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Research Article

Effect Factors of Benzene Adsorption and Degradation by Nano-TiO_2 Immobilized on Diatomite

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Difference between adsorption of benzene by diatomite and nano-TiO_2 immobilized on diatomite was investigated. And effects of temperature, light intensity, relative humidity, and initial benzene concentration on adsorption and degradation of benzene by nano-TiO_2 immobilized on diatomite were also studied. The experimental results showed that when initial benzene concentration was 2.2×10^{-3} mg L^{-1}, it could be degraded to below safe concentration (1.1×10^{-4} mg L^{-1}) after 50 h when temperature was 20°C, but it just needed 30 h at 35°C. When light intensity was 6750 Lx, it needed 30 h for benzene to be degraded to below safe concentration, but benzene could barely be degraded without light. When relative humidity was 50%, benzene could be degraded to 1.0×10^{-4} mg L^{-1} after 30 h, while its concentration could be reduced to 7.0×10^{-5} mg L^{-1} at the relative humidity of 80%.

1. Introduction

Benzene, which primarily comes from coating, painting, adhesives, and other organic solvents inside buildings, has become one of the most toxic substances and has been identified as a kind of strong carcinogenic substance by Word Health Organization. So it is very important and meaningful to remove benzene in houses and workplaces considering human health.

At present, there are some methods employed to remove benzene such as microbial degradation [1, 2], adsorption [3–7], catalytic oxidation [8–14], and so forth, among which photocatalytic degradation of benzene by TiO_2 has attracted wide attention [11–14]. This is because TiO_2 can degrade many toxic substances under mild conditions and cannot cause secondary pollution [15–18], besides being quite easy to operate, making it become a simple way to remove poisonous gases indoors. But as nano-size TiO_2 powder is inclined to aggregate to clusters and hard to be fixed, if being directly doped into coatings to paint walls or furnitures, it is very easy to fall off. So researchers have investigated many methods to fix TiO_2 on certain supports, among which diatomite is just a good carrier. As there exists a lot of silicon hydroxyls and hydrogen bonds on the surface of diatomite, it can form strong force with TiO_2, thus overcoming the difficulty of TiO_2 fixing. In addition, nano-TiO_2 immobilized on diatomite combines both large specific area of diatomite and strong oxidation ability of TiO_2, which shows broad prospect in green adornments.

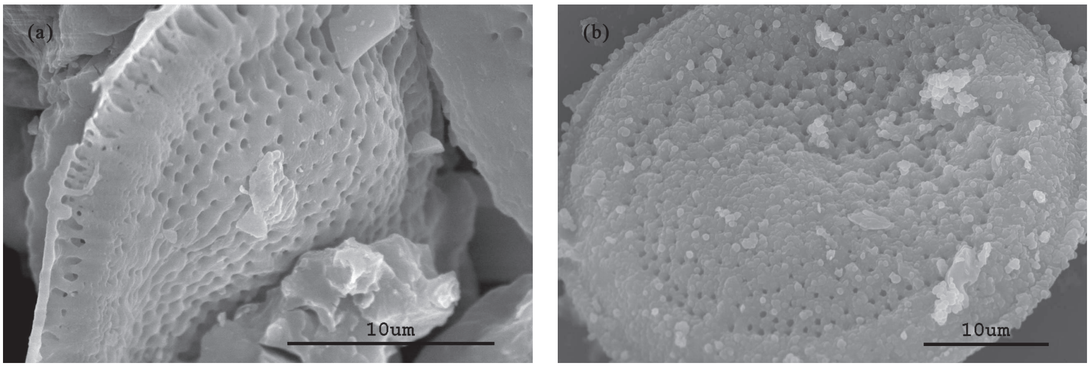
Based on our previous work [19–21], nano-TiO_2 immobilized on diatomite prepared by using $TiOSO_4$ as raw material, urea as precipitator and diatomite as support was employed to degrade benzene in this work. To verify advantage of nano-TiO_2 immobilized on diatomite, difference between adsorption of benzene by diatomite and nano-TiO_2 immobilized on diatomite was compared and effects of temperature, light intensity, relative humidity, and initial concentration of benzene on adsorption and degradation of benzene by nano-TiO_2 immobilized on diatomite were also discussed.

