Enhanced Simultaneous Photocatalytic Removal of SO₂ and CO₂ Using Powder and Coated Zeolites-Supported TiO₂ Under Concentrated Sunlight Irradiation

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Enhanced simultaneous photocatalytic removal of SO₂ and CO₂ using powder and coated zeolites-supported TiO₂ under concentrated sunlight irradiation

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Abstract

Single-step process for simultaneous removal of gaseous pollutants is more advantageous than multi-steps one. In this study, the efficiency of a novel synthetic zeolite (Ze) prepared from stone cutting sludge and a natural zeolite (clinoptilolite, Cp) as the supports of TiO₂ photocatalyst were examined for the separate and simultaneous removal of SO₂ and CO₂ under solar irradiation using a parabolic trough collector (PTC). The composites exhibited a higher efficiency than raw zeolites and TiO₂ for the removal of both gases. The maximum removal of SO₂ by TiO₂-Ze and TiO₂-Cp under sunlight was 41.9 % and 56.2 % that enhanced to 53.4 % and 78.8 %, respectively in the presence of CO₂. Correspondingly, it was 61.8 % and 68.7 % for single CO₂ removal that increased to 74.2 % and 79.0 % in the binary gas stream. This behavior could be due to the enhanced simultaneous SO₂ oxidation and CO₂ reduction. The performance of coated composite for SO₂ was higher than of powder one (54.3% vs. 41.9%) and for CO₂ removal was almost close together (58.9% vs. 61.2%). This work promises the application of photocatalytic co-removal of SO₂ and CO₂ by using synthetic and natural zeolite under solar irradiation.

Keywords: Photocatalysis; Zeolite; Air pollution and control, Greenhouse gas, Acidic gas.

Introduction

Combustion of fossil fuels including petroleum, coal, and natural gas results in the significant emissions of acidic gases such as carbon dioxide (CO₂) and sulfur dioxide (SO₂) that are harmful to human health and the environment ^{1,2}. SO₂ is an extremely toxic gas and a major

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contributor to acid rain ³. Also, CO₂ is a key greenhouse gas that promotes global climate change via global warming ⁴.

Although the flue gas desulfurization (FGD) technology especially wet scrubbing has been widely used for SO₂ treatment, the high operational costs and secondary pollution are its main disadvantages ⁵. The main technologies for CO₂ reduction are CO₂ capture and storage (CCS) as well as CO₂ capture and utilization (CCU). The major concerns associated with CCS are high cost and the risk of leakage from the storage of the gas. Among the methods, the CCU approach is more economically feasible and helps the conversion of CO₂ into a wide range of end products providing hydrocarbon recovery ⁶.

Separate technologies (i.e single-step processes) can remove pollutants from exhaust gases efficiently ⁷. However, these technologies are often multi-step processes, complex, and costly. Therefore, it is suitable to develop an integrated, economic, easy implementation and high efficient process for the purification of flue gas ^{7,8}.

Simultaneous removal of SO₂ and CO₂ as the main components in the flue gas has been greatly concerned in the air pollution control ^{2,9}. Adsorption and photocatalytic oxidation (PCO) can offer promising approaches for the simultaneous removal of gases because of low cost, relatively simple design and minimum secondary pollution ^{6,8}. During the past decade, PCO is emerged as an environmentally friendly and economically profitable technology for pollutants removal through their converting into harmless compounds or value-added chemicals ¹⁰. Besides, it can be more attractive by using of solar energy as a clean and sustainable source ¹¹.

Among various photocatalysts, TiO₂ has received tremendous attention for the photocatalysis process because of availability, non-toxicity, low cost, high photostability, abundance and environmentally friendly nature ¹². However, it suffers from several drawbacks such as low surface area, activity only under ultraviolet (UV) light (about 5% of the sunlight)

and high recombination of photo-generated electron-hole pairs ^{13,14}. To overcome these limitations, many researches have been focused on the TiO₂ modification via doping elements, coupling of semiconductors and composites synthesis of photocatalyst and adsorbent support ^{14,15}.

Zeolites, one of the most preferred supports for photocatalysts, are crystalline aluminosilicates that have many desirable properties including uniform-shaped pores, high surface area, thermal stability, hydrophilic /hydrophobic nature and polarizability ^{2,11}. These properties can improve the potential of pollutants adsorption by TiO₂-zeolite composites. Furthermore, the modification of TiO₂ with zeolite support not only can induce the shifting of the absorption affinity of the photocatalyst toward the visible light region via changing the electronic state of TiO₂ ¹⁴, but also improves the separation of photo-induced charge carriers by trapping electrons and increasing the photocatalytic activity ¹⁶.

