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

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Research Article

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**Posted Date:** September 28th, 2021

**DOI:** https://doi.org/10.21203/rs.3.rs-924529/v1

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Enhanced simultaneous photocatalytic removal of SO$_2$ and CO$_2$ using powder and coated zeolites-supported TiO$_2$ 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 TiO$_2$ photocatalyst were examined for the separate and simultaneous removal of SO$_2$ and CO$_2$ under solar irradiation using a parabolic trough collector (PTC). The composites exhibited a higher efficiency than raw zeolites and TiO$_2$ for the removal of both gases. The maximum removal of SO$_2$ by TiO$_2$-Ze and TiO$_2$-Cp under sunlight was 41.9 % and 56.2 % that enhanced to 53.4 % and 78.8 %, respectively in the presence of CO$_2$. Correspondingly, it was 61.8 % and 68.7 % for single CO$_2$ removal that increased to 74.2 % and 79.0 % in the binary gas stream. This behavior could be due to the enhanced simultaneous SO$_2$ oxidation and CO$_2$ reduction. The performance of coated composite for SO$_2$ was higher than of powder one (54.3% vs. 41.9%) and for CO$_2$ removal was almost close together (58.9% vs. 61.2%). This work promises the application of photocatalytic co-removal of SO$_2$ and CO$_2$ 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 (CO$_2$) and sulfur dioxide (SO$_2$) that are harmful to human health and the environment $^{1,2}$. SO$_2$ is an extremely toxic gas and a major

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contributor to acid rain. Also, CO$_2$ is a key greenhouse gas that promotes global climate change via global warming.

Although the flue gas desulfurization (FGD) technology especially wet scrubbing has been widely used for SO$_2$ treatment, the high operational costs and secondary pollution are its main disadvantages. The main technologies for CO$_2$ reduction are CO$_2$ capture and storage (CCS) as well as CO$_2$ 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 CO$_2$ into a wide range of end products providing hydrocarbon recovery.

Separate technologies (i.e. single-step processes) can remove pollutants from exhaust gases efficiently. 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.

Simultaneous removal of SO$_2$ and CO$_2$ as the main components in the flue gas has been greatly concerned in the air pollution control. 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. 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. Besides, it can be more attractive by using of solar energy as a clean and sustainable source.

Among various photocatalysts, TiO$_2$ has received tremendous attention for the photocatalysis process because of availability, non-toxicity, low cost, high photostability, abundance and environmentally friendly nature. 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. To overcome these limitations, many researches have been focused on the TiO$_2$ modification via doping elements, coupling of semiconductors and composites synthesis of photocatalyst and adsorbent support.

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. These properties can improve the potential of pollutants adsorption by TiO$_2$-zeolite composites. Furthermore, the modification of TiO$_2$ 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 TiO$_2$, but also improves the separation of photo-induced charge carriers by trapping electrons and increasing the photocatalytic activity.

The adsorption-photocatalysis efficiency of TiO$_2$-zeolite composites for removal of SO$_2$ and CO$_2$ was reported. Simultaneous SO$_2$ and CO$_2$ adsorption using calcium-based sorbents, zeolitic imidazolate frameworks, metal-organic frameworks, Al$_2$O$_3$, zeolite and active carbon indicated the competitive adsorption between SO$_2$ and CO$_2$ molecules to occupy active sites on the adsorbent surface. Furthermore, the co-presence of sulfide compounds and CO$_2$ provides the synergistic effect for improving their photocatalytic removal under UV irradiation.

Nevertheless, the adsorption and photocatalysis of SO$_2$ and CO$_2$ as separately and simultaneously on zeolite-TiO$_2$ composite under sunlight irradiation especially using a solar collector have not been investigated. We have previously reported the photocatalytic removal of SO$_2$ using natural and synthesized zeolites as supports of TiO$_2$ photocatalyst under sunlight irradiation in a parabolic trough collector (PTC). In the present research, the same process was used for the simultaneous removal of SO$_2$ and CO$_2$ after testing each gas separately. Furthermore, the zeolite supported TiO$_2$ 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 applications. Furthermore, the experimental data of photocatalytic degradation behavior of SO$_2$ and CO$_2$ were evaluated by isotherm and kinetic models.

