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SODIUM ON THE SURFACE OF ACTIVATED CARBONS AS A FACTOR

ENHANCING REACTIVE ADSORPTION OF DIBENZOTHIOPHENE

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Abstract

Based on the results described in the literature on the reactivity of sodium towards DBT and its derivates, the effect of sodium dispersed on the surface of a carbonaceous support on the removal of DBT from hexane solution at ambient conditions has been investigated. Since the main objective of this paper is to demonstrate the effect of sodium on the reactive adsorption of DBT from an organic solvent, hexane was chosen as a model solvent. As adsorbents, two carbons with and without sodium on the surface were investigated. The carbons are obtained by carbonization of polystyrene-sulfonic acid-co-maleic acid in sodium salt at 800 ^{o}C in nitrogen. The results show that sodium present on the surface of carbon takes part in the reaction with DBT in which sodium metallates and sodium sulfides are formed.

Key words: activated carbons, dibenzothiophene, desulfurization, reactive adsorption

INTRODUCTION

Recently desulfurization of liquid fuels on various adsorbents has been of great scientific interests [1-10]. This interest is driven by federal regulations which mandate reduction in a sulfur content of gasoline and diesel fuel from 500 and 300 ppmw to 30 and 15 ppm, respectively [11]. The reasons for lowering sulfur level are detrimental environmental effects of acid rain formed when sulfur compounds are emitted to the atmosphere, oxidized to sulfur oxides and further scavenged by atmospheric precipitation as sulfuric acid. Moreover, sulfur compounds are known to poison both automobile and fuel cell reformer catalysts.

The most difficult sulfur compounds to remove from liquid fuels are dibenzothiophene (DBT) and its derivatives. Although some research has been carried out on the use of adsorptive

techniques for removal of dibenzothiophenic compounds [12-19], so far adsorption on activated carbon has not been explored extensively [20, 21]. This is the consequence of the properties of the carbon surface. It is generally accepted that for efficient adsorbents, besides a high adsorption capacity, a selectivity is required. On carbons, owing to their hydrophobic surface, aromatic components of liquid fuels, which are the key components for high octane number, are expected to be adsorbed in significant amounts.

Recently, it has been shown that introduction of certain metals to the surface of a carbonaceous support can significantly increase its DBT removal capacity [12]. Previous studies on carbonization of transition metal-based salts of polystyrene sulfonic acid co-maleic acid showed that using this precursor, highly porous materials can be obtained and the content of metals can be controlled by selective washing [22].

The objective of this paper is to investigate the role of sodium dispersed on the surface of a carbonaceous support in the process of DBT removal from hexane solution at ambient conditions. Based on the results described in the literature on the reactivity of sodium towards DBT and its derivatives and those obtained in our study we demonstrate the effect of sodium on the reactive adsorption of dibenzothiophene from an organic solvent. In order to simplify the reaction system, hexane was chosen as a solvent. It does not represent the complex mixture of hydrocarbons in gasoline or in diesel fuel.

EXPERIMENTAL

<u>Materials</u>

As adsorbents, two carbonaceous adsorbents were investigated. The carbons were obtained by carbonization of in sodium salt at 800 ^{o}C in nitrogen (200ml/min) in a horizontal furnace with 10 ºC/min heating rate and 40 min holding time. One sample was used as-received (PS-Na) while another one was washed extensively in distilled water after carbonization in a Soxhlet apparatus to remove all sodium compounds [22]. The latter is referred to as PS. The samples after DBT adsorption are designated as PS-NaDBT and PS-DBT.

Methods

Adsorption of DBT from solution

Adsorption of DBT was carried out at room temperature in a stirred batch system. Before these experiments, the kinetic studies were performed to determine the equilibration time of the system. Different amounts of carbons (from 25 mg to 1 g) were weighed and added to 15 bottles containing 40 ml of the sulfur-containing solution with an initial concentration of 1000 ppmw of DBT (ca. 178 ppmw of S). All of the solutions were prepared in hexane. The covered bottles were placed in a shaking bath and allowed to shake for 72 h at a constant temperature. After equilibration the concentration in the liquid was determined using a UV spectrophotometer at the wavelength 312 nm. The amount adsorbed was calculated from the formula $q_e=V(C_o-C_e)/m$, where q_e is the amount adsorbed, V is the volume of the liquid phase, C_o is the concentration of solute in the bulk phase before it comes in contact with the adsorbent, C_e is the concentration of the solute in the bulk phase at equilibrium, and m is the amount of the adsorbent.

