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The adsorption performance of the TiO₂/C composites obtained by sol-gel coating route

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In this paper the preparation procedure and phenol adsorption performance of the initial carbon supports and TiO₂/C composites is studied. The effect of the surface chemistry of supporting carbon material can have a dramatic effect on the adsorption of phenol. It was found that the TiO₂ coating on the carbon adsorbents decreases the phenol uptake and analysis of the rate of adsorption was fitted the integrated first order rate equation.

Keywords: Sol-gel, TiO₂/C composite, phenol, adsorption

Адсорбционные эффективности TiO₂/C композитов полученные путем золь-гель покрытия

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В данной статье изучены процесс получения и эффективность адсорбции фенола на исходных углеродных носителей и TiO₂/C композитов. Влияние поверхностной химической структуры исходных носителей могут иметь драматический эффект адсорбции фенола. Обнаружено, что покрытие углеродных адсорбентов с TiO₂ сравнительно увеличивает удержания фенола и анализ скорости адсорбции совпадает с уравнением скорости реакции первого порядка.

Ключевые слова: золь-гель, углерод, TiO₂/C композит, фенол, адсорбция

Introduction

Water pollution has become one of the most concerning environmental problems with the rapid development of industry. The phenomena of adsorption from aqueous solution and photocatalytic oxidation of organic molecules in solution has already been described in several literatures [1, 2]. There has been a flurry of publications describing the preparation and testing of a variety of adsorbent/photocatalyst hybrids in order to utilize any synergistic effect produced with a combination of the two systems in an attempt to produce a highly efficiency means of removal of organic pollutants from both water and air. Many adsorbents have been utilized for the production of adsorbent/photocatalyst systems: carbons [3-5], clays [6], ceramics [3, 7], zeolites [3], etc. However, carbons have been studied mostly in recent years as the adsorbent used in adsorbent/photocatalyst composites.

There have been several methods to prepare carbon supported titania (TiO_2) composites: the coating of carbon surface either through the thermal decomposition of polymer [8-10], or through the use of vapor techniques, such as chemical vapor deposition (CVD) [5, 11, 12], by the thermal decomposition of titanium containing molecules with large organic ligands, such as Ti(IV) oxyacetyl acetonate [13], in an inert atmosphere. This approach has rarely been used to produce composites and techniques such as the formation of TiO_2 /polymer particles that are then subjected to a carbonization process are more commonly found in the literature for the production of composites [14].

The aim of this work was the preparation and characterization of TiO_2 /C particles using the coating of carbon supports with TiO_2 by the hydrolysis - polycondensation of titanium alkoxide via sol-gel method and their application in water borne pollution control. The specific objectives of the research were to:

- find a reliable coating with TiO_2 into the surface of Mast carbon microspheres and commercially available activated carbon Darco G-60.
- examine the location and the degree of TiO_2 coating, and also investigation of the crystal phase of the TiO_2 in these TiO_2 /C particles.
- determine the surface area of the TiO_2 /C particles to find the effect of the TiO_2 coating on the adsorption performance of TiO_2 /C composite adsorbent.

Experimental

Mast carbon microspherical particles (Mast Carbon Ltd., England) and Darco G-60 (Sigma-Aldrich) were used as a support for TiO_2 loading and were first air-modified in order to oxidize the carbon surface. Other chemicals used in this study were of reagent grade and purchased from Sigma-Aldrich Chemie GmbH, Germany. Aqueous solutions were prepared using doubly distilled water.

The titania coating was deposited chemically following the procedure by Torimoto et al. [15]. The TiO_2 was deposited on the modified carbon surface chemically using titanium isopropoxide. The titanium isopropoxide ($\text{Ti}(\text{OPr}^i)_4$) (1.85 ml) in isopropanol (70 ml) was contacted with 0.5 g of air-modified Mast carbon microspheres with a catalytic amount of nitric acid at 298 K. After 3 h the carbon was washed with water then dried and then heat treated at 623 K for 3 h to give surface TiO_x clusters.