Results and discussion
Performance of TiO$_2$, zeolites and TiO$_2$- zeolite composites in SO$_2$ and CO$_2$ removal
The performance of TiO$_2$, Cp, Ze and their composites for the removal of SO$_2$ and CO$_2$ under sunlight irradiation was shown in Figures. 1 and 2. A significant difference was observed in SO$_2$ and CO$_2$ removal in adsorption and adsorption- photocatalysis processes, separately (p<0.05). There was a low adsorption potential of SO$_2$ 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. The maximum adsorption of SO$_2$ by TiO$_2$ was 20.3 % that considering the contribution of photolysis (6.2 %), it reached up to 47.6 % under sunlight irradiation. The efficiency of TiO$_2$- Ze and TiO$_2$-Cp for the SO$_2$ 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 TiO$_2$, zeolites and their composites for SO$_2$ removal in adsorption and photocatalysis under sunlight irradiation (Initial concentration of SO$_2$: 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 SO$_2$ was in order of Cp (11.7 %)> TiO$_2$ (9.7 %) > Ze (5.5 %) that showed significant changes (P=0.024). Considering the contribution of photolysis (5.3%), the removal of SO$_2$ by TiO$_2$ under sunlight irradiation was obtained 22.8 %. The efficiency of TiO$_2$-Ze and TiO$_2$-Cp for SO$_2$ 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 TiO$_2$, zeolites and their composites for CO$_2$ removal in adsorption and photocatalysis under sunlight irradiation (Initial concentration of CO$_2$: 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 TiO$_2$ alone for the removal of SO$_2$ and CO$_2$. Clearly, TiO$_2$ 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 as confirmed by Brunauer–Emmett–Teller (BET), photoluminescence (PL) and UV–Vis diffuse reflectance spectroscopy (UV-Vis DRS) analysis. Furthermore, TiO$_2$-Cp composite showed better performance in the removal of SO$_2$ and CO$_2$ comparing to that of TiO$_2$-Ze (p<0.0001).

**Comparison of the adsorbents performance in the removal of SO$_2$ and CO$_2$**

The adsorption behavior of SO$_2$ and CO$_2$ 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. Both SO$_2$ and CO$_2$ are acidic molecules and show a high affinity for alkaline surfaces like TiO$_2$. As the polarizability of SO$_2$ ($4.3 \times 10^{-24}$ cm$^3$) is more than CO$_2$ ($1.9 \times 10^{-24}$ cm$^3$), it has a stronger tendency to bind to polar adsorbents like TiO$_2$ ($5.0 \times 10^{-24}$ cm$^3$) and zeolites. The SiO$_2$/Al$_2$O$_3$ ratio can determine the polarity of the zeolites. The smaller ratio, the greater the polarity. The Ze with a SiO$_2$/Al$_2$O$_3$ ratio of 2.7 is more polar than Cp with a ratio of 6.0. However, the lower polarity of CO$_2$ compared to SO$_2$ showed a greater adsorption tendency towards zeolites than TiO$_2$. The kinetic diameter of SO$_2$ and CO$_2$ is 0.4 and 0.3 nm, respectively. The pore diameters of TiO$_2$, Ze and Cp are 3.0, 11.0 and 23.2 nm, respectively. Therefore, the kinetic diameter can not be an obstacle to the adsorption of the studied gases by these adsorbents. The higher adsorption of both SO$_2$ and CO$_2$ gases by Cp may be due to its larger pores that can provide more adsorption sites for gas molecules.

**Comparison of the composites performance in the removal of SO$_2$ and CO$_2$**

The TiO$_2$-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 process and help to decrease the recombination rate of electron-hole pair. These properties in the TiO$_2$-Cp composite were confirmed by scanning electron microscope (SEM) and PL analysis.
revealed that the reaction of TiO$_2$ with Cp was better performed leading to higher performance in removing SO$_2$ and CO$_2$ gases.

Although the amount of TiO$_2$ 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, it was found that the amount of TiO$_2$ in the surface of the TiO$_2$-Cp sample was higher than TiO$_2$-Ze. This could be due to the presence of more oxygen groups in TiO$_2$-Cp composite. In this composite, the presence of more surface TiO$_2$ species could increase the active sites for adsorption and photocatalysis reactions. Moreover, the increase of photo excited electron-hole pairs, followed by the increase of oxidative species such as radical OH improved the performance of TiO$_2$-Cp composite for SO$_2$ and CO$_2$ photodegradation.