The equilibrium data was fitted to the so-called Langmuir-Freundlich single solute isotherm [26], which has the equation:

$$\vartheta_t = q_e \Big/ q_o = \frac{(KC)^n}{1+(KC)^n}$$

where q_e is the adsorbed amount of the solute per unit gram of adsorbent, q_o is its maximum adsorption per unit weight of the adsorbent, K is the Langmuir-type constant defined by the Van't Hoff equation, and the exponential term n represents the heterogeneity of the site energies. The fitting range was from 0 to 250 mg of S per gram of activated carbon (recalculated from its content in DBT).

Determination of porosity

Textural characterization was carried out by measuring the N_2 adsorption isotherms at 77 K using an ASAP 2010 apparatus from Micromeritics. Before the experiments, the samples were outgassed under vacuum at 393 K. The isotherms were used to calculate the specific surface area, S_{BET}, volume of micropores, V_{mic}, and total pore volume, V_{T},. The pore volumes were calculatedd using density functional theory (DFT) [24, 25].

Thermal analysis

Thermal analysis was carried out using an TA Instrument thermal analyzer. The instrument settings were heating rate 10 ^{o}C/min and nitrogen atmosphere with 100 ml/min flow rate. For each measurement about 25 mg of a ground carbon sample was used.

Textural characterization/EDX

The structure of carbon materials was characterized using a Ziess DSM 942 scanning electron microscope with EDX detector. The carbon particles were dispersed on a graphite adhesive tab placed on an aluminium stub. The images were generated using the backscattered electron signal, which yielded better quality pictures, but in some occasions, where a higher resolution was required, the settings were changed to the secondary electron mode. In any case, the information obtained was always topographic.

XRD

X-ray diffraction (XRD) patterns were recorded on a Philips instrument (Generator PW1830, goniometer PW 3020) operating at 40 kV and 20 mA and using Cu Ka radiation (k = 0.15406 nm). The powdered carbon samples were spread as thin layers on a glass slide and analyzed.

RESULTS AND DISCUSSION

Based on the sodium content of the polymer used as carbon precursor and the yield of the carbonization, it was obtained that PS-Na sample contains about 35% sodium, mainly as sulfide, sulfates and hydroxide [22] as will be later discussed. It is likely that after carbonization some sodium is present in a metallic form. Support for this is the exothermic reaction observed upon the exposure of the carbon to the atmosphere (sometimes causing self-ignition of carbon) which is linked to the reaction of sodium with the moisture). In contrast, elemental analysis of PS sample shows that most of these compounds are washed out by distilled water (3.3 % sodium content). Structural parameters of adsorbents (surface area, volumes of meso- and micropores and total pore volumes) were evaluated using adsorption of nitrogen [24, 25] and they are collected in

Table 1 along with the summary of DBT adsorption experiments. The surface area of PS sample is much larger than that for PS-Na.

Structural and chemical features of the adsorbents surface should affect DBT adsorption from hexane. Details of the experimental procedure are given elsewhere [21, 23]. Briefly, different amounts of carbons (from 25 mg to 1 g) were weighed and added to bottles with 40 ml of the DBT-containing hexane solution with an initial concentration of 200 ppm of DBT (35 ppm of sulfur). The covered bottles were placed in a shaking bath and allowed to shake for 72 h at a constant temperature. After equilibration, the concentration of DBT in the liquid was determined using a UV spectrophotometer at the corresponding wavelength. The isotherms are presented in Figure 1 along with the fit to Langmuir-Freundlich equation. From the equation, the limiting capacities, Q, were calculated in terms of the amount of sulfur adsorbed per gram of the adsorbent. Due to the extremely large difference in porosity of all samples, the adsorptive capacities were normalized by the surface area. They are listed in Table 1 as Q_S.

