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Synthesis, Characterization and Applications of Sol-Gel Derived Zirconium Oxide Adsorbent Powder: Removal from Aqueous Solution of Phenol and p-Chlorophenol

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Adsorbent powders were prepared from the uncatalysed hydrolysis-condensation reactions of different complexes that were synthesized by the reactions of $Zr(OPr^n)_4$ with different chelating ligands (such as allylacetic acid [AAH], vinylacetic acid [VAH] and citraconic acid [CAH]). The complex products were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra. The maximum combination ratios of $AAH/Zr(OPr^n)_4$, $VAH/Zr(OPr^n)_4$ and $CAH/Zr(OPr^n)_4$ were 1.7, 0.9 and 1.3, respectively. The hydrolysis-condensation products of these complexes were calcinated at 900 °C and half of them were coated with 3-glycidyloxypropyltrimethoxysilane (GLYMO). The surface area and average pore diameter of the powders were estimated by the analysis of adsorption/desorption BET isotherm data. The adsorption capacities of these powders for aqueous phenol and p-chlorophenol were calculated following spectrophotometric determination. Phenol and p-chlorophenol adsorption on all of the GLYMO-coated adsorbents were satisfactory, e.g., the adsorbent obtained from the hydrolyzed, calcinated and GLYMO-coated form of $Zr(OPr^n)_{2.3}(AA)_{1.7}$ adsorbed 63% of phenol while the uncoated form adsorbed only 10%. The adsorption isotherm has been determined and data have been analyzed according to the Freundlich model.

Key Words: adsorbent, adsorption, coating, sol-gel process, zirconium alkoxides.

Introduction

The sol-gel process is considered to be the most practical method in recent years for preparing chemically homogeneous coatings and powders with a variety of useful applications such as coating materials[1,2], adsorbents[3], catalysts[4,5] and biosensor[6−8] or for chemical separation[9]. The synthesis of the sol-gel materials consists of the following major stages: hydrolysis of the precursors (metal alkoxides) to form a homogeneous sol, condensation of the sol to form a non-crystalline gel network, several steps to remove excess solvent and unreacted precursors, and drying and calcination treatments to form the final oxide structure. Metal alkoxides, the starting materials of the sol-gel process, are known for their relatively high reactivity, especially to water. Thus high rates of hydrolysis are unavoidable, and these in turn result in the precipitation of agglomerated zirconia, rendering the process useless. In these cases it is necessary to modify the precursors so as to increase their stability toward hydrolysis[10−15]. Many different molecules are used as modifiers, such as alcohols, acetylacetone, allyl acetoacetate, diols and organic acids (mono carboxylic acids and polymerizable chelating organic acid, i.e. methacrylic acid)[16−18].

Due to the rapid development of various industries (such as textiles, paper, leather, food, cosmetics and plastics), there is growing public concern about the widespread contamination of surface water and ground water by various organic compounds, such as phenols and their derivatives. The concentrations of these compounds in wastewater usually exceed the level for safe discharge.

Adsorption is a well-established technique for the removal of organic compounds from water. Many adsorbents, such as activated carbon[19−21], fertilizer wastes[22], wood[23], rice husk[24], chitin[25], XAD-4 resin[26], sawdust[27], organobentonites[28] and the activated kernel shucks of various fruits[29] have been employed in the removal of phenolic compounds. Adsorbent powders of metal oxide origin, synthesized by the sol-gel process in this work, have not previously been used in removing phenol and its derivates from aqueous solutions.

In this work, new carboxylate derivatives of $Zr(OPr^n)_4$ were obtained by complexing with allylacetic acid, vinylacetic acid and citraconic acid, which had not been hitherto reported as chelating ligands for this alkoxide. In this process, alkoxide groups of $Zr(OPr^n)_4$ were partially exchanged with carboxylate groups of the three acids. Adsorbent powders were obtained after the appropriate treatment of these materials. The adsorption of phenol and p-chlorophenol from aqueous solutions was studied for the adsorbents.