The adsorption-photocatalysis efficiency of TiO₂-zeolite composites for removal of SO₂ ¹⁷⁻¹⁹ and CO₂ ^{20,21} was reported. Simultaneous SO₂ and CO₂ adsorption using calcium-based sorbents ²², zeolitic imidazolate frameworks ²³, metal-organic frameworks ²⁴, Al₂O₃ ²⁵, zeolite and active carbon ¹ indicated the competitive adsorption between SO₂ and CO₂ molecules to occupy active sites on the adsorbent surface. Furthermore, the co-presence of sulfide compounds and CO₂ provides the synergistic effect for improving their photocatalytic removal under UV irradiation ^{4,26}.

Nevertheless, the adsorption and photocatalysis of SO₂ and CO₂ as separately and simultaneously on zeolite-TiO₂ composite under sunlight irradiation especially using a solar collector have not been investigated. We have previously reported the photocatalytic removal of SO₂ using natural and synthesized zeolites as supports of TiO₂ photocatalyst under sunlight irradiation in a parabolic trough collector (PTC)¹⁹. In the present research, the same process was used for the simultaneous removal of SO₂ and CO₂ after testing each gas separately. Furthermore, the zeolite supported TiO₂ photocatalyst was prepared in the coated and powder

forms. The use of coated photocatalyst instead of powder one for photodegradation of air pollutants has the advantages such as easier control and more transparency regarding practical applications²⁷⁻²⁹. Furthermore, the experimental data of photocatalytic degradation behavior of SO₂ and CO₂ were evaluated by isotherm and kinetic models.

Results and discussion

Performance of TiO₂, zeolites and TiO₂- zeolite composites in SO₂ and CO₂ removal

The performance of TiO₂, Cp, Ze and their composites for the removal of SO₂ and CO₂ under sunlight irradiation was shown in Figures. 1 and 2. A significant difference was observed in SO₂ and CO₂ removal in adsorption and adsorption- photocatalysis processes, separately ($p < 0.05$). There was a low adsorption potential of SO₂ on Cp (13.9 %) and Ze (10.0 %). No photocatalytic activity was observed for zeolites under sunlight irradiation. It was reported that the aluminum silicate compounds could not adsorb the ultraviolet and visible radiation^{43,44}. The maximum adsorption of SO₂ by TiO₂ was 20.3 % that considering the contribution of photolysis (6.2 %), it reached up to 47.6 % under sunlight irradiation. The efficiency of TiO₂-Ze and TiO₂-Cp for the SO₂ removal in the adsorption process was 27.6 % and 31.7 % that increased to 70.0 % and 78.8 % through adsorption/photocatalysis under sunlight irradiation, respectively (Figure 1).

Figure 1. Efficiency of TiO₂, zeolites and their composites for SO₂ removal in adsorption and photocatalysis under sunlight irradiation (Initial concentration of SO₂: 8.0 ppm, humidity:10 %, sunlight intensity: 125.0-135.0 mW cm⁻², gas flow rate: 40.8 mL min⁻¹).

*Different letters (small and capital separately) show significant differences according to Tukey's test (p<0.05).

The adsorption of CO₂ was in order of Cp (11.7 %)> TiO₂ (9.7 %)> Ze (5.5 %) that showed significant changes (P=0.024). Considering the contribution of photolysis (5.3%), the removal of CO₂ by TiO₂ under sunlight irradiation was obtained 22.8 %. The efficiency of TiO₂-Ze and TiO₂-Cp for CO₂ adsorption was 21.1 % and 28.4 % that increased up to 61.8 % and 78.9 % by adsorption/photocatalysis under sunlight irradiation, respectively (Figure 2).

Figure 2. Efficiency of TiO₂, zeolites and their composites for CO₂ removal in adsorption and photocatalysis under sunlight irradiation (Initial concentration of CO₂: 943.8 ppm, humidity: 10 %, sunlight intensity: 119.0-127.0 mW cm⁻², gas flow rate: 40.8 mL min⁻¹).

*Different letters (small and capital separately) show significant differences according to Tukey's test (p<0.05).

The results showed that the composites had greater efficiency than the zeolite and TiO₂ alone for the removal of SO₂ and CO₂. Clearly, TiO₂ supported on zeolite integrates the photocatalytic activity and adsorptive characteristics of zeolite (the synergistic effect) providing the enhancement of gas removal. The combined effects of the high specific surface area, low recombination of photogenerated charge carrier as well as increased absorption spectrum of the photocatalyst could lead to the increase of composites activity for the pollutant

removal^{45,46} as confirmed by Brunauer–Emmett–Teller (BET), photoluminescence (PL) and UV–Vis diffuse reflectance spectroscopy (UV-Vis DRS) analysis¹⁹. Furthermore, TiO₂-Cp composite showed better performance in the removal of SO₂ and CO₂ comparing to that of TiO₂-Ze (p<0.0001).

