Preparation and Phenol Captivating Properties of Polyvinylpyrrolidone-Montmorillonite Hybrid Materials

AHMET GULTEK, TURGAY SECKIN, YUNUS ONAL, M. GALIP ICDUYGU

Chemistry Department, Inonu University, Malatya 44069, Turkey

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ABSTRACT: Montmorillonite minerals were modified in two distinct steps in order to remove hydroxlated toxicants from the aqueous environment. At first, the montmorillonite minerals were acrylated with the silylating agent γ-methcaryloxypropyl trimethoxysilane to give a product denoted as TAY-10. In the second step these materials readily reacted with vinylpyrrolidone to form copolymers covalently bonded to the clay. All hybrid materials were characterized by FTIR spectroscopy, thermogravimetry, X-ray diffractometry, SEM, and differential thermal analysis. The original montmorillonite structure was maintained for the copolymer modified surfaces. Different loadings of polyvinylpyrrolidone (PVP) were examined to arrive at the optimal conditions for the removal of toxicants from the aqueous environment. The presence of the PVP enhanced the adsorption capacity of the clay toward phenolic compounds from solution as evidenced by the retention percent that was as high as 98.9%. These results demonstrated the feasibility of utilizing a PVP modified clay as a thermally recyclable adsorbent for environmental pollutants. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 512–519, 2001

Key words: montmorillonite; clay; sol–gel hybrid materials; organic toxicants; thermal recyling

INTRODUCTION

The ability of layered silicates to undergo intercalation by a wide variety of monomers or polymers has been studied for many years, because the resulting intercalates are important in industry and agriculture.[1–5] Because these materials contain micropores larger than those of conventional zeolites and exhibit new properties, depending on the nature of the pillars, they are of interest as new types of microporous solids that can serve as a catalytic center, a separation environment, adsorbents, and so on.[6–10] In particular, clay minerals such as montmorillonite, saponite, and kaolinite have been studied for the design of inorganic composite materials.[11–15] Because of their high thermal stability, high surface areas, and intrinsic catalytic activities, clays pillared with polymers are of great importance.

The intercalation of layered silicates with polymers resulted in two types of hybrid materials. In the first type, polymer chains were inserted between the host layers, generating ordered lamella with a repeat distance of a few nanometers. In the second type, delaminated hybrids were obtained because the silicate layers were exfoliated or dispersed in the polymer matrix.[16] The direct attachment of polymers with a large number of ionizable groups to the silica surface via Si—O bonds was reported.[17] Surface modified clay materials based on Si—O bonds appeared to be much more stable to

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Correspondence to: T. Seckin (tseckin@inonu.edu.tr).

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hydrolytic decomposition than those from intercalated materials. Surface modified materials based on montmorillonite and polyvinylpyrrolidone (PVP) may be attractive from the point of view of generating new classes of stable modified clays in which the pendant polymer matrix bound covalently to the surface may contain the desired chemical functionality to remove phenolic materials.

In the past few years there has been increasing interest in designing recyclable inorganic adsorbents, particularly clay based materials, for the efficient removal of organic pollutants from aqueous solutions.[18–25] Organic molecules can bind the clay surface by a variety of mechanisms because of their hydrophilic nature, but these clays have to be modified in order to utilize their high internal surface area.

Phenolic compounds, which are one of the most challenging classes of priority pollutants to be removed from waste streams and groundwaters, can be removed by clays.[26] Adding cetylpyridinium cations to montmorillonite was also reported to remove chlorinated phenols.[27] Metal-oxide pillared clays and mesoporous delaminated smectite clays were found to be suitable for the adsorption of organic pollutants.[28]

Polycyclic amide or urethanes such as PVP form stable complexes with active hydrogen compounds such as phenols and carboxylic acids.[29]

The model studies carried out by Atobe et al.[30] showed that the interaction of phenols and vinylpyrrolidone (VP) was presumed to be weakened by steric hindrance based on the polymer chain in the complex formation of polymers having a pyrrolidone moiety bound directly to the main chain like PVP. Therefore, the primary objective of the present work was to prepare and characterize novel hybrid materials containing a PVP moiety in the clay matrix with a spacer group of silane. A secondary objective was to explore the utility of these hybrid materials in the potential removal of phenolic compounds from wastewater.