Experimental

Chemicals, Apparatus and Procedure

Zirconium(IV)-n-propoxide, $Zr(OPr^n)_4$, (70% v/v, Fluka), allylacetic acid (AAH) (98%, Fluka), vinylacetic acid (VAH) (95%, Fluka), citraconic acid (CAH) (99%, Fluka), $CDCl_3$ (99%, Aldrich) and DMSO-d_6 (99%, Sigma) were used as received. n-propanol (99%, Aldrich) was stored over molecular sieves (3ÅXL8) for a day before use. Double distilled water was used for the hydrolysis reactions.

$Zr(OPr^n)_4$ (0.001 mole) was dissolved in n-propanol (1 ml). After the production of a homogeneous solution, 1.40, 1.65, 1.75 and 1.85 mol of AAH were added slowly to the solution, for each mole of $Zr(OPr^n)_4$, respectively (these ratios were chosen as 0.85, 0.95, 1.10 and 1.50 for VAH and 1.2, 1.3, 1.45 and 1.6 for CAH). The reaction mixture was allowed to react for 2 h (required for the completion of the reaction) at ambient temperature.

Th infrared spectra of the complex products in n-propanol were taken on a MIDAC-240 Plus M-series Model FT-IR spectrophotometer.

The ^{1}H-NMR and ^{13}C-NMR spectra of these complexes were taken on GEMINI VARIAN 200 MHz model spectrometers, (the $Zr(OPr^n)_4$/AAH and $Zr(OPr^n)_4$/VAH complexes dissolved in $CDCl_3$, and the $Zr(OPr^n)_4$/CAH complex dissolved in DMSO-d_6).

Three $Zr(OPr^n)_x(L)_y$ complexes were synthesized in n-propanol by the use of the maximum combination ratios obtained in previously described experiments. The complex products in n-propanol were hydrolyzed without using a catalyst (except $Zr(OPr^n)_4$/CAH complex) by adding, drop by drop, 3 mol of water per 1 mol of $Zr(OPr^n)_4$, and stirring for 15 min at room temperature. Preliminary experiments show that the product was an extremely light powder when all the water was added instantaneously. A mixture of water with n-propanol (5 mol of H_2O/mole n-propanol) was employed in an attempt to control the rate of hydrolysis still further. The colloidal mixture, which formed immediately after the addition of water, turned into a gel as the hydrolysis reaction proceded. Gelation prevented the use of a Karl-Fischer coulometric titrator to measure the percentage of unreacted water. Solid products were obtained on removal of the solvent and the liberated alcohol under vacuum. Since $Zr(OPr^n)_4$/CAH complex is a solid, it was used as synthesized. All hydrolysis and $Zr(OPr^n)_4$/CAH complex products were first dried at room temperature for 1 h, then in a vacuum sterilizer at 95 °C for 3 h. The hydrolysis products of $Zr(OPr^n)_4$/AAH and $Zr(OPr^n)_4$/VAH were a white powder, whereas the $Zr(OPr^n)_4$/CAH complex product was cream in color. These products were ground into a powder of 175-200 mesh and calcinated at 900 °C in a muffle furnace for 90 min. Several surface characteristics of the adsorbent powders were measured using a Micromeritics ASAP 2000 BET analyzer. The BET surface area was calculated by using the many points method, but pore distribution was calculated according to the Barret-Jayner-Halenda (BJH) method[30].

GLYMO was hydrolyzed without solvent and catalyst, by adding 1, 2 and 3 mol of water per 1 mol of GLYMO. The mixture was stirred until it formed a clear and homogeneous solution at ambient temperature, and the percentage of unreacted water was measured by the use of the Karl-Fischer coulometric titrator. The alcohol that formed between the hydroxyl group of water and the methoxy group of GLYMO was removed in a vacuum at room temperature. The product thus obtained was a very viscous liquid. This product was diluted with n-propanol (0.1%, w/w) and used as a coating solution.