Comparison of the adsorbents performance in the removal of SO₂ and CO₂

The adsorption behavior of SO₂ and CO₂ depends on the nature of adsorbates such as acidity, polarity and kinetic diameter as well as the nature of adsorbents like polarity and pore size^{2,36}. Both SO₂ and CO₂ are acidic molecules and show a high affinity for alkaline surfaces like TiO₂¹. As the polarizability of SO₂ ($4.3 \times 10^{-24} \text{ cm}^3$) is more than CO₂ ($1.9 \times 10^{-24} \text{ cm}^3$), it has a stronger tendency to bind to polar adsorbents like TiO₂ ($5.0 \times 10^{-24} \text{ cm}^3$) and zeolites^{8,47}. The SiO₂/Al₂O₃ ratio can determine the polarity of the zeolites. The smaller ratio, the greater the polarity⁴⁸. The Ze with a SiO₂/Al₂O₃ ratio of 2.7 is more polar than Cp with a ratio of 6.0¹⁹. However, the lower polarity of CO₂ compared to SO₂ showed a greater adsorption tendency towards zeolites than TiO₂. The kinetic diameter of SO₂ and CO₂ is 0.4 and 0.3 nm, respectively²³. The pore diameters of TiO₂, Ze and Cp are 3.0, 11.0 and 23.2 nm, respectively¹⁹. Therefore, the kinetic diameter can not be an obstacle to the adsorption of the studied gases by these adsorbents. The higher adsorption of both SO₂ and CO₂ gases by Cp may be due to its larger pores that can provide more adsorption sites for gas molecules²

Comparison of the composites performance in the removal of SO₂ and CO₂

The TiO₂-Cp composite with a large pore size distribution has a greater tendency to remove the studied gases through the adsorption-photocatalysis processes because the large particles can reduce the agglomeration of the composite during the synthesis process⁴⁹ and help to decrease the recombination rate of electron-hole pair⁵⁰. These properties in the TiO₂-Cp composite were confirmed by scanning electron microscope (SEM) and PL analysis¹⁹. It

revealed that the reaction of TiO₂ with Cp was better performed leading to higher performance in removing SO₂ and CO₂ gases.

Although the amount of TiO₂ added to the both zeolites was the same, but based on the results of energy dispersive X-ray Spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS) analysis ¹⁹, it was found that the amount of TiO₂ in the surface of the TiO₂-Cp sample was higher than TiO₂-Ze. This could be due to the presence of more oxygen groups in TiO₂-Cp composite. In this composite, the presence of more surface TiO₂ species could increase the active sites for adsorption and photocatalysis reactions ⁵¹. Moreover, the increase of photo excited electron- hole pairs, followed by the increase of oxidative species such as radical OH ⁵² improved the performance of TiO₂-Cp composite for SO₂ and CO₂ photodegradation.

As mentioned earlier, the polarity of SO₂ is higher than CO₂. Besides, it is expected that TiO₂-Ze has more polarity compared to TiO₂-Cp. Hence, it can be inferred that TiO₂-Ze composite must have more tendency for SO₂ adsorption than TiO₂-Cp, whereas the TiO₂-Cp composite showed better performance in the removal of both gases. This indicates that the polarity was not the only parameter affecting the removal of these gases.

The TiO₂-Cp composite with a higher SiO₂/Al₂O₃ ratio than TiO₂-Ze has higher hydrophobic properties ¹¹ which can improve the photocatalytic removal of SO₂ and CO₂ in the presence of humidity ⁴⁸.

Simultaneous removal of SO₂ and CO₂ by TiO₂-zeolite composites

Table 1 shows the results of SO₂ and CO₂ removal by TiO₂-Ze and TiO₂-Cp composites in separate and simultaneous conditions. The SO₂ adsorption by TiO₂-Ze and TiO₂-Cp in the presence of CO₂ was increased about 7 and 13%, respectively. Although the adsorption of CO₂ by TiO₂-Ze was relatively reduced (around 7%), it was constant for TiO₂-Cp (36-37%). Correspondingly, the removal efficiency of SO₂ and CO₂ by both composites in the

adsorption/photocatalysis processes under sunlight was improved in the simultaneous flue of two gases comparing to their separate cases. Removal capacity of SO₂ by TiO₂-Ze in the separate and simultaneous conditions was 5.2 and 5.8 mg g⁻¹ respectively, whereas the correspondent amount for CO₂ was 368.1 and 385.2 mg g⁻¹. It revealed that the removal of both gases in simultaneous condition enhanced in comparison to the separate condition.

