

Photodegradation of humic acid using spherical activated carbon contained Zn in a fluidized bed system

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Abstract In this study, a strong acid ion-exchange resin, as the starting material of spherical activated carbon contained Zn (Zn-SPAC), was treated by 0.1 N zinc solution. Ion-exchange treatment was performed from one to three times for controlling the zinc content. The ion-exchanged resins were activated under N₂/H₂O vapor atmosphere at 900°C for 0.5 h, followed by carbonization treatment at 700°C under N₂ atmosphere. The Zn-SPAC samples were measured for their physico-chemical characteristics, such as X-ray diffraction (XRD) patterns, scanning electron microscope (SEM) images, electron probe micro analyzer (EPMA) images, energy dispersive X-ray spectroscopy (EDXS), Brunauer–Emmett–Teller (BET) specific surface area, strength, and zinc content. Also, the samples were used in order to measure photochemical activities, such as the removal efficiency of humic acid (HA) in a fluidized batch reactor. The XRD patterns appeared as the ZnS type. The Zn-SPAC had a large BET specific surface area and their shape was spherical, with a diameter of about 350–400 μm. When the Zn-SPAC was dosed in a fluidized bed reactor with UV light, the HA removal efficiency increased by up to 60%. On the other hand, the HA removal efficiency by only UV-C ($\lambda_{\max} = 254$ nm) irradiation was very low, about 15%. Therefore, we infer that Zn-SPAC has good photochemical activity and presented the possibility of being a useful photocatalyst for water purification.

Keywords HA · Resin · Spherical activated carbon · Zinc

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Introduction

The UV/photocatalyst system is the most powerful system among the advanced oxidation processes (AOPs). The heterogeneous photocatalysis can be an effective alternative solution for the elimination of humic acid (HA) from aqueous solution. With this process, it is possible to degrade the majority of organic molecules without additional chemicals. Also, this process does not produce sludge and harmful by-products. The basic mechanism of the UV/photocatalyst system is ejecting an electron from the valence band to the conduction band and then a positive h^+ hole is created in the valence band. Excited electrons react with oxide, so super oxide radicals are produced. Both positive hole and super oxide radicals are followed by the formation of extremely hydroxyl radicals on the semiconductor surface and a direct oxidation of the polluting species. The UV/photocatalyst system can be classified into two types. The first is the slurry type using the photocatalyst itself and the other is the type fixing the photocatalyst on a supporter. The former type is known to exhibit an outstanding reaction rate that is due to the dispersion of nano size particles that have high surface area. On the other hand, the slurry type has some limitations, which include a low light-utilization efficiency that is due to the absorption and scattering of the light into an aqueous suspension of illuminated powder. Indeed, a slurry type system requires post-processing such as filtration or separation processes to separate the catalyst in water after the photocatalytic reaction has completed. Such problems associated with the use of catalyst suspensions can be circumvented by immobilizing on support [1].

In the present study, the spherical activated carbon contained ZnS (Zn-SPAC) was prepared through the carbonization/activation of an ion-exchanged resin by Zn^{2+} solution. Zinc was chosen for three reasons. Zinc has photochemical activity and is easily ion-exchanged. Also, zinc has been found to show a marked antibacterial activity without the presence of light. The Zn-SPAC samples that had different zinc contents were studied for their photodegradation of HA and physicochemical characteristics.