Adsorbent powders were dipped into the coating solution and the mixture was stirred for 1 h. Then it was filtered and dried for 3 h in a vacuum sterilizer at 120 °C. The batch method was employed for all the adsorption experiments. A 0.1 g sample of GLYMO-coated and uncoated absorbent powder were mixed with solutions of phenol and p-chlorophenol (10 ppm, 10 mL) separately, and stirred for 1 h. The solutions were then filtered through a microfilter (0.2 μm). The amounts of phenol and p-chlorophenol that remained in the filtrate were measured by a Jenway 6105 Model UV/VIS spectrophotometer by measuring the absorbance value for phenol at 270 nm and for p-chlorophenol at 279.9 nm, using the calibration method. The effect of the initial concentrations of phenol and p-chlorophenol (2.5-20 mg/L) on the adsorption was observed by fixed contact time (60 min), stirrer speed (300 rpm), amount of adsorbent (0.1 g), solution pH (6.08) and the volume of phenol and p-chlorophenol solutions (10 mL). The amount of adsorption was calculated using formula based on the difference of phenol and p-chlorophenol in aqueous solution before and after adsorption, according to[31]

$$\mathrm{qe} = (\mathrm{Co} - \mathrm{Ce})\mathrm{V}/\mathrm{W}$$

where qe is the adsorption capacity (mg/g), Co is the initial concentrations of phenol and p-chlorophenol (mg/L), V is the volume of the solution (L) and W is the weight of the adsorbent prepared from hydrolyzed, calcinated and GLYMO-coated product of $Zr(OPr^n)_{2.3}(AA)_{1.7}$ (g).

Results and Discussion

Synthesis of the complexes

The maximum combination ratios in these complexes were determinated by monitoring the C=O bands of the unreacted ligand on a FT-IR. Furthermore, the observed C=C bands for all three complexes confirm the bonding of the ligand to $(ZrOPr^n)_4$. The FT-IR data for the functional groups in the ligands and complexes are summarized in Table 1.

Table 1. FT-IR data of the functional groups in the ligands and complexes.

Compound	ν (CO) (cm$^-$)	ν (C=C) (cm$^-$)	ν (COO)$_{asym}$ (cm$^-$)	ν (COO)$_{sym}$ (cm$^-$)	$\Delta\nu$
Pure AAH	1709	1643	-	-	-
AAH/$Zr(OPr^n)_4$ (1.65; 1.7; 1.75; 1.85)	-; -; 1712; 1712	1641	1564	1456	108
Pure VAH	1707	1643	-	-	-
VAH/$Zr(OPr^n)_4$ (0.85; 0.9; 0.95; 1.1)	-; -; 1710; 1710	1647	1574	1458	116
Pure CAH	1716	1657	-	-	-
CAH/$Zr(OPr^n)_4$ (1.2; 1.3; 1.45; 1.6)	-; -; 1718; 1718	1659	1527	1456	71

It is clear from the FT-IR data in Table 1 that all AAH reacts with $Zr(OPr^n)_4$ when used in 1.65 and 1.70 combination ratios, and C=O bands for the unreacted AAH are observed for higher combination ratios. Similarly, C=O bands are observed when the ratios are 0.95 and 1.45 or higher for VAH and CAH, respectively. Moreover, the frequency separation ($\Delta\nu$) for AAH/$Zr(OPr^n)_4$, VAH/$Zr(OPr^n)_4$ and CAH/$Zr(OPr^n)_4$ complexes show that three ligands were bonded to the Zr atom as bidentate chelating ligands[32,33].

According to the FT-IR data, the complexation reactions of $Zr(OPr^n)_4$ can be shown as follows:

$$Zr(OPr^n)_4 + 1.7AAH \rightarrow Zr(OPr^n)_{2.3}(AA)_{1.7} + 1.7Pr^nOH$$

$$Zr(OPr^n)_4 + 0.9VAH \rightarrow Zr(OPr^n)_{3.1}(VA)_{0.9} + 0.9Pr^nOH$$

$$Zr(OPr^n)_4 + 1.3CAH \rightarrow Zr(OPr^n)_{2.7}(CA)_{1.3} + 1.3Pr^nOH$$

The ^{1}H-NMR and ^{13}C-NMR spectra data of these complexes [$Zr(OPr^n)_{2.3}(AA)_{1.7}$ (complex I), $Zr(OPr^n)_{3.1}(AA)_{0.9}$ (complex II) and $Zr(OPr^n)_{2.7}(AA)_{1.3}$ (complex III)] are shown in Table 2.