As mentioned earlier, the polarity of SO$_2$ is higher than CO$_2$. Besides, it is expected that TiO$_2$-Ze has more polarity compared to TiO$_2$-Cp. Hence, it can be inferred that TiO$_2$-Ze composite must have more tendency for SO$_2$ adsorption than TiO$_2$-Cp, whereas the TiO$_2$-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 TiO$_2$-Cp composite with a higher SiO$_2$/Al$_2$O$_3$ ratio than TiO$_2$-Ze has higher hydrophobic properties which can improve the photocatalytic removal of SO$_2$ and CO$_2$ in the presence of humidity.

**Simultaneous removal of SO$_2$ and CO$_2$ by TiO$_2$-zeolite composites**

Table 1 shows the results of SO$_2$ and CO$_2$ removal by TiO$_2$-Ze and TiO$_2$-Cp composites in separate and simultaneous conditions. The SO$_2$ adsorption by TiO$_2$-Ze and TiO$_2$-Cp in the presence of CO$_2$ was increased about 7 and 13%, respectively. Although the adsorption of CO$_2$ by TiO$_2$-Ze was relatively reduced (around 7%), it was constant for TiO$_2$-Cp (36-37%). Correspondingly, the removal efficiency of SO$_2$ and CO$_2$ 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 SO$_2$ by TiO$_2$-Ze in the separate and simultaneous conditions was 5.2 and 5.8 mg g$^{-1}$ respectively, whereas the correspondent amount for CO$_2$ 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 SO$_2$ and CO$_2$ by composites under sunlight irradiation

| Remval               | Gas      | TiO$_2$-Ze   | TiO$_2$-Cp   |
|----------------------|----------|--------------|--------------|
|                      |          | Ads.         | Ads/PCO      | Ads.         | Ads/PCO      |
| Separate removal     | SO$_2$ (%) | 20.1±0.9$^b$ | 41.9±0.4$^B$ | 24.0±1.1$^b$ | 56.2±0.8$^B$ |
|                      | (Initial conc. 23 ppm) |              |              |              |              |
| Simultaneous removal | SO$_2$ (%) | 26.8±1.5$^a$ | 53.4±0.7$^A$ | 36.6±0.9$^a$ | 78.8±0.8$^A$ |
|                      | (Initial conc. 26 ppm) |              |              |              |              |
| Separate removal     | CO$_2$ (%) | 21.1±0.3$^a$ | 61.8±0.3$^B$ | 37.4±0.9$^a$ | 74.2±0.6$^B$ |
|                      | (Initial conc. 944 ppm) |              |              |              |              |
| Simultaneous removal | CO$_2$ (%) | 14.3±1.1$^b$ | 68.7±0.5$^A$ | 36.1±0.9$^a$ | 79.0±0.7$^A$ |
|                      | (Initial conc. 1187 ppm) |              |              |              |              |

Ads.:adsorption, PCO: photocatalysis oxidation

Condition: 50% TiO$_2$-Ze- 300 °C, 50% TiO$_2$-Cp -300 °C, composite: 0.1 g, 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 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 concentration due to more access to the active sites of composite. Consequently, it is expected that under simultaneous presence, SO$_2$ has more possibility than CO$_2$ 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.
However, as the results showed, the presence of CO$_2$ did not interfere with SO$_2$ adsorption, whereas the CO$_2$ adsorption on the TiO$_2$-Ze was slightly reduced.

The difference in the polarity of SO$_2$ and CO$_2$ molecules and their adsorption tendency on the similar active sites of the adsorbent$^{8,24}$ explain the stronger electrostatic reaction of the SO$_2$ with both composites. The relatively same kinetic diameter of SO$_2$ and CO$_2$ molecules suggests that this parameter can not be a determining factor for their adsorption by composites. Moreover, the higher density of SO$_2$ (2.6 kg m$^{-3}$) comparing to CO$_2$ (2.0 kg m$^{-3}$) provides the higher adsorption on the composite surface$^{55}$.