2. Experimental

Diatomite and nano-TiO_2 immobilized on diatomite were used as the adsorption and degradation materials, as discussed elsewhere [20]. Their morphology is shown in

Table 1: Chemical compositions and characteristics of diatomite and nano-TiO_2 immobilized on diatomite.

	Diatomite	Nano-TiO_2 immobilized on diatomite
Chemical compositions	Main: SiO_2 Other: Al_2O_3 Fe_2O_3 CaO MgO K_2O Na_2O and other organic substances	Main: SiO_2 TiO_2 Other: Al_2O_3 Fe_2O_3 CaO MgO K_2O Na_2O and other organic substances
Characteristics	Grain size and specific area were 10∼100 μm and 1.2995 m^2/g, respectively	Crystalline phase of TiO_2 was anatase, grain size was 150 nm and cover percent was 75%



(a) (b)

Figure 1: (a) The morphology of diatomite. (b) The morphology of nano-TiO_2 immobilized on diatomite.

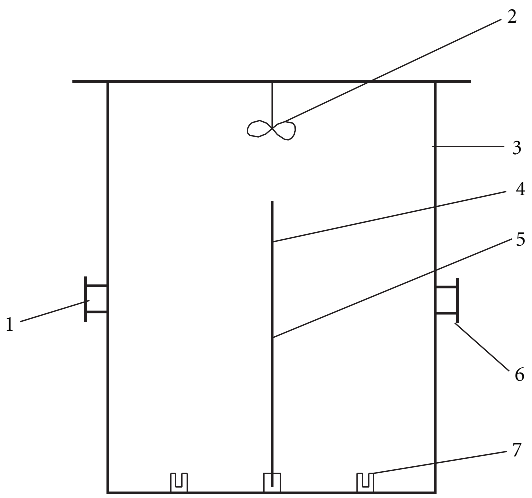


Figure 2: The innercircle reactor for degradating benzene (1-sample connection, 2-fan, 3-shell, 4-glass plate, 5-nano-TiO_2, 6-injection port, 7-slot).

Figure 1. And their chemical compositions and characteristics are shown in Table 1. Benzene obtained by evaporating its standard solution (the concentration was 100 mg L^{-1}) was used as the target degraded gas, initial concentration of which was 0.0022 mg L^{-1}. Ground glass, the effective area of which was 0.08 m^2, was used as the support of photocatalysts. The structure of the photocatalytic reactor (the volume was 5 L) is shown in Figure 2.

Adsorption by reactor: before experiment, the reactor was cleaned, dried, and sealed. Then the standard solution of benzene was injected into it. When the solvent evaporated thoroughly, it was put into illumination incubator with temperature of 35°C. During adsorption process, 1 mL gas was taken out from the reactor at regular intervals and analyzed by Gas Chromatography to determine the concentration of benzene.

Comparison of adsorption by diatomite and nano-TiO_2 immobilized on diatomite: nano-TiO_2 immobilized on diatomite of 2 g was put into the reactor and benzene's standard solution of 0.29 mL was also injected into it. Then the reactor was put into illumination incubator with temperature of 35°C and 5 fluorescent lamps opened. Like the above experiment, 1 mL gas was taken out from the reactor at regular intervals and analyzed by gas chromatography to determine the concentration of benzene. When finished, the reactor was cleaned and dried, and experiment was repeated with diatomite of 2 g under the same conditions to compare the difference of these two materials.

Effect of reaction conditions on degradation of benzene by nano-TiO_2 immobilized on diatomite: take the experiment about effect of temperature as example, nano-TiO_2 immobilized on diatomite of 2 g was put into the reactor and benzene's standard solution of 0.11 mL was also injected into it. Then the reactor was put into illumination incubator with temperature of 35°C and 5 fluorescent lamps opened. Similarly, 1 mL gas was taken out from the reactor at regular intervals and analyzed by gas chromatography to determine the concentration of benzene. The process ended when the concentration of benzene decreased to below its safe