The presence of natural organic matter (NOM) in both surface and ground water supplies has received much public attention in recent years. The HA form among the NOM has a significant role in aquatic systems for several reasons. HA generally forms the major fraction of dissolved organic matter (DOM) in surface water that represents 90% of DOM. HA imparts a brown or yellow color in water and can make complexes with metals and organic pollutants, such as pesticides, insecticide, and herbicides [2, 3]. Most significantly, HA is the precursor of disinfection by-products in chlorination and ozonation processes [4, 5]. In conventional processes, HA is eliminated from water before chlorination by coagulation with aluminum sulfate and filtration. However, coagulation processes bring two main problems. Firstly, the residual sludge has high aluminum concentration. Secondary, treated water needs high-quality monitoring of its aluminum concentration. If the water contains more than 0.2 mg/L of aluminum, it is not recommended for drinking by the World Health Organization (WHO). Moreover, it needs to be mentioned that, during this conventional treatment process, only 10–50% of the total organic carbon (TOC) is removed [6]. Therefore, HA was chosen to investigate

Zn-SPAC photochemical activity and the possibility of its application in a floating UV/photocatalyst system.

Experimental

A strong acid ion-exchange resin (SK1BH, Diaion) was used as the starting material for the preparation of Zn-SPAC. The strong acid ion-exchange resin that consists of polystyrene and divinylbenzene (DVB) has the sulfonate group as the exchangeable functional group. This resin was treated using 0.1 N zinc ion solution for 1 h because the resin's operating pH range is from 0 to 14 and the rate of ion-exchange is rapid. The weight ratio was 1:0.86 (zinc solution:dry resin). For controlling the zinc content in SPAC samples, ion-exchange treatment was performed from one to three times. The resin was activated under nitrogen/H₂O vapor at 900°C for 0.5 h, followed by carbonization treatment at 700°C under N₂ atmosphere.

Morphologies and shapes of the Zn-SPAC samples were observed using a scanning electron microscope (SEM, JEOL, JSM-6700F). Crystal structures of zinc compounds in the SPAC samples were identified by X-ray diffraction patterns (XRD) using an X-ray diffractometer (Rigaku, D/MAX-IIIB) with Cu- $k\alpha$ radiation, and operating at 2.0 kW. The XRD data was collected from 20° to 80° (2θ) at a scanning rate of 0.5°/min. For determining the spatial distribution of zinc ions on the SPAC samples, an electron probe micro analyzer (EPMA, JEOL, JXA-8100) and an energy dispersive spectroscope (EDS, Phoenix, EDAX) were used. The specific surface area of the Zn-SPAC samples was measured using the Brunauer–Emmett–Teller (BET) method (Micrometrics, ASAP 2010). The photochemical activity was measured using electron spin resonance (ESR) (JEOL, JES-FA100). After the Zn-SPAC samples were oxidized at 900°C under air atmosphere for 3 h, residues of the Zn-SPAC samples were dissolved in nitric acid for determining the zinc content by means of an atomic adsorption spectroscope (AAS, Varian, SpectrAA 220). HA concentration was measured using a total organic carbon analyzer (TOC, Shimadzu, TOC-5000A) and the chemical oxygen demand using chromate (COD_{Cr}) method. In the method of compressive strength, one unit of the Zn-SPAC sample was placed on the strength test instrument and then force was vertically applied until the Zn-SPAC was broken. The applied force was indicated in units kg.

The Zn-SPAC samples were used for HA removal to investigate photochemical activity. The photocatalytic reactors were batch-type reactors. When the UV source was a low-pressure mercury lamp UV-C ($\lambda_{\max} = 254$ nm, G18T5C, LightTech), the batch-type reactor had 3.1 L capacity and was 45 cm in height and 10 cm in diameter. The other batch-type reactor had 3.1 L capacity and was 31.5 cm in height and 10 cm in diameter, and the UV source was a low-pressure mercury lamp UV-A lamp ($\lambda_{\max} = 365$ nm, TI105, Philips). The reason for this was the different heights of UV lamp. Each of the Zn-SPAC samples that had different zinc contents were dosed to 20 g/L in the UV/photocatalysis system to remove HA. Actually, the ZnS weights in 20 g of Zn-SPAC are 0.9–2.7 g when considering the zinc content in SPAC. Also, the Zn-SPAC loading amount was changed from 10 to 50 g/L to

estimate a reasonable Zn-SPAC dosage. Moreover, ZnS (Aldrich, powder, 10 micron) was used in the photodegradation of HA for comparison with the photochemical activity of the Zn-SPAC samples. The concentration of ZnS was 2 g/L in the reactor. The reaction was carried out in the neutral pH range at 25°C. Air was supplied to the reactor for the dispersion of the Zn-SPAC samples during the photochemical reaction. The HA (sodium salt, Aldrich) was dissolved in distilled water overnight, and the HA solution was filtrated using a 0.45- μm membrane filter to remove the ash. The initial concentration of HA was controlled to 10 ppm.