In order to give a more controlled loading of TiO_2 , further work was carried out using different amounts of $\text{Ti}(\text{OPr}^i)_4$. 1.5 g of air-modified Mast carbon microspheres were added to 25 ml of isopropanol with rapid stirring. A known amount of $\text{Ti}(\text{OPr}^i)_4$ added in order to give either a 5%, 7%, 10% or 15% (w/w) TiO_2 coating on the carbon surface. The mixture was stirred continued for 1 h. The mixture was then 'aged' for 24 h before filtering and drying at 373 K for 24 h. Heat treatment was then carried out at 623 K for 16 h.

The N_2 sorption characterization on the powdered samples was done on a Micromeritics, Inc. A Micromeritics ASAP 2010 surface area and pore size analyzer at -196°C (liquid nitrogen). The samples were degassed at 90°C and 1 Pa overnight prior to N_2 adsorption-desorption measurement. The surface and pore parameters were calculated using the accompanying software from Micromeritics, Inc. The location of the TiO_2 coating in the TiO_2 /C samples was observed under a scanning electron microscope A Philips 3200N SEM in conjunction with an Oxford Instruments EDX analyzer. X-ray diffraction (XRD) patterns were recorded on a Panalytic X'Pert Pro MPD powder diffractometer with a $\text{Cu K}\alpha$ ($\lambda=1.54\text{\AA}$) X-ray source.

Adsorption experiments were carried out using a Pyrex jacketed reactor equipped with a magnetic stirrer, thermometer and sample syringe needle. The cylindrical reactor

(internal dimensions: 50.8 x 127mm) containing 250 ml of solution was stirred at 60 rpm \pm 2rpm by a magnetic stirrer. It was held at the desired temperature by pumping water at 120 cm³ /min through the water jacket of the reactor from a water bath held at the desired temperature. The temperature of the solution in the kinetic reactor was monitored to within 0.5 K. The kinetic parameters of an adsorbent and specific adsorbate under defined conditions were determined by using simple integrated rate laws according to [16, 17]. The initial rate constants were determined from the gradient using Equation $[A]=[A]_0 e^{-kt}$. The half-life of a reactant was calculated by $t_{1/2} = \ln 2/k$.

Results and discussion

The sol-gel method was used for the preparation of titania coated carbon particles, TiO₂/C, through the hydrolysis of titanium isopropoxide (Ti(OPrⁱ)₄) for the coating of Mast carbon spherical particles (Mast Carbon Ltd., England). The advantage of this method is contacting of the carbon spheres with a pre-formed TiO_x gel would be able to give a large loading of TiO₂ on the outer surface of the carbon spheres. The degree of TiO₂ coating on the surface of the carbon supports was determined by the use of mass burn-off. For analysis of samples in this work, a known amount of a sample was placed in a dry, pre-weighed ceramic crucible were reweighed in order to determine the amount of inorganic matter. After determination of the amount of inorganic matter contained within the parent carbons used, the amount of TiO₂ then coated onto a carbon could easily be determined.

In order to examine the location and the degree of TiO₂ coating onto the surface of Mast carbon microspheres via sol-gel process scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis was studied. The SEM could also be used to image the external surface of the TiO₂/C particles. The distribution and morphology of the TiO₂ coating can easily be identified using this technique. The SEM images of the coating of Mast carbon spheres using the sol-gel method are shown in Figure 1. The acid-catalyzed hydrolysis of Ti(OPrⁱ)₄ resulted in Mast carbon spheres coated with 7% by weight of TiO₂ (see Figure 1). Subsequent coatings by hydrolysis of Ti(OPrⁱ)₄ were carried out with different target loadings.

The SEM images show a coating on the surface of the carbon support (Figure 1), which is confirmed as comprising of titanium and oxygen by the EDX spectra (not shown), strongly indicates that the coating is TiO₂. However the coating looks fragile and non-homogeneous in that the coating appears to cover most of the outer surface of the carbon microsphere, but some areas a quite clearly is seen that they have a very thin coating of TiO₂.