Additionally, the simultaneous presence of SO$_2$ and CO$_2$ and increasing the mass density of total gases could have a significant effect on the Henry’s law solubility of SO$_2$ (1.2 mol L$^{-1}$) but a little effect on CO$_2$ (0.03 mol L$^{-1}$)$^{56}$. Therefore, in the simultaneous presence of SO$_2$ and CO$_2$ in the system containing moisture, the SO$_2$ 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 SO$_2$ and CO$_2$ molecules prevents the substantial decrease of the CO$_2$ adsorption in the presence of SO$_2^{23}$.

In the photocatalytic process, the CO$_2$ conversion requires a reducing agent and SO$_2$ conversion requires an oxidizing agent (reactions of 1-6). The conversion of SO$_2$ and CO$_2$ at the same time can be a reduction–oxidation (redox) reaction. Although H$_2$O and SO$_2$ can act as reducing agents for CO$_2$, the oxidation potential of H$_2$O is about 1.2 V (reaction 3) and SO$_3^{2-}$ (resulting from SO$_2$ conversion) is 0.9 V (reaction 4). This indicates that the presence of SO$_2$ for CO$_2$ reduction is better than H$_2$O 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 SO$_2$ removal by photocatalytic oxidation in the presence of humidity was sulfate (SO$_4^{2-}$). More details were presented in the previous study$^{19}$. According to the literature, the products of CO$_2$ photocatalytic degradation
on TiO$_2$-zeolite photocatalysts in the presence of humidity could be methane (CH$_4$) 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 CH$_4$ and CO, respectively), it was not possible to measure the exact amount of these gases. The redox process of SO$_2$ and CO$_2$ can be described as the following reactions $^{4,10}$.

\[
\begin{align*}
\text{SO}_2_{(\text{gas})} + 2\text{OH}^-_{(\text{sites})} & \rightarrow \text{SO}_3^{2-}_{(\text{ads})} + \text{H}_2\text{O} & (1) \\
\text{SO}_2_{(\text{gas})} + \text{O}^{2-}_{(\text{sites})} & \rightarrow \text{SO}_3^{2-}_{(\text{ads})} & (2) \\
4\text{OH}^- & \rightarrow \text{O}_2_{(g)} + 2\text{H}^+ + 4e^- & (3) \\
\text{SO}_3^{2-}_{(\text{ads})} + 2\text{OH}^-_{(\text{ads})} & \xrightarrow{\text{light}} \text{SO}_4^{2-}_{(\text{ads})} + \text{H}_2\text{O} + 2e^- & (4) \\
\text{CO}_2 + 2\text{H}^+ + e^- & \rightarrow \text{CO} + \text{H}_2\text{O} & (5) \\
\text{CO}_2 + 8\text{H}^+ + 8e^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} & (6)
\end{align*}
\]

The effect of sulphide compounds as the reducing agent in the increase of photocatalytic conversion rate of CO$_2$ 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 CO$_2$ conversion including formic acid (HCOOH) and formaldehyde (HCOH) increased in the presence of H$_2$S. Li et al. (2019) $^4$ indicated that the oxidation energy of SO$_2$ improved the CO$_2$ reduction and led to the increase of SO$_4^{2-}$ and CO/HCOOH formation, respectively.

**Efficiency of the powder and coated TiO$_2$-Ze composites in SO$_2$ and CO$_2$ removal**

As shown in Table 2, despite the use of a very less amount of TiO$_2$-Ze composite in the coated form (0.1 of powder), its performance for SO$_2$ removal in both adsorption and adsorption/photocatalysis processes was higher than the powder form. Although the same trend was observed for CO$_2$ adsorption, the results of the adsorption/photocatalysis process showed almost the same removal of CO$_2$ 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 TiO$_2$-Ze composite in the powder and coated forms to remove SO$_2$ and CO$_2$.

| 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% TiO$_2$-Ze- 300 ºC, 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 SO$_2$ removal than CO$_2$. This can be due to the slow movement of heavy SO$_2$ molecules 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 processes.$^{27-29}$