Results and discussion

Physicochemical characteristics of the Zn-SPAC samples

After the ion-exchange treatment was performed from one to three times, each of treated resins had 1.5, 3, and 4.5 wt% of zinc content, respectively. The treated resins were activated for changing spherical activated carbon contained zinc. The sample code, the zinc content, the compressive strength, and the specific surface area of the Zn-SPAC samples are listed in Table 1. The amounts of zinc ion content in Zn-SPAC-1, Zn-SPAC-2, and Zn-SPAC-3 were 3, 6, and 9 wt%, respectively. The above results are attributed to the fact that the burn-off weight percent of carbon is 50 wt% during carbonization/activation. Therefore, these results indirectly proved that zinc was not lost during the carbonization/activation treatment. All of the Zn-SPAC samples had compressive strengths of 9 kg/unit. The value of compressive strength was enough to apply in the UV/photocatalyst system. The specific surface areas of Zn-SPAC samples increased with increasing zinc content; that is, the values were increased in the range from 420 to 519 m^2/g . Zinc is a chemical reagent that is used in chemical activation for increasing the activated carbon pore width [7]. Also, zinc may promote the formation of cross-linking, leading to the formation of a rigid matrix, which is less prone to volatile loss and volume contraction upon heating to high temperature [8]. Therefore, zinc content wt% increased with increasing BET specific surface areas of Zn-SPAC samples.

Figure 1 shows the SEM images of the Zn-SPAC samples. All of the sample shapes were spherical, with diameters in the range 350–400 μm . As shown in Fig. 2, the X-ray diffraction peak was appropriate to the pattern, coinciding with the ZnS crystal of zincblende type from the JCPDS file. This kind of result was obtained

Table 1 Sample code, compressive strength, zinc content, and specific surface area of spherical activated carbon contained zinc (Zn-SPAC) samples

Sample code	Time of ion-exchange treatment	Compressive strength (kg/unit)	Zinc content (wt%)	BET surface area (m^2/g)
Zn-SPAC-1	1	9	3	420
Zn-SPAC-2	2	9	6	509
Zn-SPAC-3	3	9	9	519

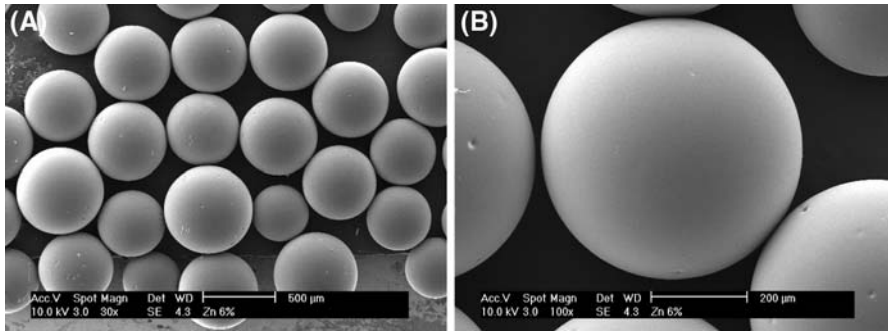
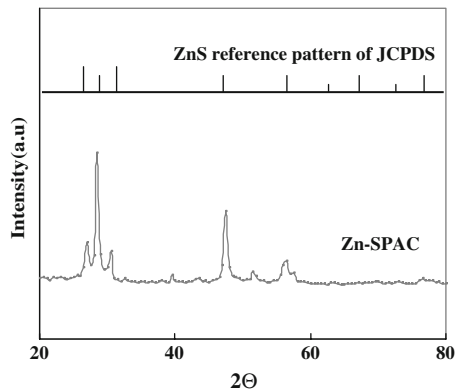
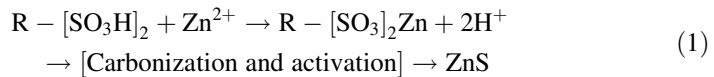