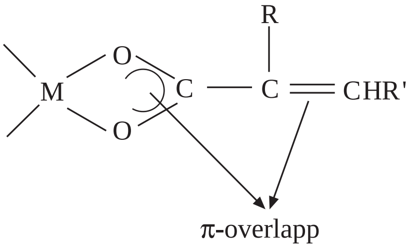
The acidic protons of the ligands were not observed in the ^{1}H-NMR spectra of these complexes. The absence of carboxylic protons in the ^{1}H-NMR spectrum of the complexes is evidence of bonding of the ligand to Zr. Moreover, in the ^{13}C-NMR spectra, expanding and displacing spectra of carbon atoms of carbonyl groups verified the FT-IR results and that the ligands were bonded to the Zr atom as bidentate chelating ligands.

Table 2. ^{1}H-NMR and ^{13}C-NMR spectra data of the carboxylate groups in ligands and complexes.

Compound	^{1}H-NMR (*) ppm	^{13}C-NMR (+) ppm
Pure AAH/complex I - C^{+} O_2 H*	11.8/–	181.8/180
Pure VAH/complex II - C^{+} O_2 H*	11.4/–	180.3/179
Pure CAH/complex III a) = CH - C^{+} O_2 H* b) = (CH_3) - C^{+} O_2 H*	12.2/– 12.2/–	167.8/172 171.7/170.5

Synthesis of adsorbent powders

Our various preliminary experiments on the hydrolysis reactions of different alkoxides and their complexes show that condensation occurred by the interaction of hydroxyl and alkoxyl (no chelating group) groups that are bonded to the metal atom. It was observed that the amount of alcohol liberated in the condensation reaction is much less than was formed in the hydrolysis of metal-chelate complexes. In the case of metal-alkoxide-chelate complexes, the chelating bonds are expected to be more resistant than the alkoxide bonds to hydrolysis and condensation due to π-overlapping. This is due to the extra stability of the O–M bond resulting from conjugation of the π-bond of C=C to the carboxylate group, i.e., π-overlapping. Conjugation of this type is known to stabilize carboxylate modified metal alkoxides[3].



$Zr(OPr^{n})_4$/CAH complex and hydrolysis products of the other two complexes were calcinated at 900 °C for 90 min, then coated with the hydrolysis product of GLYMO and were finally hot-treated overnight at 120 °C to realize both condensation and inorganic polimerization. The surface areas, micropore areas and particle sizes of GLYMO-coated and uncoated powder are different from each other. These properties of the powders are shown in Table 3.

Table 3. The surface areas and micropore areas of GLYMO-coated and uncoated powder.

Powder	BET surface areas (m^2/g)	Micropore areas (m^2/g)
Uncoated powder		
$Zr(OPr^{n})_{2.3}(AA)_{1.7}$	1.55	0.97
$Zr(OPr^{n})_{3.1}(VA)_{0.9}$	4.21	1.04
$Zr(OPr^{n})_{2.7}(CA)_{1.3}$	2.92	1.11
Coated powder		
$Zr(OPr^{n})_{2.3}(AA)_{1.7}$	1.00	0.83
$Zr(OPr^{n})_{3.1}(VA)_{0.9}$	3.34	2.24
$Zr(OPr^{n})_{2.7}(CA)_{1.3}$	1.38	1.16

The results show that both the BET surface areas and micropore areas of GLYMO-coated powder are smaller than those of the uncoated powders. The discrepancy between the micropore areas of $Zr(OPr^n)_4$/CAH could be attributed to the fact that this complex could not be hydrolyzed.