Table 1- Separate and simultaneous removal of SO₂ and CO₂ by composites under sunlight irradiation

Removal	Gas	TiO ₂ -Ze		TiO ₂ -Cp	
		Ads.	Ads/PCO	Ads.	Ads/PCO
Separate removal	SO ₂ (%) (Initial conc. 23 ppm)	20.1±0.9 ^b	41.9±0.4 ^B	24.0±1.1 ^b	56.2±0.8 ^B
Simultaneous removal	SO ₂ (%) (Initial conc. 26 ppm)	26.8±1.5 ^a	53.4±0.7 ^A	36.6±0.9 ^a	78.8±0.8 ^A
Separate removal	CO ₂ (%) (Initial conc. 944 ppm)	21.1±0.3 ^a	61.8±0.3 ^B	37.4±0.9 ^a	74.2±0.6 ^B
Simultaneous removal	CO ₂ (%) (Initial conc. 1187 ppm)	14.3±1.1 ^b	68.7±0.5 ^A	36.1±0.9 ^a	79.0±0.7 ^A

Ads.:adsorption, PCO: photocatalysis oxidation

Condition: 50% TiO₂-Ze- 300 °C, 50% TiO₂-Cp -300 °C, composite: 0.1 g, humidity:10 %, sunlight intensity: 119.0-127.0 mW cm⁻²gas flow rate: 40.8 mL min⁻¹.

*Different letters (small and capital separately) show significant differences in each column for each gas according to Tukey's test (p<0.05).

It should be noted that the maximum gas removal has basically occurred in the low concentration¹⁹ due to more access to the active sites of composite^{53,54}. Consequently, it is expected that under simultaneous presence, SO₂ has more possibility than CO₂ to occupy the sites. On the other hand, in the combined gas system, the increased concentration of one gas prevents the adsorption of other pollutants or excludes them from the preferred adsorption sites

^{23,25}. However, as the results showed, the presence of CO₂ did not interfere with SO₂ adsorption, whereas the CO₂ adsorption on the TiO₂-Ze was slightly reduced.

The difference in the polarity of SO₂ and CO₂ molecules and their adsorption tendency on the similar active sites of the adsorbent ^{8,24} explain the stronger electrostatic reaction of the SO₂ with both composites. The relatively same kinetic diameter of SO₂ and CO₂ molecules suggests that this parameter can not be a determining factor for their adsorption by composites. Moreover, the higher density of SO₂ (2.6 kg m⁻³) comparing to CO₂ (2.0 kg m⁻³) provides the higher adsorption on the composite surface ⁵⁵.

Additionally, the simultaneous presence of SO₂ and CO₂ and increasing the mass density of total gases could have a significant effect on the Henry's law solubility of SO₂ (1.2 mol L⁻¹) but a little effect on CO₂ (0.03 mol L⁻¹) ⁵⁶. Therefore, in the simultaneous presence of SO₂ and CO₂ in the system containing moisture, the SO₂ adsorption by the composites would be higher. However, it seems that as sufficient active sites are available on the adsorbent surface, the interaction between the SO₂ and CO₂ molecules prevents the substantial decrease of the CO₂ adsorption in the presence of SO₂ ²³.

In the photocatalytic process, the CO₂ conversion requires a reducing agent and SO₂ conversion requires an oxidizing agent (reactions of 1-6). The conversion of SO₂ and CO₂ at the same time can be a reduction–oxidation (redox) reaction. Although H₂O and SO₂ can act as reducing agents for CO₂, the oxidation potential of H₂O is about 1.2 V (reaction 3) and SO₃²⁻ (resulting from SO₂ conversion) is 0.9 V (reaction 4). This indicates that the presence of SO₂ for CO₂ reduction is better than H₂O because it requires less energy. Therefore, the photogenerated holes and electrons would be instantaneously consumed and their separation was improved ⁴. In the current study, the main product of SO₂ removal by photocatalytic oxidation in the presence of humidity was sulfate (SO₄²⁻). More details were presented in the previous study ¹⁹. According to the literature, the products of CO₂ photocatalytic degradation

on TiO₂- zeolite photocatalysts in the presence of humidity could be methane (CH₄) and carbon monoxide (CO) ⁵⁷⁻⁵⁹. However, as the online outlet concentration of these gases was below the detection limit of the gas analyzer (i.e. less than 0.2 ppm and 0.13 ppm for CH₄ and CO, respectively), it was not possible to measure the exact amount of these gases. The redox process of SO₂ and CO₂ can be described as the following reactions ^{4,10}.