The crystal phase and dispersion of the TiO₂ in the TiO₂/C particles were carried out using X-ray diffraction (XRD) analysis. The hydrolysis of Ti(OPrⁱ)₄ has been reported to result in anatase TiO₂ [18], the kinetically favored crystal phase, which is the desired crystal phase due to its higher photoactivity. The XRD profile for sol-gel TiO₂ coated Mast carbon microspheres are shown in Figure 2. It shows that TiO₂ in the TiO₂/C prepared by the hydrolysis of Ti(OPrⁱ)₄ has a similar XRD pattern to TiO₂ formed using the method in the absence of the carbon support, and is identified as mostly comprising of anatase TiO₂. The peaks in the diffraction pattern for the TiO₂/C are much wider than those for TiO₂ only.

The growth of TiO₂ crystals within the porous structure of the carbon support will limit their size and even the crystals of TiO₂ which form on the outer surface of the carbon may have their growth limited by the carbon support. Using line broadening to determine the crystallite size for the TiO₂ from the hydrolysis of Ti(OPrⁱ)₄, using the same peak at 2 θ

- 25.27° , is given as 7.6 nm. The TiO_2 crystals grown on the support are a third of the size of the sol-gel derived TiO_2 crystals prepared in the absence of a carbon support. In the XRD pattern for the TiO_2/C composite in Figure 2 the additional peaks at positions 2θ - 43.07° and 44.90° are attributed to a C_{12} structure within the carbon support [19]. Hence these peaks are not present in the TiO_2 only XRD pattern.

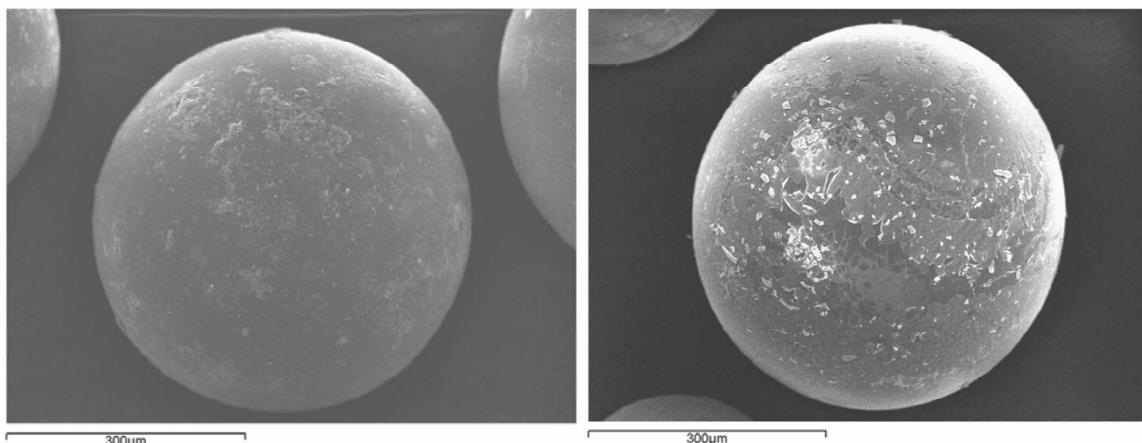


Fig. 1. Air modified precursor (*left*) and 7 wt% TiO_2 coated Mast carbon microspheres produced using the acid-catalyzed sol-gel method (*right*)

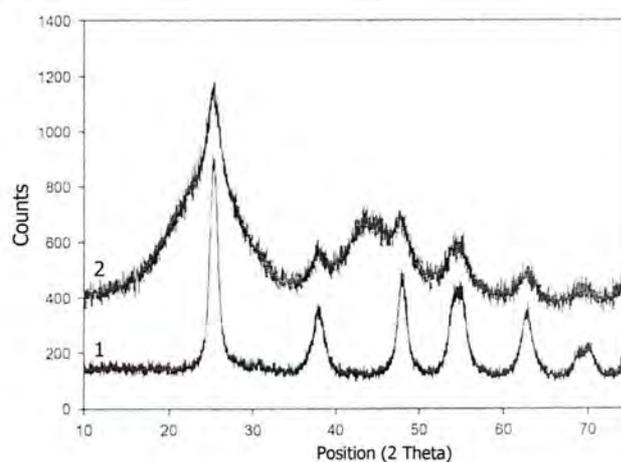


Fig. 2. XRD patterns of (1) TiO_2 formed from the hydrolysis of $\text{Ti}(\text{OPr})_4$ and (2) Mast carbon spheres coated with TiO_2 by hydrolysis of $\text{Ti}(\text{OPr})_4$