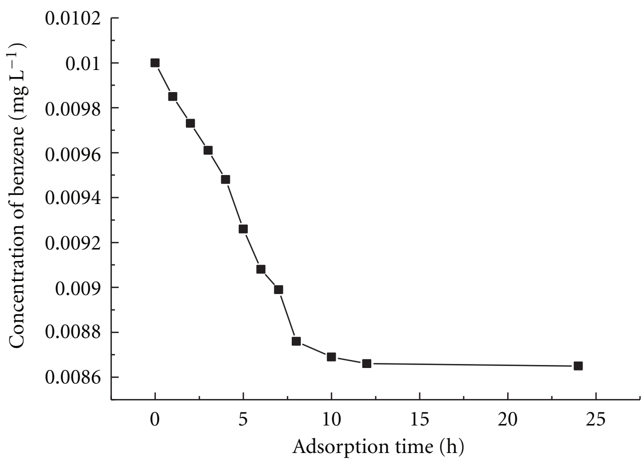


Figure 3: Curve of adsorption equilibrium by reactor.

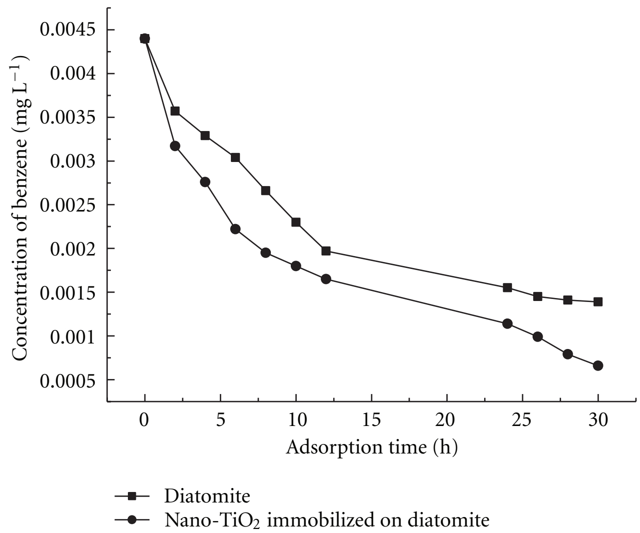


Figure 4: Comparison of adsorption between diatomite and nano-TiO_2 immobilized on diatomite.

concentration. Experiment was repeated at 20°C to study the effect of temperature on degradation of benzene.

3. Results and Discussion

3.1. Adsorption by Reactor. When benzene is injected into a closed reactor, some gas will be adsorbed to the wall of the reactor. Accordingly, the degradation ability of nano-TiO_2 immobilized on diatomite will be artificially increased if this part of adsorption capacity does not be excluded. In order to reduce this kind of error, the experiment about the adsorption of benzene by the reactor was conducted and the curve of adsorption equilibrium was obtained, as seen in Figure 3.

From Figure 3, it can be seen that the adsorption at the first 8 h was almost linear. The concentration of benzene reduced from 0.01 mg L^{-1} to 0.00866 mg L^{-1} after adsorption for 12 h and almost maintained unchanged until 24 h, implying the saturated concentration of benzene for the reactor was 0.00134 mg L^{-1}. To avoid relative error, in the following experiments, the real adsorbed concentration of benzene by nano-TiO_2 was the concentration obtained by experiment minus 0.00134 mg L^{-1}.

3.2. Comparison of Adsorption by Diatomite and Nano-TiO_2 Immobilized on Diatomite. The concentration changes of benzene adsorbed by diatomite and nano-TiO_2 immobilized on diatomite under the same mass are shown in Figure 4.

It can be seen from Figure 4 that adsorption and degradation of benzene by different materials were quite different. Diatomite has strong adsorption capacity owing to its many holes, as seen in Figure 1(a). At the first 12 h, the concentration of benzene decreased sharply. At this period, the adsorption rate of benzene on diatomite was much larger than the desorption rate. While at the later 12 h, the slope of the curve greatly decreased and tended to become unchanged, which demonstrated that the adsorption rate of benzene on diatomite was almost equal to the desorption rate and the concentration of benzene kept steady. From the figure, it can be found that after adsorption by diatomite of 2 g, the concentration of benzene reduced from 0.0044 mg L^{-1} to 0.00139 mg L^{-1}.