The effect of sulphide compounds as the reducing agent in the increase of photocatalytic conversion rate of CO₂ under UV irradiation was reported by other researchers ^{4,26}. Aliwi and AL-Jubori (1989) ²⁶ found that the formation of two main products from CO₂ conversion including formic acid (HCOOH) and formaldehyde (HCOH) increased in the presence of H₂S. Li et al. (2019) ⁴ indicated that the oxidation energy of SO₂ improved the CO₂ reduction and led to the increase of SO₄²⁻ and CO /HCOOH formation, respectively.

Efficiency of the powder and coated TiO₂-Ze composites in SO₂ and CO₂ removal

As shown in Table 2, despite the use of a very less amount of TiO₂- Ze composite in the coated form (0.1 of powder), its performance for SO₂ removal in both adsorption and adsorption/photocatalysis processes was higher than the powder form. Although the same trend was observed for CO₂ adsorption, the results of the adsorption/photocatalysis process showed almost the same removal of CO₂ by the coated and powder sample. Although the amounts of 15, 20 and 30 mg of the coated composite were also investigated, the whole gas was almost

removed in the adsorption process, so there was no possibility of determining the effect of photocatalytic removal of these gases.

Table 2- Performance of TiO₂-Ze composite in the powder and coated forms to remove SO₂ and CO₂.

TiO ₂ -Ze	SO ₂ removal (%)		CO ₂ removal (%)	
	(Initial conc. 23 ppm)		(Initial conc. 944 ppm)	
	Ads.	Ads/PCO	Ads.	Ads/PCO
Powder (100 mg)	20.1±0.9 ^b	41.9±0.4 ^B	21.1±1.1 ^b	61.2±1.3 ^A
Coated (10 mg)	37.8±1.1 ^a	54.3±1.2 ^A	32.8±0.9 ^a	58.9±1.5 ^A

Ads. : adsorption, PCO: photocatalysis oxidation

Condition: 50% TiO₂-Ze- 300 °C, humidity:10 %, sunlight intensity: 119.0-127.0 mW cm⁻², gas flow rate: 40.8 mL min⁻¹)

*Different letters (small and capital separately) show significant differences in each column according to Tukey's test (p<0.05).

The coating has the greatest effect on the contact surface of gases and composites, so it increases the adsorption amount and consequently improves the photocatalysis removal of gases. The results showed that the dip-coating method influence more on the SO₂ removal than CO₂. This can be due to the slow movement of heavy SO₂ molecules⁶⁰ providing more contact surface and more adsorption. The coated technique has many advantages including prevention of particles scattering and their collision with the reactor, prevention of fluidization of the adsorbent in the presence of moisture, easy sample collection, a decrease of the overlap of the adsorbent or photocatalyst layers, as well as prevention of clogging the pores, decreasing turbidity of the adsorbent sample and better penetration of the light for photocatalysis processes²⁷⁻²⁹.

Adsorption isotherms

Adsorption isotherms of SO₂ and CO₂ onto the TiO₂-Ze composite at various concentrations are shown in Figure 3. The results demonstrated that the equilibrium adsorption capacity (q_e)

236 of SO₂ and CO₂ was significantly influenced by the initial concentration of gases. The
 237 experimental data was better fitted with the Langmuir isotherm ($R^2 = 0.94$ for SO₂ and $R^2 =$
 238 0.99 for CO₂). Based on these results, the adsorption process mainly involved monolayer
 239 adsorption of SO₂ and CO₂ on the homogeneous active sites of the composite. The maximum
 240 adsorption capacity of SO₂ and CO₂ on the TiO₂-Ze composite (q_m) was 6.1 and 400 mg g⁻¹,
 241 respectively. From the data calculated in Table 3, the R_L is between 0 and 1 indicating the
 242 favorable adsorption. Yi et al. (2012)⁸ and Luo et al. (2017)¹ reported the suitability of
 243 Langmuir isotherm and the monolayer adsorption mechanism of SO₂ and CO₂ on the zeolite
 244 adsorbents.

Figure 3. The adsorption isotherms of SO₂ and CO₂ onto TiO₂-Ze (50% TiO₂-Ze 300°C, humidity:10%, composite: 0.1g, gas flow rate: 40.8 mL min⁻¹).

Table 3- Isotherm and kinetic parameters for the removal of SO₂ and CO₂ on the TiO₂-Ze.