Although the absolute capacities for DBT adsorption differ significantly and the high uptake is obtained for the carbon without sodium, when the capacities are normalized per unit surface area (Qs), the importance of sodium for DBT retention on the surface (Table 1) is clearly visible (Figure 2). While the isotherm on PS shows the limiting effect of the pore sizes/ pore volume for the physical adsorption process (type-L isotherm in the Giles classification), the linear uptake on Ps-Na suggests that the chemical reaction is involved in DBT retention on the surface of this material (likely belonging to type C-isotherm). Although, as mentioned above, the content of sodium in this sample is about 35 % we expect that a vast majority of this sodium is not

accessible to DBT molecule (large clusters) or it does not react with it owing to difference in the chemical state (salts, hydroxides, metallic sodium). As seen from Table 1, the surface of PS-Na consists of only about 5% of the surface available after removal of all sodium. Nevertheless, the adsorption of DBT is measurable on this material, and when the amount adsorbed is normalized to the available surface area, the PS-Na sample outperforms the PS of almost two times. When the concentration of sulfur in the solution is higher, this ratio is even better.

The chemistry of samples exposed to DBT was evaluated using TA analysis in nitrogen. The DTG curves are presented in Figure 3. The peaks represent weight loss related to the removal of adsorbed species (DBT and hexane) [21]. Comparison of the initial samples, without and with sodium shows clear differences in materials' chemistry. Since for PS-Na the peaks seen on the DTG curve related to weight loss between 600 and 900 ^{o}C disappear after extensive washing (absent for the PS sample) we assign them to the decomposition of sodium sulfides (between 600-750 ^{o}C) and sodium sulfate (at 880 ^{o}C) [22, 27]. It is important to mention that the weight loss for PS-Na carbon at T> 600 ^{o}C consists of over 50% of this sample mass, which is in agreement with its content of an inorganic matter.

After DBT adsorption on the PS sample, the DTG analysis reveals two peaks, which are linked to weak physical adsorption of DBT in small pores (at 250 ^{o}C) and strong adsorption on oxygen and sulfur heteroatoms built to the carbon matrix [21]. The low temperature peaks are related to desorption of the solvent.

In the case of the sample with sodium, PS-NaDBT, the DTG profile looks different form that for the PS sample exposed to DBT discussed above. When comparing to the initial sample, PS-Na, the only new feature is a low temperature peak related to the removal of solvent (between 100-200 ^{o}C). It is interesting that the peaks revealed at T > 500 ^{o}C have the same positions as those for the PS-Na sample. Moreover, the peaks over 800°C remain practically unchanged. As assigned based on the chemistry of the initial polymer, and the detection of H$_2$S in the off-gases, [22] they represent decomposition of sodium sulfides. The peak at 880 ^{o}C remains unchanged suggesting that no new sulfates were formed on the surface upon exposure to DBT.

Another important feature is the difference between the weight losses of both samples exposed to DBT adsorption. Although the amount adsorbed on PS is much higher than that on PS-Na, the weight loss for the latter one is much more pronounced. This may have the reason in the combined effects of decomposition of an inorganic matter/organic matter and its influence on gasification of carbons. Apparently after DBT adsorption, decomposition of sodium sulfide promotes gasification. Moreover, the DBT immobilized on the surface/ new aromatic derivatives (the products of reactive adsorption) also undergoes pyrolysis affecting the gasification process. The changes in the carbon after this complex carbonization, however very interesting, are beyond the scope of this paper.