While for the nano-TiO_2 immobilized on diatomite, the adsorption rate at the first 12 h was greater than that of diatomite. This was because benzene was not only adsorbed to the diatomite through physical effect but also oxided to CO_2 and H_2O by light-generated holes on the surface of the nano-TiO_2, which led to more adsorption of benzene on nano-TiO_2 immobilized on diatomite than on diatomite alone. Moreover, the concentration of benzene still kept decreasing untill 30 h, although the degradation rate was smaller than that of the first 12 h. At this stage, desorption of benzene from the nano-TiO_2 immobilized on diatomite gradually appeared, but the desorption rate was still smaller than the adsorption rate, so the concentration of benzene still kept reducing, indicating that the nano-TiO_2 had lasting degradation effect on benzene.

3.3. Effect of Temperature on Adsorption and Degradation of Benzene by Nano-TiO_2 Immobilized on Diatomite. The change tendencies of benzene's concentration under different temperature are shown in Figure 5.

It demonstrated that the degradation rate of benzene increased with the rise of reaction temperature. From the figure, it can be seen that when the temperature was 20°C, it needed 50 h for benzene of 0.0022 mg L^{-1} to be degraded to below the safe concentration, while it just needed 32 h when the reaction temperature was 35°C. This may be explained as follows. First, the internal energy of benzene molecules increased with the rise of temperature and their irregular movement became fiercer, which made the cyclic process of benzene's adsorption and desorption on the surface of nano-TiO_2 much faster, but the adsorption rate and degradation rate were larger than that of desorption, so the concentration of benzene kept decreasing. Second, when the temperature

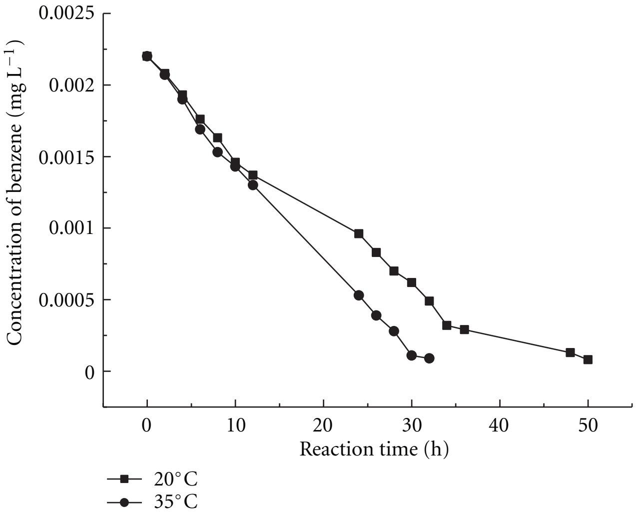


Figure 5: Effect of temperature on degradation of benzene by nano-TiO_2 immobilized on diatomite.

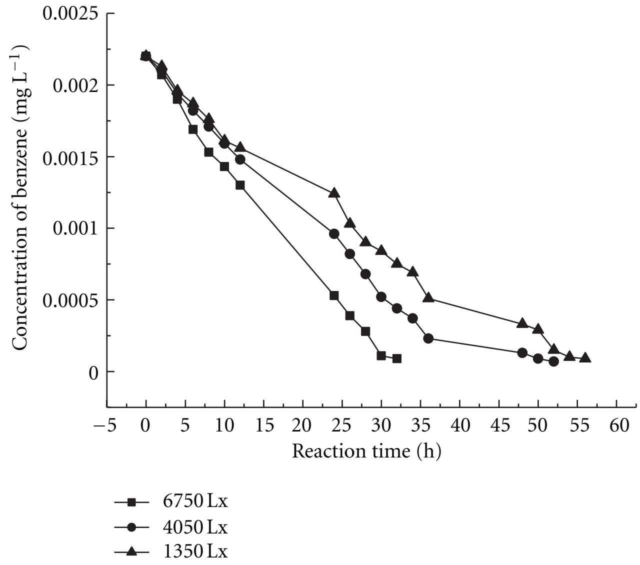


Figure 6: Effect of light intensity on degradation of benzene by nano-TiO_2 immobilized on diatomite.

Table 2: The average light intensity for different number of lamp.

N (number of lamps)	E_{av} (Lx)
1	1350
3	4050
5	6750

was high, the saturation vapor pressure of steam increased, which led to decrease of relative humidity in the reactor. In this case, the nano-TiO_2 would release the steam and other dissolved gases adsorbed before to relieve the decrease of humidity. So the diatomite would adsorb more benzene and more benzene could be oxided to nontoxic gases by nano-TiO_2. While at low temperature, the benzene molecules were relatively steady and the rates of adsorption, degradation, and desorption were much slower, so the decrease rate of benzene's concentration at high temperature was relatively larger.