Fig. 1a, b Scanning electron microscope (SEM) images of the Zn-SPAC-2 sample. **a** 30×. **b** 100×

Fig. 2 X-ray diffraction (XRD) pattern of spherical activated carbon contained zinc (Zn-SPAC)



because the resin had an exchangeable functional group of sulfonate, so Zn-SPAC samples had the ZnS form as per the below presumed reaction:



An EPMA is a commonly used means to determine the spatial distribution of major elements precisely. In this study, the ZnS distribution on the Zn-SPAC was determined using EPMA. It is shown from the EPMA results of Fig. 3 that Zn elements were uniformly distributed on the Zn-SPAC. Moreover, the distribution level area percentage was shown to increase as the content of the zinc increased.

ESR studies were carried out to verify the existence of paramagnetic species such as $\bullet\text{OH}$ and $\text{HO}_2\bullet$ on the UV irradiation of photocatalysts [9]. Figure 4 show the ESR spectra of the Zn-SPAC. In general, the intensity of ESR absorption is proportional to the concentration of the free radical or the paramagnetic materials that are present [10]. Therefore, it is possible to produce paramagnetic species of the Zn-SPACs under UV irradiation.

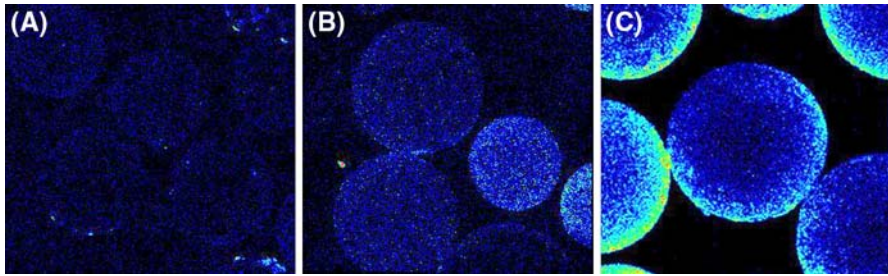
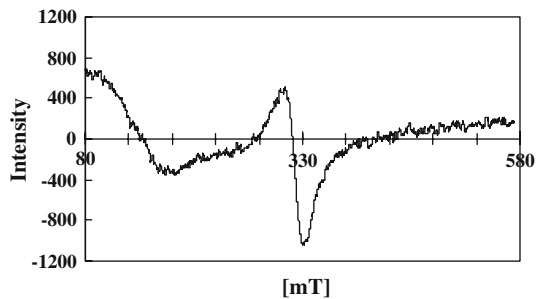


Fig. 3a–c Electron probe micro analyzer (EPMA) images of the Zn-SPAC samples. **a** 3 wt%. **b** 6 wt%. **c** 9 wt%