Based on the results presented above, and the data published in the literature addressing activity of sodium in desulfurization [3,29], it is likely that on a sodium active center, mono- and disodium thiophene metallates along with sodium sulfides are formed:
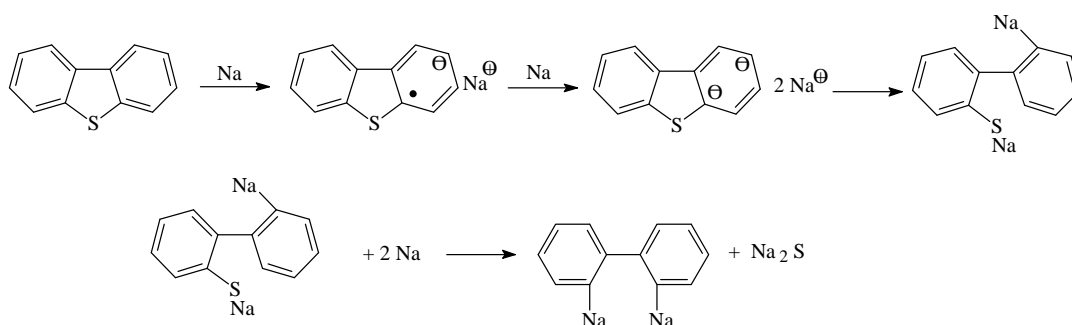
These species decompose during heat treatment resulting in a partial gasification of the carbon. Of course, the hypothesized above mechanism "consumes" the active centers so the capacity for DBT removal is expected to last until either all accessible active centers are exhausted or pores spaces accommodating the surface adsorption and/or reaction products are occupied. This emphasizes the importance of the porosity along with the catalyst amount and its dispersion in our materials. Taking this into account, we evaluated the ratio of the number of moles of sodium present in PS-Na to the number of moles of sulfur retained on the surface. The obtained 100:1 ratio clearly shows the excess of sodium, which is likely inaccessible to DBT molecules or it is not in the metallic form as suggested by the reaction scheme. With the ratio of metallic sodium to sulfur 4:1 the catalysts/adsorbent can be efficiently used. An increase in the capacity is likely to happen as a result of various levels of sodium present in the structure of the initial polymer. It is important to have that sodium in carbon nanospace where its oxidation/reactivity with the atmosphere can be limited. This aspect is the subject of our ongoing research. It is worth to mention that hypothetically, if even only 1/4 of sodium were accessible for the above-mentioned reaction, the capacity of this hypothetical adsorbent would be over 100 mg of S/g. The performance would be certainly enhanced if the reaction products were immobilized in the high volume of pores.

Support for the above mentioned mechanism are the changes observed on DTA curves before and after DBT adsorption. While for PS sample only two broad endothermic peaks related to the removal of hexane and physically adsorbed DBT are observed, the curves for PS-Na are much more complex. That broad endothermic peak on PS- Na between 100 and 250 ^{o}C is linked to decomposition of sodium hydroxide formed when the sample was exposed to the atmosphere. This process is also observed as a weight loss on TA curve (a peak on the DTG curve in Figure 3). On the other hand, the sample exposed to DBT adsorption exhibits three exothermic peaks in this range, which are assigned to the reaction of freshly formed sodium with physically adsorbed DBT according to the mechanism presented above. Exothermic effect of this reaction can explain the quite significant weight loss at this range (more than for the initial sample). Besides water released form the decomposition of sodium hydroxide, some carbon can be also consumed in this process and released as CO_2. Na_2S formed as the product of reaction adsorbs on the surface and decomposes as two endothermic peaks between 600-700 ^{o}C. Of course, based on this hypothesis one can argue that formation of Na_2S happens only as a result of the heat treatment applied to the sample.

To emphasize the role of sodium in the reactive DBT adsorption at room temperature, the amounts adsorbed on two samples, with and without sodium, are normalized taking into account the active pore volume. The pore size distributions for PS before and after DBT adsorption indicated that mainly small pores (micropores) are involved in this process [21]. If these pores are the only active sites for physical adsorption, and the sodium is not chemically involved, the normalized amount adsorbed (per volume of micropores) on these two carbons should be comparable. The data collected in Table 1 shows that this is not the case. The amount adsorbed

on Ps-Na (Q_{mic}) is three times higher that that on the PS sample. This is consistent with the difference existing when the amount adsorbed is normalized to the unit surface area of the adsorbed (Q_s).

The differences in the textures and chemistries of the samples are clearly seen on SEM images and EDX data, respectively (Figure 5 and Figure 6). While the surface of PS-Na seems to be smooth, the PS sample shows the light texture of the matrix, which is the result of open porosity. In PS-Na a lot of sodium is present whereas in PS only traces of this metal are found. Indeed elemental analysis shows significant differences in the content of this metal (Table 1).