Isotherm/kinetic parameters	SO ₂	CO ₂
Langmuir		
$q_{\max}$ (mg g ⁻¹)	6.1	400.0
K_L (L mg ⁻¹)	0.2	0.001
R_L	0.2-0.7	0.2-0.4
R^2	0.94	0.99
Freundlich		
K_f (mg g ⁻¹)(mg L ⁻¹) ^{1/n}	0.01	6.1
n	1.7	1.9
R^2	0.87	0.94
Langmuir–Hinshelwood		
k_{app} (min ⁻¹)	0.007	0.03
R^2	>0.999	>0.999

Langmuir–Hinshelwood (L-H) kinetic

As shown in Figure 4, the experimental data was in good agreement with a pseudo-first-order kinetic model ($R^2 = 0.92$ for SO_2 and $R^2 = 1.0$ for CO_2). The applicability of the Langmuir–Hinshelwood (L-H) kinetic model for the photocatalysis removal of SO_2 and CO_2 pollutants has been confirmed by the linearity in the plot of $1/r$ against $1/C_e$ ($R^2=1$ for both gases). The value of k was found to be 0.007 min^{-1} for SO_2 and 0.03 min^{-1} for CO_2 , respectively (Table 3). A good fitness of the data with this kinetic model represented that the adsorption of gases on the composite was a prerequisite for their efficient photocatalysis⁴¹. Also, according to this model, the most important factor limiting the rate of adsorption-photocatalysis reaction of SO_2 and CO_2 gases was the fixed active site of the composite^{42,53}.

Figure 4. Langmuir–Hinshelwood Kinetic of SO₂ and CO₂ onto TiO₂-Ze (50% TiO₂-Ze 300°C, humidity:10%, composite: 0.1g, gas flow rate: 40.8 mL min⁻¹).

Conclusion

The adsorption and photocatalysis processes for the separate and simultaneous removal of SO₂ and CO₂ using natural (clinoptilolite) and synthetic X zeolites- supported TiO₂ composites was investigated in a designed solar collector. The TiO₂- synthetic and natural zeolite composites showed the higher efficiency for the both gases removal than the raw zeolites and TiO₂. The simultaneous presence of SO₂ and CO₂ gases in the photoreactor improved the SO₂ removal from 41.9 to 53.4 % by TiO₂-Ze and from 56.2 to 78.8% by TiO₂-Cp, and the corresponding CO₂ removal from 61.8 to 68.7% by TiO₂-Ze and from 74.2 to 79.0% by TiO₂-Cp. The coated TiO₂-Ze composite acted better than powder one for the removal of gases especially for SO₂, so that the adsorption of this gas increased about two times and the adsorption-photocatalytic removal was promoted more than 10%. The CO₂ removal by coated and powder composite was in the range of 58.9 to 61.2%. The adsorption behavior of SO₂ and CO₂ gases on TiO₂-Ze composite was well described by the Langmuir isotherm with the maximum adsorption capacity 6 and 400 mg g⁻¹, respectively. The application of the synthesized composites for the removal of other binary or multi-gas systems is necessary to develop the process.

277 **Materials and methods**

278 **Materials**

279 The synthetic zeolite X with 80 % purity hereafter named as Ze, was previously synthesized
280 from the stone cutting sludge using the alkali fusion method ³⁰. The natural zeolite,
281 clinoptilolite (Cp), with 73 % purity was purchased from Aria Tamadon Company, Tehran,
282 Iran. Titanium tetraisopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$, 97%) was purchased from Sigma-Aldrich
283 (Germany).

284 **Preparation of zeolites**

285 Synthetic zeolite (Ze) with a particle size of less than 500 μm was used without any treatment.
286 Natural zeolite, clinoptilolite (Cp) was also used to compare the effect of zeolite type on SO_2
287 and CO_2 removal in adsorption and photocatalytic processes. Cp sample was washed with
288 distilled water to remove the surface dust and dried in an oven at 70 $^\circ\text{C}$ ³¹. Then it was ground
289 and sieved into a size of 53–105 μm . Both zeolites were separately used and as the support of
290 TiO_2 . The characterization of the used samples were reported in our previous study ¹⁹.

291 **Synthesis of TiO_2 particles and zeolite-supported TiO_2 composites**

292 TiO_2 particles and TiO_2 -based composites containing TiO_2 -Cp and TiO_2 -Ze (with 50 wt %
293 TiO_2 loading to zeolites) were prepared by the sol-gel method ¹⁹. Then, the samples were
294 calcined at 300 $^\circ\text{C}$ for 3 hours to obtain the powder form. The characterization of the composites
295 were also described in our previous study ¹⁹.

