, the desulfurization rate increased slightly. In theory, the bigger the concentration of inlet SO₂, the faster the adsorption reaction, which can increase the conversion rate of the adsorbent.

3.10 The Effect of Water Vapor Content on SO₂ Adsorption

From Fig 11, in presence of without water, the adsorption performance of K-PC on SO₂

Fig. 10. Desulfurization curve of K-PC under different SO_2 concentrations. Reaction conditions: 5% O_2 , 8% H_2O , $\text{SV} = 5732 \text{ h}^{-1}$, $T = 120^\circ\text{C}$.

Fig. 11. Desulfurization curve of K-PC under different water vapor content. Reaction conditions: 1000 ppm SO_2 , 5% O_2 , $\text{SV} = 5732 \text{ h}^{-1}$, $T = 120^\circ\text{C}$.

molecules was very poor. It is found that the removal of SO_2 was more advantageous under water vapor content of 8%. For the catalytic oxidation of SO_2 at low temperature, the increasing gas humidity can accordingly increase the concentration of the gas-adsorption phase. This could be due to the presence of H_2O could favor the formation of alkaline water membrane, which would facilitate the removal of acidic SO_2 (Liu and Adanur, 2015; Xu *et al.*, 2016). On the other hand, the addition of H_2O could take part in the reactions ($\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$), which accelerated the desorption of adsorbed SO_3 from the active center of activated carbon (Molina-Sabio *et al.*, 1995; Andrey *et al.*, 2002). However, when the H_2O content was up to 16%, a thicker water film could be formed on the surface of the activated carbon (Watts and Dick, 2014), which restricted the transmission of O_2 and increased the transmission resistance of the flue gas, which reduced the chemical reaction rate, thereby reducing the desulfurization efficiency.

3.11 The Effect of O_2 Concentrations on SO_2 Adsorption

The adsorption rate of SO_2 increased first and then decreased with the increasing O_2 concentrations (Fig. 12). The suitable O_2 concentration for SO_2 adsorption in K-PC system was about 5%.

Fig. 12. Desulfurization curve of K-PC under different O₂ concentrations. Reaction conditions: 1000 ppm SO₂, 8% H₂O, SV = 5732 h⁻¹, T = 120°C.

The desulfurization efficiency was very low in the absence of O₂, which may be owing to most of the adsorption was physical adsorption, and only a small part of SO₂ reacted with water to form H₂SO₃ (Rosas *et al.*, 2017). In the presence of O₂, the chemical adsorption process dominated the total desulfurization reaction. In detail, the active lattice oxygen produced by adsorbed O₂ had the ability to catalytically oxidize SO₂ to SO₃, and the generated SO₃ would further react with water vapor to form final product H₂SO₄, resulting in the significantly enhanced desulfurization efficiency of K-PC. In addition, Raymundo-Piñero *et al.* (2001) believed that intermediate C-O may also appear in the intermediate process and can be react with SO₂ molecules around to SO₃. However, the C-O intermediate would tend to be a stable group if there is no SO₂ around, hindering SO₂ adsorption. Thus, the decreased desulfurization efficiency may be due to more stable C-O intermediate formed on the surface when O₂ concentration was up to 10%.

4 CONCLUSIONS

Samples of petroleum coke, a low-cost carbonaceous substance, were prepared as adsorbents for flue gas desulfurization using six common techniques of activation, viz., hydrothermal, high-temperature, acid-based, alkali-based, H₂O₂-based and Cu²⁺-based treatment.

1. Raw petroleum coke exhibited a very low desulfurization efficiency, which hovered between 35% and 45%, as well as a miniscule specific surface area (2.67 m² g⁻¹).
2. High-temperature activation modified the structure and chemical properties of the petroleum coke, leading to an initial desulfurization efficiency of 76.4%, with a specific surface area of 59.0 m² g⁻¹.
3. The desulfurization efficiency was further enhanced by adding a suitable amount of acid-based activator, which consumed the petroleum coke's ash content and carbon skeleton and thereby formed structures consisting of micropores and mesopores.
4. Petroleum coke activated with the alkali KOH at a ratio of 4:1 displayed the maximum desulfurization efficiency, 96.3%, and a specific surface area of 476.4 m² g⁻¹.
5. The optimal conditions for adsorption comprised an atmosphere of 5% O₂ and 8% H₂O, a reaction temperature of 120°C and a space velocity of 5732 h⁻¹.

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