Similar conclusion can be drawn from the analysis of X-ray diffraction patterns presented in Figure 7. Whereas the pattern of PS sample shows only the broad peaks of the stacking structure of carbon layers, the surface of PS-Na revealed many peaks that have been identified as sodium oxide, sodium sulfide and sodium sulfate.

CONCLUSIONS

The results presented in this paper indicate that sodium present on the surface of activated carbons takes an active part in the process of DBT immobilization at room temperature. As a result of reactive adsorption on a sodium active center, mono- and disodium thiophene metallates along with sodium sulfides are formed along with sodium sulfide. The capacity for DBT removal is expected to last until either all accessible active centers are exhausted or pores spaces accommodating the surface adsorption and/or reaction products are occupied. This emphasizes the importance of the porosity along with the catalyst amount and its dispersion on the surface of carbon support

Acknowledgement:

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CAPTIONS TO THE FIGURES

Figure 1.

DBT adsorption isotherms on the samples studied.

Figure 2.

 Normalized DBT adsorption isotherms.

Figure 3.

DTG curves for samples before and after DBT adsorption.

Figure 4.

 DTA curves in nitrogen.

Figure 5.

SEM images of PS-Na (A) and PS (B) samples.

Figure 6.

EDX spectra of PS-Na and PS samples.

Figure 7.

X-ray diffraction patterns for PS and PS-Na samples.

CAPTIONS TO THE TABLES

Table 1.

Structural parameters evaluated from nitrogen adsorption isotherms measured at - 196 ºC and the adsorption capacity toward DBT removal. Q is expressed as the amount of sulfur per gram of adsorbent.

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Structural parameters evaluated from nitrogen adsorption isotherms measured at - 196 ℃ and the adsorption capacity toward DBT removal. Q is expressed as the amount of sulfur per gram of adsorbent.