296 The coated composite was prepared using a sol-gel-based dip-coating method. Before
297 coating, the borosilicate beads with a diameter of 4-5 mm were initially soaked in ethanol
298 solution under ultrasonic bath for 30 min at room temperature (25 $^\circ\text{C}$), then rinsed in distilled
299 water for 15 min. The supports were again immersed for 5 min in ethanol solution with stirring
300 and finally immersed in distilled water with constant stirring for 15 min. The supports were
301 oven-dried at 60 $^\circ\text{C}$ for 1 h ^{32,33}. The powder composite (1 g) prepared previously (before

calcination) was dispersed in 100 mL of the ethanol solution under magnetic stirring for 4 h³². The prepared beads were transferred to a filter and kept after 1 min in contact with the composite sol. Then, they were allowed to drain freely. The coated beads were dried in the oven at 100°C and weighted³⁴. The difference in the weight of beads before and after coating indicated the coated composite amount on the supports. Finally, the coated composite was calcinated at 300°C for 3 h.

Experimental set-up

The adsorption and photocatalytic experiments of SO₂ and CO₂ gases were carried out in a 2 L Pyrex reactor (length of 100 cm, the external diameter of 5 cm, the internal diameter of 4.8 cm) placed in a designed solar parabolic trough collector (PTC) with a concentration ratio (CR) of more than 32.2 times¹⁹. The other equipments used in the SO₂ and CO₂ removal experiments included SO₂ gas tank, CO₂ gas, tank carrier gas tank (N₂), gas mixing tank, mass flow controller (MFC), and the gas analyzer. K-type Thermocouple (Thermometer autonics-T4W1) and solar power meter (SPM-1116SD) were used to measure the temperature and incident sunlight irradiance intensity. The pressure was adjusted with a manual valve.

Gas removal experiments

In the single gas experiments, the gas flow (CO₂ or SO₂) supplied from a cylinder with a pressure of 0.5 atmospheres was first mixed with nitrogen gas (0.5 atm) and then passed into the reactor with an adjusted gas flow rate by MFC. Under the simultaneous presence of two gases, the pressure of each gas was 0.5 atm (without combining with nitrogen gas) to keep 1 atm pressure in the photoreactor. After placing the prepared samples (TiO₂, zeolites and composites) in the reactor, the pollutant gas was involved in the different reactions with solid-phase and finally, the outlet concentration of SO₂ and CO₂ was continuously measured using the gas analyzer online (Vario plus industrial SE) during 5 and 10 min for CO₂ and SO₂ respectively. The removal efficiency of SO₂ and CO₂ was calculated using Eq.(1)³⁵:

$$Removal (\%) = \frac{C_{Inlet} - C_{Outlet}}{C_{Inlet}} \times 100 \quad \text{Eq.(1)}$$

where C_{Inlet} and C_{Outlet} are the inlet and outlet concentration of gas (ppm) respectively.

The removal experiments of SO₂ and CO₂ gases were conducted under defined conditions as following:

The photolysis reaction of the two pollutant gases was performed under sunlight irradiation in the absence of any photocatalyst or adsorbent. In the adsorption process, the reactor was completely covered by aluminum foil (dark conditions) and the removal of the gases by the prepared adsorbents including TiO₂, raw zeolites and TiO₂- zeolite composite samples was evaluated. To study the hybrid reactions of adsorption and photocatalysis, the removal of gases by the raw zeolites, TiO₂ and TiO₂- zeolite composites were tested under sunlight irradiation.

The simultaneous removal of SO₂ and CO₂ by the composites was investigated in the adsorption and photocatalysis processes under sunlight irradiation. Ultimately, the performance of powder and coated TiO₂-Ze composite for the separate and simultaneous removal of SO₂ and CO₂ was studied through adsorption and photocatalysis processes under sunlight.

The performance of TiO₂, zeolites and their composites for the removal of SO₂ and CO₂ was done in the optimized conditions that were already obtained in the preliminary experiments. The concentrations of SO₂ and CO₂ were 8.0 and 943.8 ppm, respectively. The relative humidity (10 %) was adjusted by injection of water to the surface of composites using the micropipette. The maximum sunlight intensity through the experiments was in the range of 119.0 to 135.0 mW cm⁻² from 11:30 AM to 14:30 PM. The hold time of gas (15 and 30 min for CO₂ and SO₂, respectively) presented the time that was kept in the reactor in contact with adsorbents and/or composites before exiting for analysis. All experiments were performed in three replications.