The adsorption performance of the TiO_2/C composites is studied in the adsorption of phenol under varying conditions of temperature and pH as well the concentration of the selected pollutants. The effect of the surface chemistry of supporting material - carbon can have a dramatic effect on the adsorption of phenols and its derivatives, and therefore the effect of different activation regimes on the physical and chemical nature of the carbon surface and the subsequent effect on the degree of adsorption of phenol were studied. Table 1 shows the monolayer coverage seen in the adsorption of phenol on the five different adsorbents at 298 K. The differences in the monolayer coverage can be explained in terms of the surface chemistry for the adsorption of phenol by activated carbon spheres.

The difference in the surface coverage (capacity) of Darco G-60 and the reduced Darco G-60 (for comparison) is a very clear indication of the effect of surface functionality on the uptake of phenol. Both these carbons have the same surface area and pore size distribution, the only difference between the two carbons is the distribution of surface functional groups. The functional group distribution for the two carbons shows that the

reducing treatment of Darco G-60 has removed over half of the acidic functional groups from the surface and generated more basic sites. This large decrease in the surface acidity seems to be responsible for the ca. 25% increase in the phenol monolayer coverage on the reduced Darco G-60 over the as received Darco G-60. Coughlin and Ezra also showed that surface treatments which altered the amount chemisorbed oxygen on the surface of a carbon have a strong effect on the adsorptive capacity for phenol [20].

Table 1. The surface area and the phenol monolayer coverage at 298 K for the five adsorbents studied

Carbon or TiO ₂ /C	S _{BET} (m ² /g)	Phenol monolayer capacity (μmol/m ²)	Mass Uptake (% wt)
Mast Carbon Microspheres	737	3.13	21.7
Darco G-60	1000	2.06	19.4
Reduced Darco G-60	1000	2.47	23.2
TiO ₂ /Mast Carbon microspheres	457	3.11	13.4
TiO ₂ /Darco G-60	655	2.82	17.4

The adsorption of phenol by the two TiO₂/C composites shows similar to that for the two supports used, i.e. that Mast carbon based TiO₂/C system has a higher monolayer coverage than the Darco G-60 based system. The Darco G-60, however, shows a large increase in the monolayer capacity over the carbon support alone. Again this difference in monolayer coverage per m² can be explained in terms of the surface chemistry [3]; the coating of the carbon support with a new layer of carbon and the use of high temperatures in the preparation of the TiO₂/C particles will both act to reduce the concentration of acidic functional groups on the carbon surface of the TiO₂/C particles.

The % mass uptake is more relevant to real applications of carbons as adsorbents i.e. phenol uptake per unit volume is the usual term used for industrial applications as the amount of carbon used is determined by the volume of the absorber system, but these values were not available. Phenol uptakes of around 20 wt% are observed for the three uncoated adsorbents (Table 2). The coating reduces the surface area of the adsorbents by ca. 35% and although the monolayer coverage (in moles adsorbed/ m²) is high for the TiO₂/C composites, the weight uptake of phenol decreases. However, the weight phenol uptake for the TiO₂/Darco G-60 composite is still very respectable (17.4%).

The kinetics of adsorption of phenol was studied on the two carbon adsorbents and the two prepared TiO₂/C systems. Figure 3 shows the uptake of phenol by the carbon adsorbent and the TiO₂/C composites. What is immediately evident is the high performance of Darco G-60 compared to the Mast carbon microspheres.

The TiO₂ coating on the carbon adsorbents decreases the phenol uptake. However, the plots mirror those of the parent adsorbents indicating that the nature of the parent adsorbents is important in determining the rate of phenol uptake for the TiO₂/C systems. Analysis of the rate of adsorption was carried out by plotting the integrated rate laws for each reaction in order to determine the order of reaction. The kinetic data from the adsorption of phenol by all four adsorbents fitted the integrated first order rate equation as has been demonstrated for the adsorption of phenol by Mast Carbon microspheres.