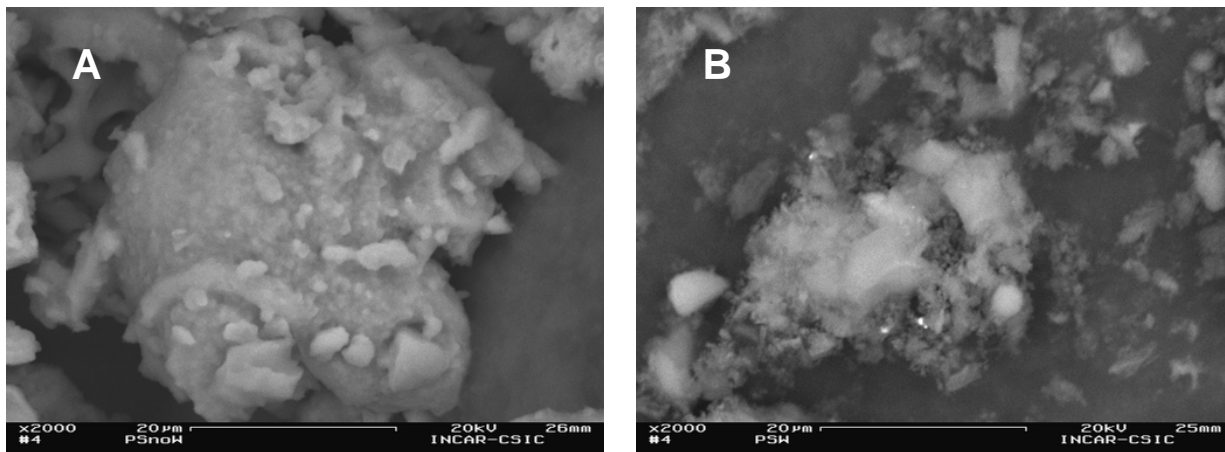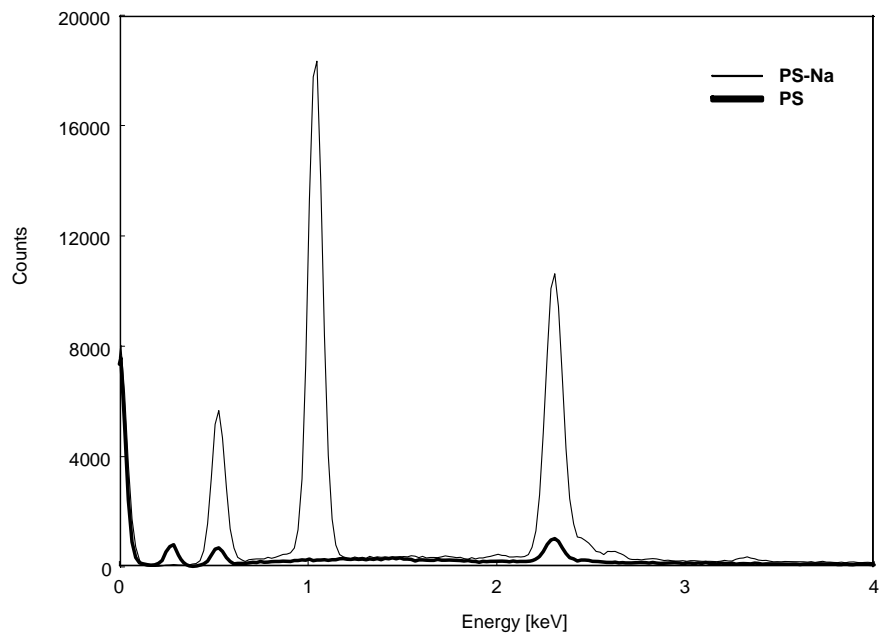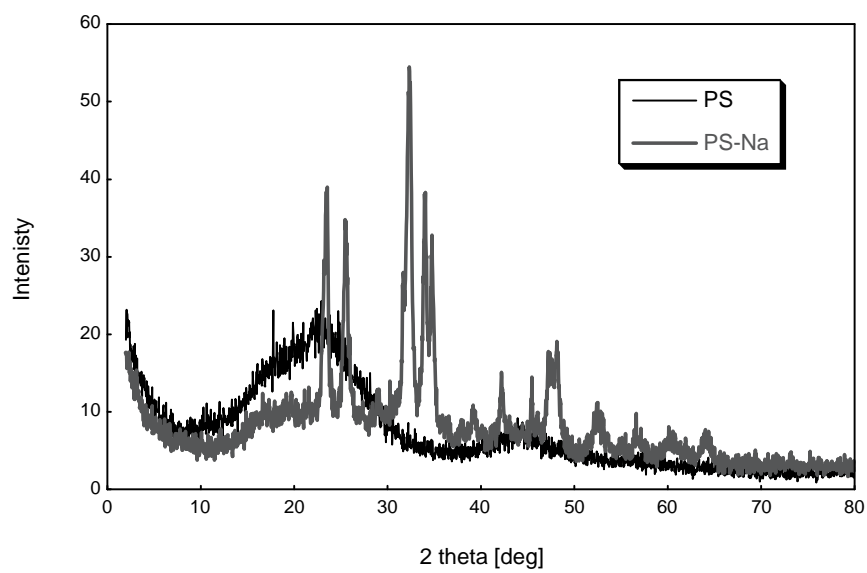| Sample	S_{BET}	V_{mic}	V_{mes}	V_t	Q	Q_S	Q_{mic}	Na/S
	[m^2/g]	[cm^3/g]	[cm^3/g]	[cm^3/g]	[mg S/g]	[mg S/m^2]	[mg S/cm^3]	[mol Na/mol S]