We prepared a series of hybrid materials and investigated their adsorption parameters toward phenolic contaminants in aqueous solution. The results reported here demonstrate that the adsorption of phenols was facilitated and the ease of thermal recyclability was achieved.

EXPERIMENTAL

Materials

The clay used in this study was montmorillonite obtained from Çanakkale, Turkey; it had a stoichiometry of [$Na_{0.43}(Al_{1.67}Mg_{0.36})Si_{4.75}O_{10}(OH)_2 \cdot nH_2O$] and a cation exchange capacity of 125 mmol/100 g and was used with further purification. The mineral was fractionated to 2 μm by gravity sedimentation and purified by standard methods. The sample was washed with distilled water, transferred into dialysis tubes in order to obtain chloride-free clays, and then dried at room temperature.

The 4-VP (95%) was obtained from Aldrich and was distilled before use. The γ-methacryloxypropyltrimethoxysilane was used as received. Phenols were obtained from Aldrich. Standard solutions of phenols (1000 mg/L) were prepared in acetonitrile and kept in the dark at 4°C.

The development of montmorillonite γ-methacryloxypropyltrimethoxysilane (A-174)-PVP sol–gel materials was carried out as a two-step process. First the γ-methacryloxypropyltrimethoxysilane was prehydrolyzed with different amounts of water in the presence of an acid catalyst, and the water concentration was varied between 1.5 and 3 mol/mol silane. The progress of the hydrolysis was followed by Karl Fischer titration. In the second step montmorillonite was placed in a vacuum oven and dried at 120°C under reduced pressure (0.1 Pa) for 24 h. The dried clay (3.01 g) was suspended in a solution consisting of 10 mL of dried benzene and 10 mL of prehydrolyzed A-174. The mixture was stirred under dry N_2(g) at room temperature for 20 h and then refluxed under N_2(g) at 85°C by heatin in an oil bath for another 24 h. The resulting mixture was distilled, the excess benzene and A-174 were removed, and the resulting solid was placed in a Soxhlet apparatus and extracted with methanol for 2 days. The remaining solid was dried under a vacuum at room temperature for 16 h and yielded 3.45 g of white hybrid materials coded as TAY-10.

Preparation of Hybrid Materials

The TAY-10 was suspended in benzene (2 wt %) and heated to 40°C with stirring. Different amounts of 4-VP were added to this suspension, and the temperature was maintained at 40 °C. Then a radical initiator, benzoyl peroxide, was added to the benzene and the temperature was raised to 85°C and held at that point for 18 h under nitrogen. The viscous suspension obtained was washed several times with methanol and distilled water and the side product was distilled off. The hybrid product was dried in a vacuum at 125°C and coded as TAYVP-5 to -15 (Table I).

Table I Preparation of PVP-Montmorillonite Hybrid Materials

	Clay + A-174/PVP (w/w)	Clay Yield[a,b] Obsd (%)	Clay Yield[a,b] Calcd (%)	T_g[a,c]
TAYVP-0	1	77.8	81.3	—
TAYVP-5	1/4	67.3	64.2	287
TAYVP-10	3/7	37.5	43.4	202
TAYVP-15	1/1	34.5	37.1	305

[a] Properties of the hybrid materials.

[b] The clay yield was calculated by thermogravimetry. The samples were heated to 900°C in air.

[c] The glass-transition temperature (T_g) values of hybrid materials as calculated from DTA: PVP = 84.8°C, poly-A174 = 212°C.

The prehydrolyzed A-174 solution in benzene was mixed with various amounts of VP (A-174/VP ratio of 6 mmol/g), and a 2 wt % suspension of clay was added to this solution. The mixture was heated at 40°C for 2 h, the radical initator was added to the system, and the temperature was raised over the θ temperatures of the monomers. The resulting viscous mixture was purified by extraction and dried in a vacuum oven at 125°C (TAYVP-11).

Montmorillonite particles were dispersed in the electrolyte solution for at least 24 h. Aliquot portions of montmorillonite and PVP with molecular weights of 5000 g/mol TAY-P5, 10.000 g/mol TAY-P10, 44,000 g/mol TAY-P44, and 400,000 g/mol TAY-P40 solution were mixed and shaken for 3 days at room temperature. The concentration of clay in these comparative tests was generally 5 g/L. The total added concentration of PVP varied from 15 to 300 mg/L. The adsorption experiments were performed at various concentrations of phenols in water. The nonadsorbed PVP was determined using a Shimadzu UV-1601 UV–visible spectrophotometer ($\lambda = 265$ nm).