3.4. Effect of Light Intensity on Adsorption and Degradation of Benzene by Nano-TiO_2 Immobilized on Diatomite. Light intensity is another factor which has important effect on degradation of benzene by nano-TiO_2 immobilized on diatomite. As known, TiO_2 can be activated by ultraviolet light. After being activated, the photogenerated electronics and holes will reduce or oxide the organics and inorganics adsorbed to the surface of the nano-TiO_2. When the wavelength is definite, the intensity of the light will determine the number of electronics and holes generated by illumination, thus determining the concentration of benzene degraded by TiO_2. It is the same for ultraviolet in visible light. Besides, as the light intensity at every point in the light range is different for different light source and different light space, so average light intensity is used as the intensity in certain space. According to the following formula [22]:

$$E_{av} = \frac{N \times \Phi_s \times U \times K}{A}, \quad (1)$$

E_{av}—average light intensity, Lx; N—number of fluorescent lamp; Φ_s—light flux of a fluorescent lamp, Lm; U—use coefficient, generally 0.4; K—maintenance coefficient, 0.8; A—Incubator's bottom surface area, 0.2 m^2 the average light intensity with different number of fluorescent lamp is listed in Table 2.

The changes of benzene's concentration at different light intensity are shown in Figure 6.

It can be found that when the light intensity was definite, the concentration of benzene decreased with time going on. For example, when the light intensity was 4050 Lx, the concentration of benzene reduced sharply at the first 35 h, while the rate became much smaller after that; this was also because at the first 35 h, the adsorption rate and the degradation rate were much greater than the desorption rate, so decrease of benzene's concentration was significant, with time increasing, the desorption of benzene from the surface of photocatalyst gradually became apparent, causing the decrease rate of benzene's concentration become small. Besides, it can be seen that the stronger the light intensity was, the larger the decrease rate of benzene was. When the light intensity was 6750 Lx it just needed 30 h for benzene to be degraded to below the safe concentration, while it cost more than 30 h when the light intensity was 1350 Lx and 4050 Lx. This was because more holes were generated at large light intensity than at small light intensity, leading to faster degradation of benzene.

3.5. Effect of Relative Humidity on Adsorption and Degradation of Benzene by Nano-TiO_2 Immobilized on Diatomite. Relative humidity is also an effect which has important impact on degradation of benzene. In this section, the standard solution of 0.27 mL was first injected into the reactor, implying the water's volume was 0.27 mL. To realize

Table 3: Volume of deionized water needed to be added at different relative humidity.

Relative humidity (%)	Volume of deionized water (mL)
50	0.110
60	0.132
70	0.154
80	0.176

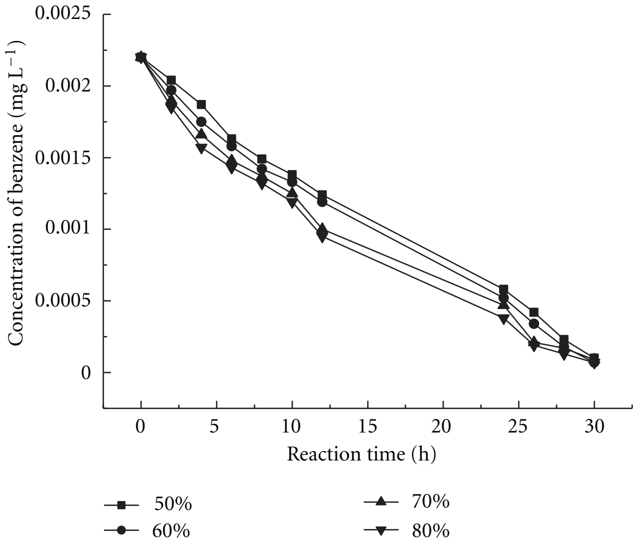


Figure 7: Effect of relative humidity on degradation of benzene by nano-TiO_2 immobilized on diatomite.

relative humidity of 50%, 60%, 70%, and 80%, the volumes of deionized water needed to be added into the reactor were calculated according to gas state equation when the temperature was 35°C. The results are listed in Table 3.