Fig. 4 Electron spin resonance (ESR) spectra of the Zn-SPAC



Photodegradation of HA

The photodegradation results of HA are shown in Fig. 5. To measure the adsorption affect of HA on the Zn-SPAC samples, all of the Zn-SPAC samples were dispersed in a batch-reactor without UV irradiation. Because the HA had a large-scale molecular structure for being adsorbed to the Zn-SPAC, the adsorption did not occur. The HA removal efficiency was approximately 15% under conditions of only UV-C irradiation. But the case of adding the Zn-SPAC samples rather than only UV-C irradiation improved the removal efficiencies of HA. Consequently, the HA removal efficiencies for Zn-SPAC-1, Zn-SPAC-2, and Zn-SPAC-3 were 48, 61, and 62%, respectively. The HA removal efficiency increased with the zinc content until it became 6 wt%. On the other hand, the HA removal efficiencies when the zinc content exceeds 6 wt% analogously showed the removal efficiency of the zinc content 6 wt% case. Therefore, 6 wt% zinc content in SPAC was suitable for removing HA. The HA removal efficiency of Zn-SPAC-2 in which the zinc content is 6 wt% was four times higher than that of the UV-C irradiation only case. Compared with UV/ZnS, the HA removal efficiency of Zn-SPAC-2 was approximately 86% relative to the HA removal efficiency of UV/ZnS. Especially, the ZnS amount in Zn-SPAC-2 was similar to the ZnS amount in UV/ZnS, which was about 1.8 g/L. As shown in Fig. 5, we obtained similar results in photodegradation test when UV-C was used (Fig. 5a) as when UV-A was used (Fig. 5b).

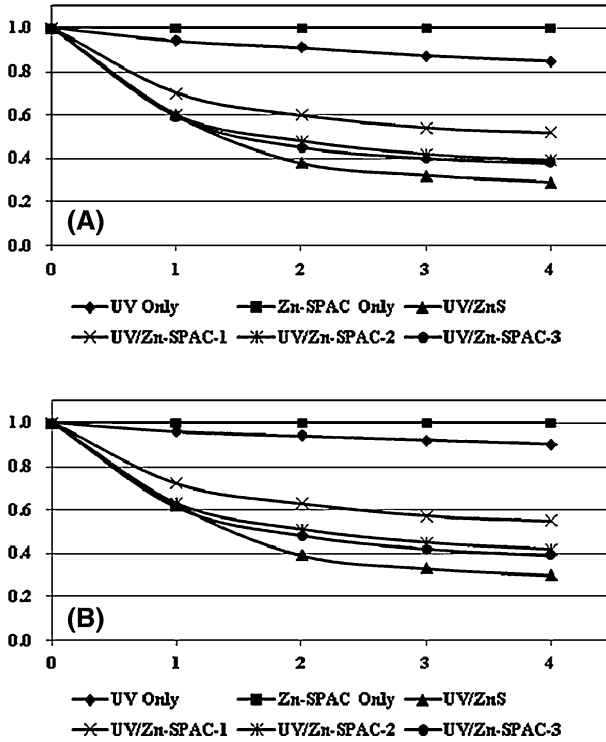


Fig. 5a, b Degradation efficiencies of humic acid (HA) by UV only, Zn-SPAC only, UV/ZnS, and UV/Zn-SPAC samples. **a** UV-C. **b** UV-A

To investigate the stability of the Zn-SPAC samples during the photochemical reaction, HA solution in the UV/photocatalyst reactor that was collected at each sampling time was analyzed by AA spectrometers for determining the leached zinc ion concentration. Figure 6 shows the results of the leached zinc concentration. Zn-SPAC-1 and Zn-SPAC-2 samples were stable without leaching of the zinc fraction,

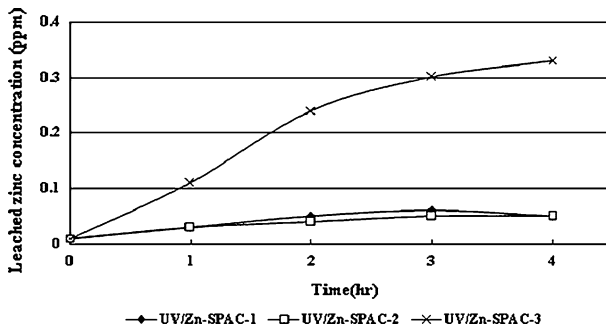
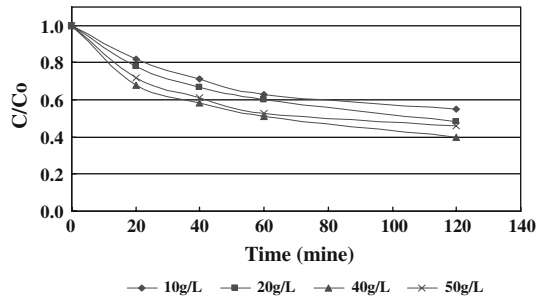