Adsorption Isotherms

Hybrid material (250 mg) was packed dry into a 50 × 6 mm polyethylene column containing polyethylene frits to support the resin. The column was activated with a subsequent addition of 5 mL of acetone, 5 mL of acetonitirile, and 5 mL of distilled water. The acidified standards and samples were passed through the column at 5 mL/min. The column was washed with 5 mL of water/acetone (95:5, v/v) and dried under nitrogen for 1 h. Elution was achieved with 2 mL of 10 mmol/L NH_3 in acetone/water (70/30, v/v). The eluate was acidified with 25 μL of 1 mol/L HNO_3 and then analyzed.

The X-ray diffraction (XRD) data were collected on a Rigaku (RadB system) X-ray diffractometer equipped with a graphite monochromator employing Cu radiation with a scan rate of 1°C/min and a secondary beam graphite monochromator. The spectra were recorded in the 2θ range.

The IR spectra in the region of 400–4000 cm^{-1} were measured on a Mattson 1000 FTIR.

The nitrogen adsorption experiments were carried out employing a Quantachrome analyzer and using the volumetric method to calculate the adsorbed amount of nitrogen. The surface area was obtained from these isotherms using the Brunauer–Emmett–Teller (BET) method.[31]

Thermal experiments were performed on a Shimadzu Net Work System 60 at a constant heating rate of 10°C/min in an air atmosphere.

The SEM studies were carried out using a Jeol microscope with a field emission gun operating at a 2–5 kV acceleration voltage. The samples were coated with gold films to a thickness of 2–3 nm using a magnetron coating system.

RESULTS

Although clay, organoclay, and other polymer matrices are reported in the literature for the removal of phenols, relatively little evidence was found concerning the phenol removal by PVP modified hybrid materials.[28–30,32] Therefore, it was necessary as a first step to characterize some of the physical properties of the hybrid materials. Moreover, each sample was characterized with regard to phenol adsorptive properties. Three methods were utilized to prepare hybrid materials. The first one was to prepare a material based on covalent bonding of silane to clay via Si—O linkages and then using this spacer to prepare a

Table II Adsorbed Amount of PVP on Montmorillonite at pH 5.5

	Adsorbed Amount (mg/m^2)	BET N_2 (m^2/g)
TAY-P40	0.67 ± 0.02	195
TAY-P44	0.52 ± 0.03	148
TAY-P10	0.44 ± 0.04	126
TAY-P5	0.31 ± 0.04	90

The nonadsorbed PVP concentration in the supernatant was determined using a UV spectrophotometer at 196 nm.

copolymer with VP. In the second method the preparation was carried out in a manner that intercalation and surface bonding took place together. In the third method PVPs with different molecular weights were intercalated with activated montmorillonite. Table II presents the results of the last method. The amount of PVP adsorbed onto the montmorillonite was determined in terms of the nonadsorbed quantity of PVP found with a UV spectrophotometer at 196 nm. The increase in basal spacing indicated that the intercalation of PVP into the montmorillonite would take place. Due to the difference in the basal spacing between the final material and raw montmorillonite, it was assumed that PVP was mostly arranged as a monolayer between the layers of the montmorillonite. The BET surface area remained approximately constant at 200 m^2/g. For higher loading of PVP, the BET surface area was drastically decreased from 200 to 90 m^2/g. This could be explained in terms of filling of the micropores by PVP at high loading.

Among multilayered structures of the montmorillonite minerals are hydrated layered alkali-metal silicates that exhibit some interesting properties such as interlamellar sorption of water and organic molecules and ion exchange of surface cations. The structures of these minerals were of continuous interest in past decades because the physical and chemical properties of these materials are largely structure dependent. For this reason, the exact structure of montmorillonite had to be outlined. Powder XRD, FTIR, SEM, and thermal techniques provided valuable structural information.