Preparation of the surface coating material

According to the Karl-Fischer titrations, 1.50 mol of water was used per 1 mol of GLYMO. This product was used as a coating material for adsorbent powder. The hydrolysis reaction of GLYMO is shown as follows:

$$R - Si(OMe)_3 + 3/2H_2O \rightarrow R - Si(OMe)_{3/2}(OH)_{3/2} + 3/2MeOH$$

R:

Adsorption of phenol and p-chlorophenol

The percentages for phenol and p-chlorophenol adsorption of GLYMO-coated and uncoated adsorbents are given in Table 4.

Table 4. Phenol and p-chlorophenol adsorption results of coated and uncoated adsorbents.

Adsorbent	(%) Phenol adsorption	(%) p-chlorophenol adsorption
Uncoated adsorbents		
$Zr(OPr^n)_{2.3}(AA)_{1.7}$	10	31
$Zr(OPr^n)_{3.1}(VA)_{0.9}$	17	44
$Zr(OPr^n)_{2.7}(CA)_{1.3}$	—	47
Coated adsorbents		
$Zr(OPr^n)_{2.3}(AA)_{1.7}$	63	62
$Zr(OPr^n)_{3.1}(VA)_{0.9}$	61	31
$Zr(OPr^n)_{2.7}(CA)_{1.3}$	63	50

The data given in Table 4 indicate that the adsorption of p-chlorophenol is superior to that of phenol, which can be attributed to the stronger dipole-dipole interactions favored by the higher acidity of p-chlorophenol. On the other hand, both phenol and p-chlorophenol adsorptions on all of the GLYMO-coated adsorbents are satisfactory.

The adsorption of phenol and p-chlorophenol on GLYMO-coated and uncoated adsorbents was systematically studied by investigating the constant parameters as described above and the different initial concentrations of phenol and p-chlorophenol to optimize the adsorption isotherm test. Depending on the initial concentrations, the adsorption percentages of phenol and p-chlorophenol for the hydrolyzed, calcinated and GLYMO-coated $Zr(OPr^n)_{2.3}(AA)_{1.7}$, and the adsorption capacities of this adsorbent for phenol and p-chlorophenol are presented in Figure 1 (a) and (b).

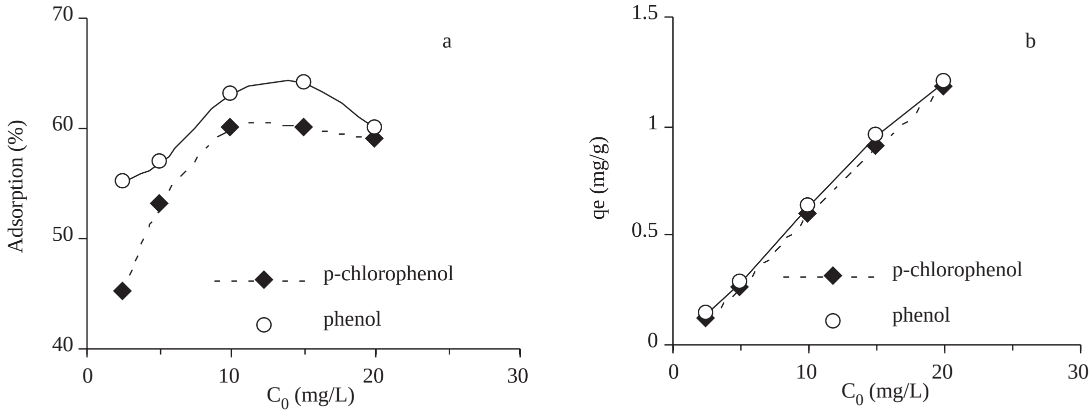


Figure1. The effect of initial concentration on the adsorption percentages of phenol and p-chlorophenol (a) and adsorption capacity (b) of GLYMO-coated adsorbent.

According to Figure 1, the percentages of phenol and p-chlorophenol adsorption for GLYMO-coated adsorbent decreased while the adsorption capacities increased as the initial concentrations of phenolics rose.

In order to quantify the engineering aspects of adsorption, an equilibrium study was performed on the different initial concentrations of phenol and p-chlorophenol. Other parameters such as contact time, stirrer speed, temperature and amount of adsorbent were kept constant.