Fig. 6 Leached zinc concentration during photodegradation at varying zinc contents

Fig. 7 Photodegradation efficiencies of HA at various dosages of Zn-SPAC-2



whereas the zinc concentration was leached with a maximum of 0.33 ppm when the Zn-SPAC-3 sample was used in the fluidizing UV/photocatalyst reactor. As with the results of not only the HA removal efficiency but also the zinc elution, Zn-SPAC-2 with 6 wt% zinc content was the most suitable for the UV/photocatalyst reactor.

The loading amount of Zn-SPAC-2 was varied in the range 10–50 g/L in order to estimate the reasonable amount. The HA removal efficiency increased with the loading amount of Zn-SPAC-2 until it became 40 g/L, as shown in Fig. 7. When Zn-SPAC-2 was dosed to 50 g/L in the UV/photocatalyst reactor, the HA removal efficiency decreased from 60 to 54%. This result is due to the low light-utilization efficiency by absorption and the scattering of the light into the Zn-SPAC [1]. Therefore, an optimal dosage of the Zn-SPAC-2 was determined as 40 g/L (ZnS amount in Zn-SPAC-2 is 3.6 g/L).

Conclusion

The spherical activated carbon (SPAC) containing ZnS, which was uniformly dispersed on the SPAC, was prepared through manufacturing process of AC for applying to UV/photocatalyst systems. The Zn-SPAC samples were prepared through carbonization/activation, wherein strong acid ion-exchange resin was treated by Zn²⁺ solution. These Zn-SPAC samples together had characteristics of activated carbon and photocatalysts. These Zn-SPAC samples were used for removing humic acid (HA) to investigate the photochemical activity and the application possibility in a UV/photocatalyst system. The Zn-SPAC-2 samples could effectuate the UV/photocatalyst system to remove pollutants in aqueous processes without leaching zinc. As the results show, the method of zinc immobilization in this study can be inferred as a new way of photocatalyst immobilization. Also, this Zn-SPAC sample presented the applicability to the UV/photocatalyst system for water purification. Consequently, hazardous pollutants will be easily removed or transformed to harmless substances, because the use of these samples could possibly be used to facilitate the adsorption of pollutants by supporter (AC) and the photodegradation of pollutants by the photocatalyst.

References

1. C.S. Turchi, D.F. Ollis, J. Phys. Chem. **92**, 6852 (1988)
2. E.B. Louise, D. Mary, Water Res. **27**, 1209 (1993)
3. M. Hiraide, Y. Arima, A. Mizuike, Anal. Chim. Acta **2000**, 171 (1987)
4. P.C. Singer, Water Sci. Technol. **40**, 25 (1999)
5. B. Lasnglais, D.A. Reckhow, D.R. Brink (eds.), *Ozone in water treatment application and engineering* (Lewis publishers, Michigan, 1991)
6. G.S. Wang, S.T. Hsieh, C.S. Hong, Water Res. **34**, 3882 (2000)
7. A. Ahmadpour, D.D. Do, Carbon **34**, 471 (1996)
8. H. Teng, T.S. Yen, L.Y. Hsu, Carbon **36**, 1387 (1998)
9. T.K. Kim, M.N. Lee, S.H. Lee, Y.C. Park, C.K. Jung, J.H. Boo, Thin Solid Films **475**, 171 (2005)
10. C.N. Banwell, E.M. McCash (eds.), *Fundamentals of molecular spectroscopy* (Mcgraw-Hill, New York, 1994)