The FTIR spectra of the montmorillonite (BP-1), TAY-10, TAYVP-10, and PVP are given in Figure 1. The spectra of these materials can be divided in two regions. The first region covered the frequency range of 4000–1700 cm^{-1} where stretching and bending vibrations of water molecules appeared. The second region below 1400 cm^{-1} included the vibrations due to the silicate layer and charge balancing cations. The peak assignments for the hybrid materials were as follows: the peaks at 3360 (m), 3585 (m), and 3293 cm^{-1} (w) were attributed to ν(OH); the peaks at 3230 (w), 1668 (m), 1628 (m), 1235 (m), and 1200 cm^{-1} (s) were assigned to δ (HOH); the Si—O—Si (ν_{asym}) peaks appeared at 1174 (s), 1087 (s), and 1061 cm^{-1} (sh) whereas the Si—O—Si (ν_{sym}) peaks showed up at 939 (w), 822 (m), 783 (m), 709 (w), 693 (v), 620 (m), 577 (m), and 443 cm^{-1} (sh); and the peaks at 353–310 cm^{-1} (w) were given for the external modes of H_2O and δSi—O—Si and δO—Si—O. In general, the C═O bond resulting from the in-phase coupling appeared in the region of 1680 cm^{-1}, whereas N—H stretching appeared at 3419 and 3675 cm^{-1}.

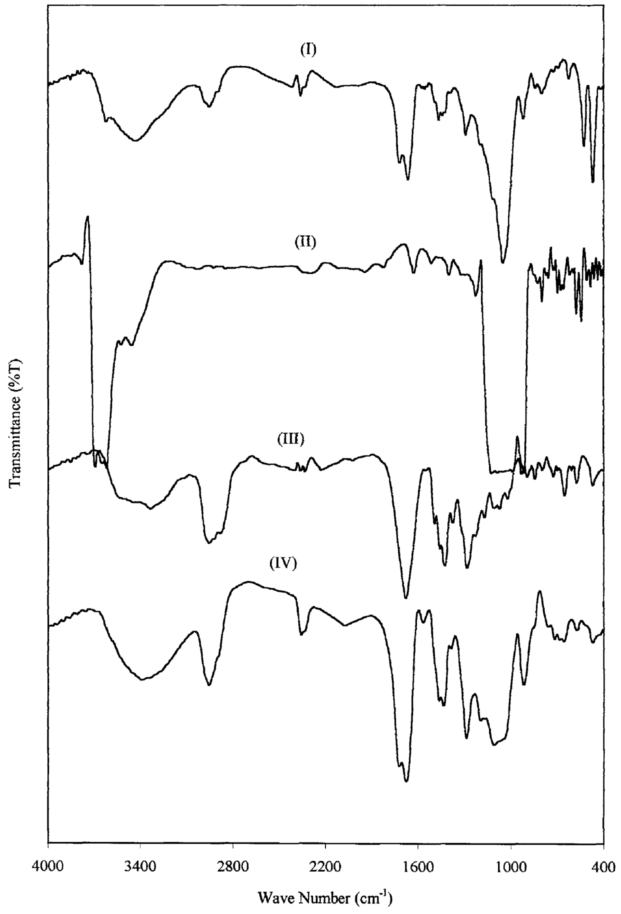

Figure 1 FTIR spectra of TAYVP-15 (spectrum I), montmorillonite (spectrum II), polyvinylpyrrolidone (spectrum III), and copolymer of PVP-A174 (spectrum IV).

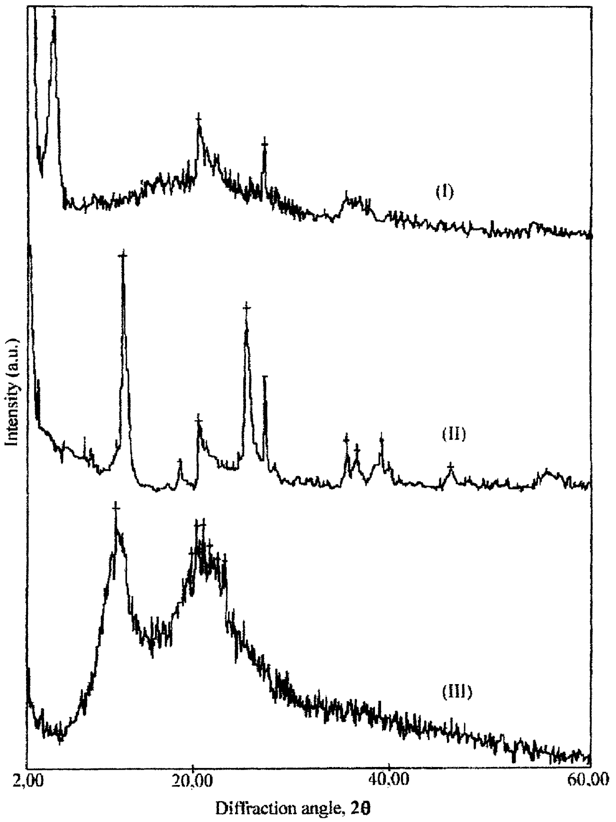

Figure 2 XRD patterns of TAYVP-15 (spectrum I), montmorillonite (spectrum II), and polyvinylpyrrolidone (spectrum III).