Adsorption isotherms

Adsorption isotherms of SO$_2$ and CO$_2$ onto the TiO$_2$-Ze composite at various concentrations are shown in Figure 3. The results demonstrated that the equilibrium adsorption capacity ($q_e$)
of SO₂ and CO₂ was significantly influenced by the initial concentration of gases. The experimental data was better fitted with the Langmuir isotherm ($R^2 = 0.94$ for SO₂ and $R^2 = 0.99$ for CO₂). Based on these results, the adsorption process mainly involved monolayer adsorption of SO₂ and CO₂ on the homogeneous active sites of the composite. The maximum adsorption capacity of SO₂ and CO₂ on the TiO₂-Ze composite ($q_m$) was 6.1 and 400 mg g⁻¹, respectively. From the data calculated in Table 3, the $R_L$ is between 0 and 1 indicating the favorable adsorption. Yi et al. (2012)⁸ and Luo et al. (2017)¹ reported the suitability of Langmuir isotherm and the monolayer adsorption mechanism of SO₂ and CO₂ on the zeolite adsorbents.

![Graphs showing the adsorption isotherms for SO₂ and CO₂.](image-url)
Figure 3. The adsorption isotherms of SO$_2$ and CO$_2$ onto TiO$_2$-Ze (50% TiO$_2$-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 SO$_2$ and CO$_2$ on the TiO$_2$-Ze.

| Isotherm/kinetic parameters | SO$_2$ | CO$_2$ |
|-----------------------------|--------|--------|
| **Langmuir**                |        |        |
| $q_{\text{max}}$ (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**   |        |        |
| $k_{\text{app}}$ (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 $\text{SO}_2$ and $R^2 = 1.0$ for $\text{CO}_2$). The applicability of the Langmuir–Hinshelwood (L-H) kinetic model for the photocatalysis removal of $\text{SO}_2$ and $\text{CO}_2$ 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 $0.007 \text{ min}^{-1}$ for $\text{SO}_2$ and $0.03 \text{ min}^{-1}$ for $\text{CO}_2$, 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 photocatalysis. Also, according to this model, the most important factor limiting the rate of adsorption-photocatalysis reaction of $\text{SO}_2$ and $\text{CO}_2$ gases was the fixed active site of the composite.

![Graphs](image-url)
Conclusion

The adsorption and photocatalysis processes for the separate and simultaneous removal of SO$_2$ and CO$_2$ using natural (clinoptilolite) and synthetic X zeolites- supported TiO$_2$ composites was investigated in a designed solar collector. The TiO$_2$- synthetic and natural zeolite composites showed the higher efficiency for the both gases removal than the raw zeolites and TiO$_2$. The simultaneous presence of SO$_2$ and CO$_2$ gases in the photoreactor improved the SO$_2$ removal from 41.9 to 53.4% by TiO$_2$-Ze and from 56.2 to 78.8% by TiO$_2$-Cp, and the corresponding CO$_2$ removal from 61.8 to 68.7% by TiO$_2$-Ze and from 74.2 to 79.0% by TiO$_2$-Cp. The coated TiO$_2$-Ze composite acted better than powder one for the removal of gases especially for SO$_2$, so that the adsorption of this gas increased about two times and the adsorption-photocatalytic removal was promoted more than 10%. The CO$_2$ removal by coated and powder composite was in the range of 58.9 to 61.2%. The adsorption behavior of SO$_2$ and CO$_2$ gases on TiO$_2$-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.
Materials and methods

Materials

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

Preparation of zeolites

Synthetic zeolite (Ze) with a particle size of less than 500 μm was used without any treatment. Natural zeolite, clinoptilolite (Cp) was also used to compare the effect of zeolite type on SO$_2$ and CO$_2$ removal in adsorption and photocatalytic processes. Cp sample was washed with distilled water to remove the surface dust and dried in an oven at 70 °C. Then it was ground and sieved into a size of 53–105 μm. Both zeolites were separately used and as the support of TiO$_2$. The characterization of the used samples were reported in our previous study.

Synthesis of TiO$_2$ particles and zeolite-supported TiO$_2$ composites

TiO$_2$ particles and TiO$_2$-based composites containing TiO$_2$-Cp and TiO$_2$-Ze (with 50 wt % TiO$_2$ loading to zeolites) were prepared by the sol-gel method. Then, the samples were calcined at 300°C for 3 hours to obtain the powder form. The characterization of the composites were also described in our previous study.