PS	1737	0.514	0.288	0.974	55	0.032	107	------
PS-Na	77	0.014	0.037	0.085	5	0.064	357	100
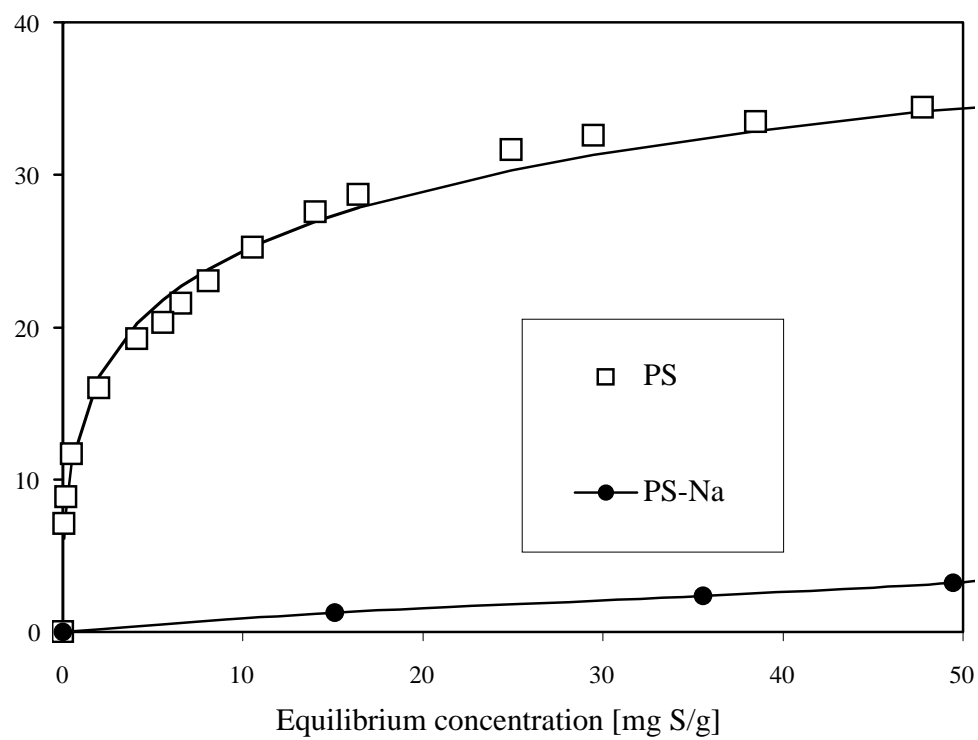
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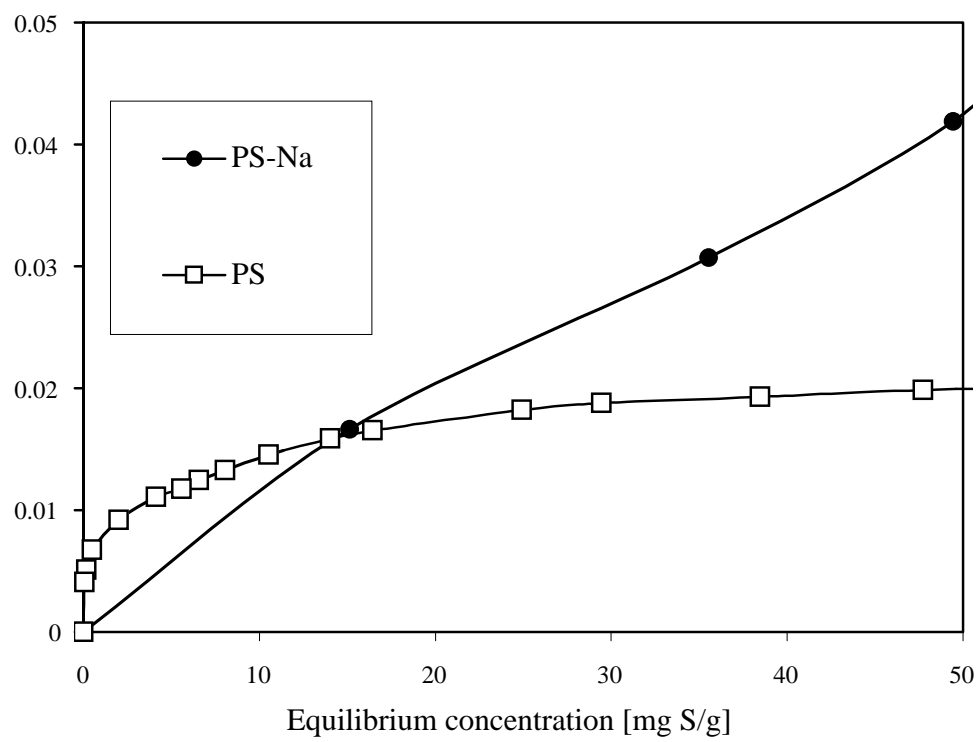