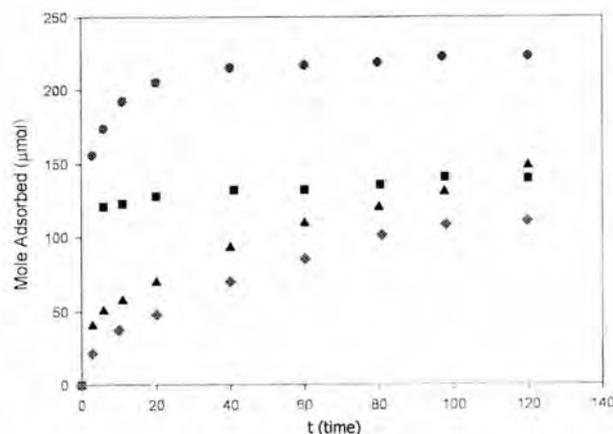


Fig. 3. The adsorption of phenol from aqueous solution at pH 7 by four adsorbents as a function of time. ● – Darco G – 60; ■ – TiO₂/Darco G – 60; ▲ – Mast Carbon Microspheres; ◆ - TiO₂/Mast Carbon Microspheres.

The initial rate constants and half-lives summarize Table 2, the rate constants for the Darco G-60 based adsorbents are better than the Mast Carbon based adsorbent. Indeed the half-life for Darco G-60 is less than 20% of the half-life for phenol adsorption on Mast carbon spheres. This would massively influence the decision on which of the two adsorbent to choose for any application. The reason for the large difference in the rate of adsorption comes down to the amount of available surface area of Darco G-60 (1000 m²/g) and Mast Carbon (747 m²/g) and the pore size distribution. The pore volume and pore size distribution for Darco G-60 is much greater than for the Mast Carbon spheres. And as was stated above the method and extent of the activation of the carbon has a large impact on the pore structure of the resultant activated carbon and thus it will have an impact on the initial rate of phenol adsorption.

Table 2. The initial first-order rate constants and half-lives for the adsorption of phenol at 298 K for four adsorbents

Adsorbent	k (s ⁻¹)	Half-Life (min)
Mast carbon	1.49 x 10 ⁻⁴	77.5
TiO ₂ /Mast carbon	1.32 x 10 ⁻⁴	87.5
Darco G-60	7.80 x 10 ⁻⁴	14.8
TiO ₂ /Darco G-60	3.87 x 10 ⁻⁴	29.8

There is a clear temperature effect on the rate of phenol adsorption. This is demonstrated in Table 3, where the half-life of the adsorption of phenol at 318 K is less than half the half-life for the adsorption at 298 K. Therefore changing the temperature has a significant effect on the rate but it also impacts on the maximum uptake for phenol.

Table 3. The integrated initial-first-order rate constant and half-life for the phenol adsorption by TiO₂/Mast carbon spheres and the monolayer coverage as a function of temperature

Temperature	k (s ⁻¹)	Half-Life (min)	Phenol Monolayer Coverage (μmol/m ²)
298 K	1.49 x 10 ⁻⁴	77.5	3.13
308 K	2.64 x 10 ⁻⁴	43.8	2.48
318 K	3.43 x 10 ⁻⁴	33.6	2.19

In most applications of carbon-based adsorbents and the intended application for the TiO₂/C composites, the temperature of the system is not controlled, and so the system cannot be optimized in this respect. This information is required by the operators of these systems so that the performance of the system can be predicted during the design phase for any new system.

Conclusion

The adsorption capacity of the TiO₂/C composites for phenol showed that the amount of phenol adsorbed at defined condition per m² of adsorbent surface was comparable in the case of TiO₂/Mast and Mast carbon microspheres and the TiO₂/Darco composite was much better than Darco G-60. This result is attributed to the fact that the carbon adsorbent will make up the vast majority of the surface area of the TiO₂/C composite and the method of preparation will produce a surface chemistry that is favourable for phenol adsorption. The kinetic performance of both initial adsorbents and the TiO₂/C composites would benefit from further activation treatments to widen existing pores and open up new pores within the carbon structure. This information is crucial for the efficient application of adsorbents and for this body of work has laid the foundations for the study of the photocatalytic activity of the TiO₂/C composites.

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