The coated composite was prepared using a sol–gel-based dip-coating method. Before coating, the borosilicate beads with a diameter of 4-5 mm were initially soaked in ethanol solution under ultrasonic bath for 30 min at room temperature (25 °C), then rinsed in distilled water for 15 min. The supports were again immersed for 5 min in ethanol solution with stirring and finally immersed in distilled water with constant stirring for 15 min. The supports were oven-dried at 60 °C for 1 h. The powder composite (1 g) prepared previously (before
calcination) was dispersed in 100 mL of the ethanol solution under magnetic stirring for 4 h 32. 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 weighted 34. 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 times 19. 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_{\text{Inlet}} - C_{\text{Outlet}}}{C_{\text{Inlet}}} \times 100 \quad \text{Eq.(1)}

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

The removal experiments of SO\(_2\) and CO\(_2\) 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 TiO\(_2\), raw zeolites and TiO\(_2\)-zeolite composite samples was evaluated. To study the hybrid reactions of adsorption and photocatalysis, the removal of gases by the raw zeolites, TiO\(_2\) and TiO\(_2\)-zeolite composites were tested under sunlight irradiation.

The simultaneous removal of SO\(_2\) and CO\(_2\) by the composites was investigated in the adsorption and photocatalysis processes under sunlight irradiation. Ultimately, the performance of powder and coated TiO\(_2\)-Ze composite for the separate and simultaneous removal of SO\(_2\) and CO\(_2\) was studied through adsorption and photocatalysis processes under sunlight.

The performance of TiO\(_2\), zeolites and their composites for the removal of SO\(_2\) and CO\(_2\) was done in the optimized conditions that were already obtained in the preliminary experiments. The concentrations of SO\(_2\) and CO\(_2\) 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 CO\(_2\) and SO\(_2\), 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. For the study of adsorption isotherms, 0.1 g composite was used for different initial concentrations of \( \text{SO}_2 \) (2.8, 8.0, 16.2 and 23.3 ppm) and \( \text{CO}_2 \) (943.8, 1834.2, 2337.8 and 2961.5 ppm). These concentrations were obtained based on mixing the target gases (\( \text{SO}_2 \) and \( \text{CO}_2 \)) and \( \text{N}_2 \) 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. The linear Langmuir equation can be represented as follows Eq.(2):

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
\]

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 \( C_e \). A dimensionless constant, commonly known as separation factor \( (R_L) \) can be represented as Eq.(3):

\[
R_L = \frac{1}{1 + K_L C_0}
\]

\( R_L \) 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.

The linear Freundlich equation is as follows Eq.(4):
\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

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 \( \log (C_e) \) plots \(^{38} \).

### Photocatalysis kinetic

The Langmuir–Hinshelwood (LH) model is the most commonly used kinetic model for investigating the photo-oxidation rate of the pollutants \(^{41} \). 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 \((\text{L mg}^{-1})\), \( k_r \) 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 \((k_{app}; \text{min}^{-1})\). 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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Acknowledgments

The financial support for synthesis of zeolite from stone cutting sludge under the project contract 941035 by the Iran National Science Foundation (INSF) is appreciated.

Author contributions

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

Competing interests

The authors declare no competing interests.
Figure legends

**Figure 1.** Efficiency of TiO$_2$, zeolites and their composites for SO$_2$ removal in adsorption and photocatalysis under sunlight irradiation (Initial concentration of SO$_2$: 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 TiO$_2$, zeolites and their composites for CO$_2$ removal in adsorption and photocatalysis under sunlight irradiation (Initial concentration of CO$_2$: 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 SO$_2$ and CO$_2$ onto TiO$_2$-Ze (50% TiO$_2$-Ze 300$^\circ$C, humidity: 10 %, composite: 0.1 g, gas flow rate: 40.8 mL min$^{-1}$).

**Figure 4.** Langmuir–Hinshelwood Kinetic of SO$_2$ and CO$_2$ onto TiO$_2$-Ze (50% TiO$_2$-Ze 300$^\circ$C, humidity: 10 %, composite: 0.1 g, gas flow rate: 40.8 mL min$^{-1}$).