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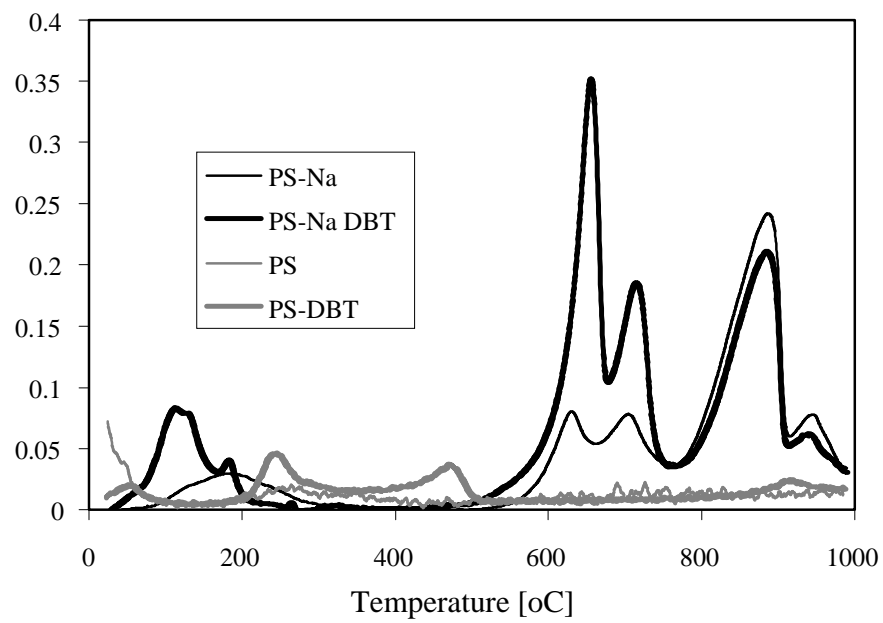
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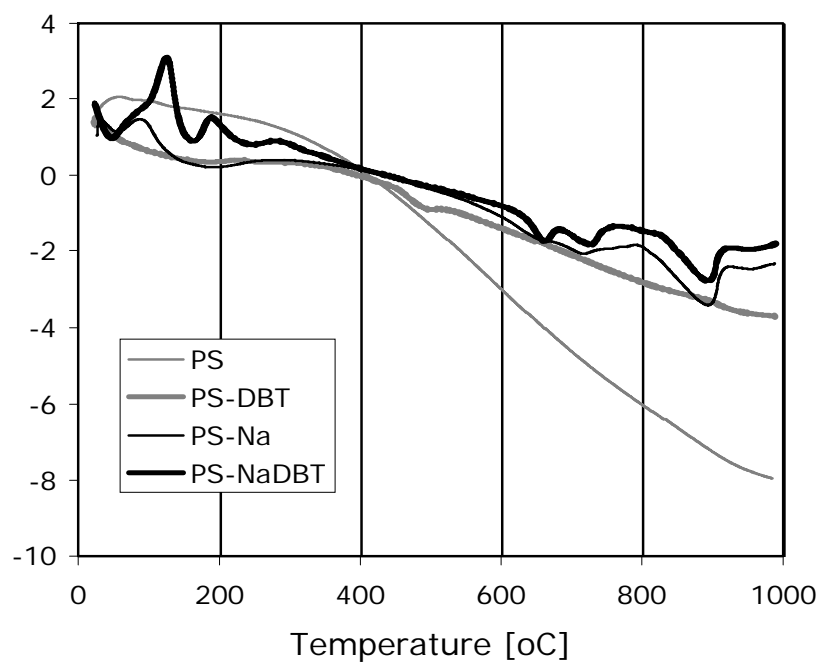
Figure 4

Figure 5

Figure 6.

Figure 7.