On the basis of the above discussion, we decided that the covalent bond formation might take place at the surface; however, some intercalation was also observed.

Montmorillonite has a sheet-type structure that consists of two inverted tetrahedral layers sharing oxygen with the octahedral layer. Two of the octahedral vacancies are occupied by Al(III) and Mg(II). These sheets are superimposed, forming microcrystals that can be expanded by absorbing polar molecules. The XRD spectra recorded for montmorillonite and the hybrid materials (dried for 24 h at 300°C) exhibited one prominent peak in the region of $2\theta < 10°$ (Fig. 2). An obvious loss of the ordered crystalline structure of the clay when copolymer chains were incorporated, which was shown by the loss of the $d_{001} = 12.4$ Å peak, was also reconfirmed by thermal analysis. The crystal nature of PVP itself is identified in Figure 2.

Typical dynamic thermal analysis (DTA) curves obtained for the hybrid materials are given in Figure 3. In the montmorillonite (Fig. 3) endothermic behavior was obtained from room temperature to nearly 430°C. This kind of behavior was ascribed to the loss of hydroxyl water in the material. This process accelerated when the temperature increased and was followed by a major endothermic effect at 545°C that was attributed to the partial melting of the material. However, this particular endothermic curve between 490 and 570°C and a dip at 545°C was believed to be a combination of various endothermic activities, together with partial melting such as the complete loss of lattice water and the decomposition process. These effects must also be taken into account.

The exothermic behavior with a maximum at around 600°C can be explained by the heat associated oxidation of the Si—O network in the clay; as a result of this, partial crystallization may have occurred. However, the remaining pattern after 600°C obviously showed continuous decomposition and melting of the material. In the composite material shown in Figure 3 the three characteristics of the nonisothermal DTA investigation were obtained. A loss of hydroxyl water at the low temperature region between room temperature and 200°C was clearly observed. This kind of character did not involve

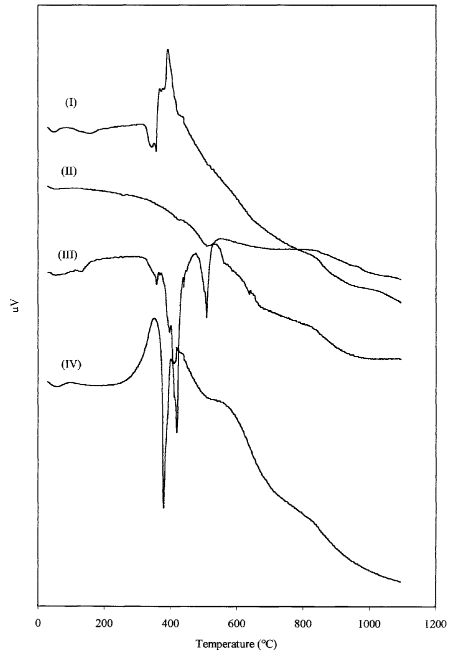

Figure 3 DTA thermograms of TAYVP-15 (spectrum I), montmorillonite (spectrum II), polyvinylpyrrolidone (spectrum III), and copolymer of PVP-A174 (spectrum IV).