Figure 7 shows the changes of benzene's concentration with reaction time under different relative humidity.

As is known, when the photogenerated holes transfer to the surface of TiO_2, they can accept electrons from O_2 and H_2O to generate $^{\bullet}O^{2-}$ and $^{\bullet}OH$, which have strong oxidation ability. Undoubtedly, the more H_2O there is, the more free radical there can produce. So it is beneficial for degradation of benzene when the relative humidity increases. It can also be found from Figure 7 that the degradation rate of benzene increased with the relative humidity ranging from 50% to 80%. But it is not to say the relative humidity can be infinite. In practice, there is certain range of humidity for people to endure, about 40% to 70%. So for degradation of benzene, the principle is the bigger the relative humidity is, the better the effect is, but people's comfort is the first to be considered.

3.6. Effect of Benzene's Initial Concentration on Adsorption and Degradation of Benzene by Nano-TiO_2 Immobilized on Diatomite. When benzene's initial concentration is different, the degradation situation will be quite different. To verify effect of initial concentration on the degradation of benzene by nano-TiO_2 immobilized on diatomite, two groups of

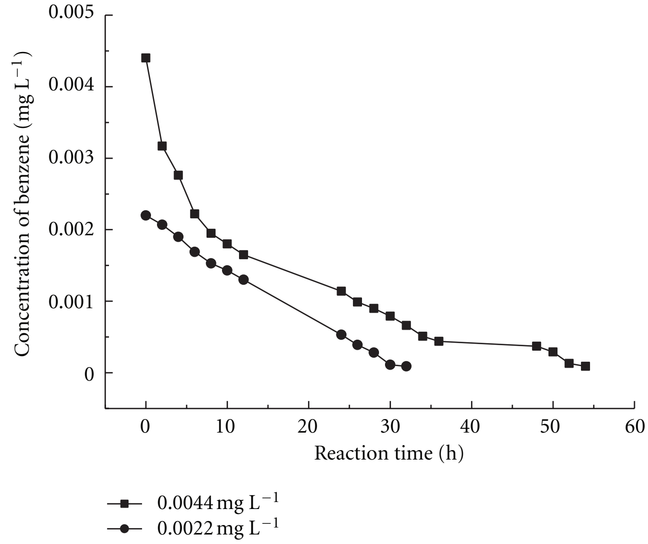


Figure 8: Effect of initial concentration on degradation of benzene by nano-TiO_2 immobilized on diatomite.

experiments were carried out and the results are shown in Figure 8.

As Figure 8 shown, at first hours, the higher the initial concentration was, the larger the degradation rate was. This could be explained by degradation process of benzene by TiO_2. First, benzene was adsorbed to the surface of TiO_2. Second, it was oxided to nontoxic organics or even CO_2 and H_2O. Third, the products were desorbed from the surface of TiO_2. When the initial concentration of benzene was higher, there was more benzene adsorbed to the surface of TiO_2, so the decrease rate of benzene was larger at first hours. But with time going on, the desorption of benzene from the surface of catalyst gradually appeared, which hampered the further adsorption and degradation of benzene, so the decrease rate of benzene's concentration became smaller. When initial concentration was 0.0022 mg L^{-1}, it could decrease about 95% after 30 h, which was higher than that of Pd/TiO_2 [11] in efficiency.

4. Conclusions

Diatomite can only adsorb benzene, while nano-TiO_2 immobilized on diatomite not only can adsorb benzene but also can degrade benzene to nontoxic organics. Experiments about effect of reaction conditions on adsorption and degradation of benzene by nano-TiO_2 immobilized on diatomite showed that temperature had great effect on the adsorption and degradation process, when the initial concentration of benzene was 0.0022 mg L^{-1}, it could be degraded to below the safe concentration by nano-TiO_2 immobilized on diatomite after 30 h when temperature was 35°C, while 50 h was needed when temperature was 20°C. Light intensity was direct driving of the degradation process. TiO_2 could not play role of degradation when there was no light, while it just needed 32 h to degrade benzene to below the safe concentration when light intensity was 6750 Lx. Relative humidity also impacted the degradation process. When relative humidity was 50%, the concentration of benzene could reduce from 0.0022 mg L^{-1} to 0.0001 mg L^{-1} after 30 h, but it could reduce to 0.00007 mg L^{-1} at humidity of 80%. Besides, when initial concentration was 0.0022 mg L^{-1}, it could decrease to below safe concentration after 30 h, while the time was 54 h when initial concentration was 0.0044 mg L^{-1}. In short, the nano-TiO_2 immobilized on diatomite not only showed high adsorption and degradation capacity for benzene, but also could be used in decorative materials to remove benzene indoors conveniently.