To arrive at the adsorption capacity at the adsorbent surface, equilibrium adsorption isotherm data were analyzed using the Freundlich isotherm. This isotherm has proved useful in describing the adsorption behavior of the adsorbents for organic compounds[34]. The Freundlich isotherm is given by the equation[35]

$$Lnq_e = \ln K_F + alnC_e$$

where q$_e$ is the amounts of phenol and p-chlorophenol adsorbed per unit weight of adsorbent (mg/g), C$_e$ is the final or equilibrium phenol and p-chlorophenol concentrations (mg/L), a is the Freundlich constant and K$_F$ is the adsorption coefficient. The values of the Freundlich constants, K$_F$ and a, calculated from the intercept and the slope of the linear plots of lnq$_e$ versus lnC$_e$, prepared using the values of q$_e$ and C$_e$ obtained from the experimental adsorption data determined in solutions of different initial phenol and p-chlorophenol concentrations in solution using a constant amount (0.1 g) of adsorbent is given in Figure 2.

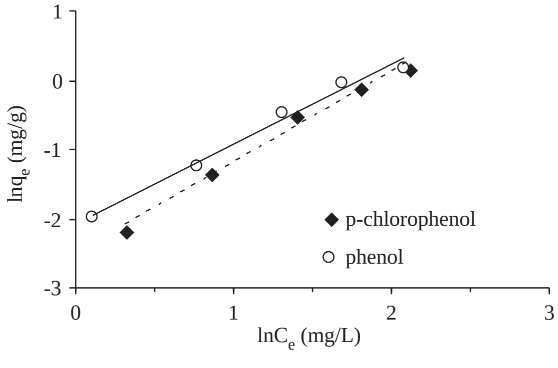


Figure 2. Freundlich isotherm for the adsorption of phenol and p-chlorophenol on GLYMO-coated adsorbent.

The Freundlich constants, K$_F$ and a, and the correlation coefficient (r^2) for phenol and p-chlorophenol are presented in Table 5.

Table 5. Freundlich constants and correlation coefficients for the adsorption of phenol and p-chlorophenol on hydrolyzed, calcinated and GLYMO-coated product of $Zr(OPr^n)_{2.3}(AA)_{1.7}$.

Adsorbed	K_F	a	r^2
phenol	0.125	1.15	0.99
p-chlorophenol	0.082	1.33	0.99

The Freundlich constant a is a measure of deviation from adsorption linearity. If a is equal to unity the adsorption is proved to be linear, which means that adsorption sites are homogeneous or these sites of the adsorbent are not limiting in quantity and are not modified by the adsorption process itself. If a is less than unity, this implies that increased adsorption modifies the adsorbent, giving rise to an increase in the adsorption capacity, such as forming new adsorption sites on the adsorbent surface. If a is greater than unity the adsorption bond becomes weak, and the q_e changes significantly, with small changes in C_e. It is clear that specific chemical reactions occurs between the phenol and the adsortion sites of adsorbent, and physical adsorption occur between p-chlorophenol and adsorbent surface, which results in a high adsorption capacity for the adsorbent.

Conclusions

This study has made the following achievements:

1. New metal alkoxides were synthesized and characterized.
2. These results show that organic acid modified metal alkoxides and that their hydrolysis-condensation products can be used as adsorbent materials.
3. New metal-organic adsorbent powders were prepared and tested for phenol and p-chlorophenol, which are known contaminants in many industrial wastewaters.
4. This work has also demonstrated that the adsorptive properties of the adsorbents could be improved by coating their surfaces.
5. The surface areas and micropore areas of uncoated and GLYMO-coated adsorbents can be altered.
6. The adsorptive capacity of the adsorbent was limited (0.11-1.20 mg/g). Adsorption was strongly dependent on the initial concentrations of the solutions. The capacity increased with the increase in the initial concentrations of phenol and p-chlorophenol.
7. The Freundlich constant, a, was 1.15 and 1.33 for phenol and p-chlorophenol, respectively. We observed that a is almost equal to unity. Therefore, the adsorption of phenol is more favorable than p-chlorophenol adsorption.

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