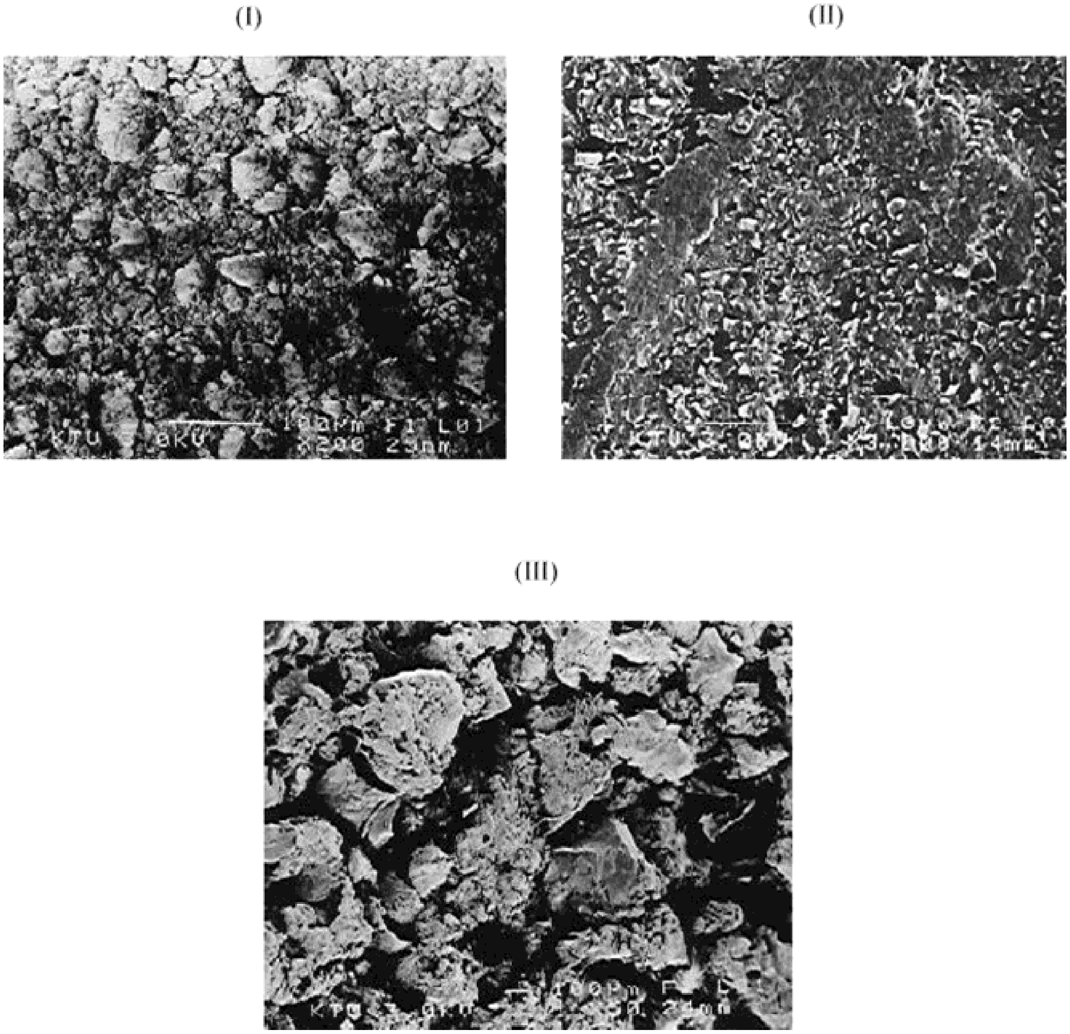

Figure 4 SEM images of TAYVP-15 (spectrum I), montmorillonite (spectrum II), and polyvinylpyrrolidone (spectrum III).

major changes in the basic physical properties of the material, but it was associated with the changes in specific heat and free volume. Exothermic peaks at 260 and 390°C clearly indicated the structural reorganization. The first peak was attributed to crystallization of the amorphous structure and the second peak was believed to be associated with the second-order phase transition that was enhanced in the structure by heating.

Figure 4 shows SEM photographs of the surface of the TAYVP-10 hybrid materials. The copolymer–clay hybrid particles were dispersed as platelets within the matrix and showed no microscopic voids. This indicated that the copolymer component of these materials did not agglomerate.