Adsorption isotherms

The adsorption isotherm describes the relationship between the equilibrium concentration of adsorbate and its adsorbed amount at the surface of solid materials ³⁶. For the study of adsorption isotherms, 0.1 g composite was used for different initial concentrations of SO₂ (2.8, 8.0, 16.2 and 23.3 ppm) and CO₂ (943.8, 1834.2, 2337.8 and 2961.5 ppm). These concentrations were obtained based on mixing the target gases (SO₂ and CO₂) and N₂ gas in the maximum tolerable pressure of 1 atm in the system.

The Langmuir model is based on the monolayer adsorption on the adsorbent surface with an identical distribution of the sorption sites and sorption energies ³⁷. The linear Langmuir equation can be represented as follows Eq.(2) ³⁸:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad \text{Eq.(2)}$$

where q_e is the amount of pollutant adsorbed per unit mass of adsorbent (mg/g), q_m (mg/g) is the maximum adsorption capacity and K_L is the Langmuir constant (L/mg) related to the binding strength, respectively. The constants in the Langmuir isotherm can be determined by plotting (C_e/q_e) versus C_e ³⁷. A dimensionless constant, commonly known as separation factor (R_L) can be represented as Eq.(3) ³⁹:

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{Eq.(3)}$$

R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich model is based on the adsorption on heterogeneous surfaces with different adsorption sites where high energy sites are occupied first, and with the increase of adsorbate concentration, the low energy sites will then be occupied resulting from the weak adsorption ^{39,40}. The linear Freundlich equation is as follows Eq.(4) ³⁸.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{Eq.(4)}$$

C_e and q_e were defined earlier, K_F is the Freundlich isotherm constant ($\text{mg g}^{-1}/(\text{mg L}^{-1})^n$) related to the adsorption capacity. $1/n$ is a measure of the surface heterogeneity, ranging between 0 (more heterogeneity) and 1 (more homogeneity)³⁷. The values of K_F and n were determined from the slope and intercept of the $\log (q_e)$ versus $\log (C_e)$ plots³⁸.

Photocatalysis kinetic

The Langmuir–Hinshelwood (LH) model is the most commonly used kinetic model for investigating the photo-oxidation rate of the pollutants⁴¹. The model is expressed by the Eq. (5)⁴²:

$$\frac{1}{r} = \frac{1}{k_r K_e C_e} + \frac{1}{k_r} \quad \text{Eq. (5)}$$

where r is the rate of degradation, K_e is the equilibrium adsorption constant (L mg^{-1}), k_r is the reaction rate constant ($\text{mg L}^{-1} \text{min}^{-1}$). The term $k_r K_e$ is generally evaluated as an apparent rate constant (k_{app} ; min^{-1}). In most photocatalysis kinetic studies, it is assumed that in the low pollutant concentration ($K_e C_e \ll 1$), so Eq. (6) can be transformed to a classical first-order Eq.(6)⁴¹:

$$\ln \left(\frac{C_e}{C_0} \right) = -k_{app} t \quad \text{Eq. (6)}$$

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539 **Author contributions**

540 Z. R. conceptualized, investigated, carried out experiments and wrote the manuscript. N. M.
541 conceptualized and supervised the research. M.S. conceptualized and supervised the research.
542 All authors contributed and approved the final version of the manuscript.

543 **Competing interests**

544 The authors declare no competing interests.

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Figure legends

Figure 1. Efficiency of TiO₂, zeolites and their composites for SO₂ removal in adsorption and photocatalysis under sunlight irradiation (Initial concentration of SO₂: 8.0 ppm, humidity:10 %, sunlight intensity: 125.0-135.0 mW cm⁻², gas flow rate: 40.8 mL min⁻¹).

*Different letters (small and capital separately) show significant differences according to Tukey's test (p<0.05).

Figure 2. Efficiency of TiO₂, zeolites and their composites for CO₂ removal in adsorption and photocatalysis under sunlight irradiation (Initial concentration of CO₂: 943.8 ppm, humidity: 10 %, sunlight intensity: 119.0-127.0 mW cm⁻², gas flow rate: 40.8 mL min⁻¹).

*Different letters (small and capital separately) show significant differences according to Tukey's test (p<0.05).

Figure 3. The adsorption isotherms of SO₂ and CO₂ onto TiO₂-Ze (50% TiO₂-Ze 300°C,., humidity:10%, composite: 0.1g, gas flow rate: 40.8 mL min⁻¹).

Figure 4. Langmuir–Hinshelwood Kinetic of SO₂ and CO₂ onto TiO₂-Ze (50% TiO₂-Ze 300°C, humidity:10%, composite: 0.1g, gas flow rate: 40.8 mL min⁻¹).