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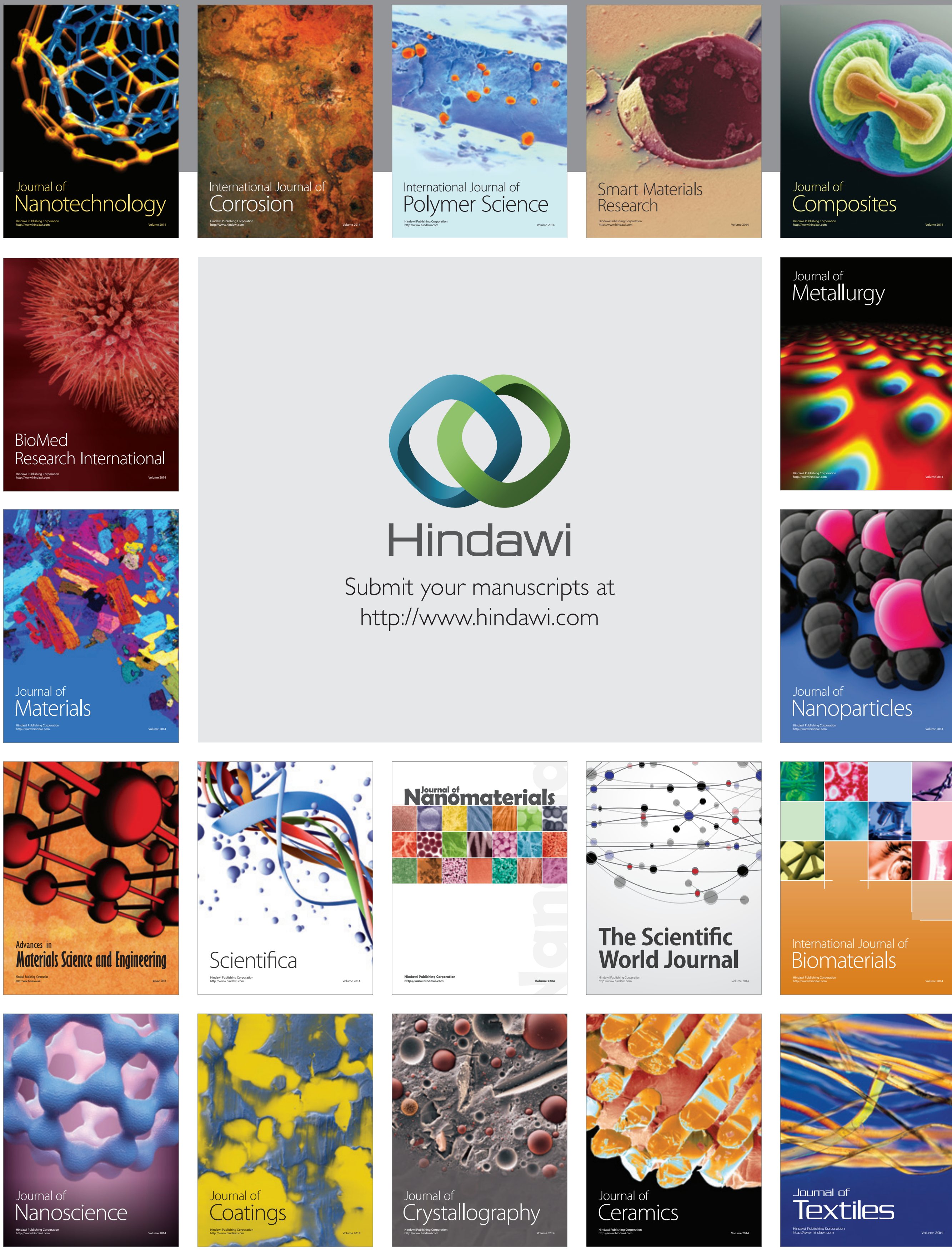
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