DISCUSSION

Although nonionic polyether surfactants and cetylpyridinium chloride intercalated into clays were reported,[33–35] relatively little is known about the nature of PVP covalently bonded to the clay that forms complexes with hydroxy groups of phenols. In this work the physical properties of the hybrid complexes were characterized and the results are given in Tables I and III. Table III presents the caption exchange capacity (CEC), BET surface area, and basal spacing. Clay analysis of the hybrid materials as given in Table I shows that the hybrid material contained 35–63% PVP. The X-ray basal spacing showed that no pillaring took place in the hybrid TAYVP-5 to -15 materials. For the TAYP-5 to -44 series the

Table III Properties of Hybrid Materials

Material	CEC (meq/100 g)	d_{001} (Å)	Surface Area N_2 (m^2/g)
BP-1	125.0	12.8	206
TAY-10	98.0	—	87
TAYVP-10	92.0	—	65
TAYVP-15	87.0	13.4	45
TAY-P40	55.0	14.8	206
TAY-P44	61.0	13.2	148
TAY-P10	58.0	14.3	126
TAY-P5	51.0	14.4	90

The CEC was measured by the Co(II) procedure.

basal spacings were constant at approximately 14.4 Å that indicated that intercalation was likely to take place. In these series of materials the intercalated PVP content was determined by the nonadsorbed PVP concentration in the supernatant employing a UV spectrophotometer at 196 nm. Surface area measurements showed that the BET surface area of BP-1 decreased to 87 m^2/g in TAY-10 and to 45 m^2/g in TAYVP-15, indicating that the surface was more likely to be covered with polymer. Table IV presents the retention values of the phenols. The maximum adsorbed quantities per gram of clay were about 1.65 mg pentachlorophenol (PCP), 1.69 mg 3,4,5-trichlorophenol (3,4,5-TCP), 1.83 mg 3,5-dichlorophenol (3,5-DCP), and about 1.59 mg 3-chlorophenol (3-CP). 4-Chlorophenol (4-CP), 3-CP, resorcinol, *o*-cresol, 4-nitrophenol (4-NP), and 3-NP had values of 1.56, 1.62, 1.75, 1.60, 1.59, and 1.58 mg/phenol/g clay, respectively. These results suggested that the presence of PVP at the surface greatly enhanced the adsorptivity of the hybrid materials. However, when the micropores were filled by intercalation as in TAYP-40 and -44, a decrease in adsorptivity was noted; therefore, it was essential to use PVP covalently bonded to clay via the A-174 linkage. The increase in the chain length increased the complex formation, so the spacer group was necessary to obtain high absorptivity.

This was evidenced by the higher adsorptivity obtained when the TAYP-15 hybrid material was used for the removal of phenol in which the PVP spacer was longer than the corresponding materials. When the PVP intercalation was preferred, the leaching took place so the reuse was limited. Recyclability experiments showed that the PVP modified clay would be capable of thermal recycling by combustion of the adsorbed phenols at nearly 400°C. The results indicated that after removal of organic phenols, there was no need to readsorb the CPC(Hexadecylpyridinium) or polyether onto the clay.

CONCLUSION

On the basis of the experimental results, it was demonstrated here that PVP modified montmorillonite-A-174 hybrid materials exhibited interesting adsorption properties with regard to phenols. The PVP increased the affinity toward phenol. In the PVP intercalation the adsorption toward phenol decreased. Recovery of the material by ther-

Table IV Retention of Phenols on Hybrid Materials

	Retention (%)					
Constituent	BP-1	TAYVP-5	TAYVP-10	TAYP-15	TAYP-40	TAYP-44
PCP	13.4	78.2	89.5	97.4	67.5	75.4
3,4,5-TCP	24.5	67.5	84.4	98.2	57.5	59.5
3,5-DCP	12.6	74.3	87.7	97.4	47.4	51.2
4-CP	11.7	79.2	91.0	95.7	51.4	54.3
3-CP	9.4	82.8	90.3	96.3	38.9	44.5
Resorcinol	54.8	71.9	88.3	97.1	57.1	58.5
o-Cresol	12.8	64.5	91.3	95.4	39.5	45.3
4-NP	8.81	81.9	93.2	98.9	57.4	62.1
3-NP	4.5	87.2	91.8	96.1	61.2	63.4

The column was activated with a subsequent addition of 5 mL of acetone, 5 mL of acetonitrile, and 5 mL of distilled water. The acidified standards and samples were passed through the column at 5 mL/min. The column was washed with 5 mL of water/acetone (95 : 5, v/v) and dried under nitrogen for 1 h. Elution was achieved with 2 mL of 10 mmol/L NH_3 in acetone/water (70/30, v/v). The eluate was acidified with 25 μL of 1 mol/L HNO_3 and then analyzed. BP-1, original clay material as control.

mal recycling via combustion at 400°C indicated that after removal of phenols from the wastewater the matrix could be used many times. Work on the reuse and regeneration parameters is in progress in our laboratory.

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