



Adsorption of phenolic compounds on some hybrid xerogels

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ABSTRACT

The ability of some hybrid xerogels (HyXs) to adsorb phenolic compounds from aqueous media was studied. It was shown that by incorporating n-alkylormosils (30–50%, v/v) into the composition of the HyXs the ability to adsorb phenolic compounds was improved. Aging of the HyXs was also shown to have an effect on the adsorptive capacity. Sol–gels dried at room temperature had higher adsorptive capacity compared with the analogous gels aged at 4 °C. All HyXs with an ormosil content between 0 and 80% exhibited a base reaction with the phenolic substances. It was also shown that hydrogen bonding appeared to have a negligible effect on the adsorption of the selected phenolic substances for the HyXs studied. It is proposed that adsorption occurs as a result of non-ionic but strong intermolecular Van der Waals interactions and as a consequence is geometry and weight dependant. Considering the molecular weights of the selected phenolic compounds for this study, it is proposed that phenolic substances with a $pK_a < 7$ and $MW > 180$ will be adsorbed by the HyXs selected. In addition, the non-ionic-based adsorption of the phenolic compounds did not follow the Langmuir monolayer adsorption model.

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1. Introduction

Studying the adsorptive ability of different materials provides important information which can be used in a variety of diverse fields. Treatment of polluted air and water, selective separation of substances and fuel and energy storage are just some examples of the adsorption applications [1]. Adsorption is also an important parameter to consider for successful encapsulation and immobilization of biologicals. Favorable interactions might lead to successful encapsulation or a more stable sorbate or might be considered as a hindrance when the transfer of some species in and out of the matrix is affected. Both of these phenomena are important in the xerogel field as they are increasingly being considered for use in the immobilization of different biologicals [2,3].

Development of the cold process of sol–gel preparation revolutionized the glass and ceramic field and related applications. The convenient three-step process of sol, gel, and xerogel formation was primarily based on the hydrolysis of tetraalkylated silicates like tetramethoxysilane (TMOS) and tetraethylorthosilane (TEOS) by means of acid or base treatment at ambient temperature [4]. It was also quickly realized that modification of the starting materials would affect the properties of the final products. One of the rapidly growing sub-families of xerogels are made from organically modified silanes called ormosils.

Ormosils have at least one organic group attached directly to silicon. The attached organic moiety can range from simple alkyl, alkenyl, and aryl to those bearing additional mixed functionalities [5,6]; however, Si–C bonds are hydrolytically stable in all of them. The inorganic siloxane skeleton of the resulting sol–gel contains the pendant organic residues [7], which render these materials with three new distinct features in comparison with the classic TMOS and TEOS sol–gels. First, ormosils show lower rates of hydrolysis and polymerization during the sol–gel process because of the electronic and steric effects of the organic residues. Second, the adaptability of ormosils to non-conventional media is improved due to their higher hydrophobicity. Third, in contrast to classic sol–gels, ormosils can be further modified if the chosen precursor has modifiable chemical functionality [8,9].

Given the aqueous basis of sol–gel processing and considering the increasing application of ormosils for bio-encapsulation, this research focused on investigating the adsorption of phenolic compounds onto a spectrum of hybrid xerogels (HyXs) consisting of TMOS and TEOS with an n-alkyl (methyl or propyl)ormosil. This was done for several reasons including that similar to ormosils, phenolic compounds can be involved in both hydrophilic and hydrophobic interactions. As a result of such interactions, there is an opportunity for adsorption of phenolic compounds to the surface of the HyXs. This phenomenon might be considered as a hindrance where ormosils or HyXs are meant to be used for encapsulation of enzymes or biologicals which act on phenolic substrates. In addition, phenolic compounds are both biologically and industrially important. They are present in many common industrial wastewaters such as

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coal conversion or those that deal with resin and plastic manufacture, petroleum refineries, iron and steel, textiles, dyes, pulp and paper [8]. There is also growing concern regarding the toxicity of phenolic pollutants as the number of reports regarding the possible risks to living organisms by these substances increases [10,11].

2. Experimental

2.1. Chemicals

TMOS (98% purity), TEOS (98% purity), methyltri-propoxy-silane (MeTPS, 97% purity), propyltrimethoxysilane (Pr-TMS, 97% purity), phenol, 4-chlorophenol (CP), 2,6-dichlorophenol (dCP), 1,5-dihydroxynaphthalene (dHN), and *p*-coumaric acid were purchased from Aldrich (Oakville, ON, Canada) and were used without further purification. Methylene blue (MB) was obtained from Fischer Scientific. 4-[(4-Methylphenyl)azo]-phenol (MePAPh), 4-[(4-nitrophenyl)azo]-phenol (NAPh), 2-methoxy-4-[(4-methylphenyl)azo]-phenol (MMPAPh), and 3-amino-4-(phenylazo)-aniline (APA) were prepared according to reported methods [12]. Deionized water was used throughout this study. Due to the low solubility of the phenolic compounds in water, stock solutions of these compounds were prepared in 2-propanol as solvent. To ensure comparable concentrations of the co-solvent and to avoid using extra 2-propanol, 50 μ l of the stock solution was diluted with deionized water in all the experiments. The stability of the phenolic solutions was determined by measuring the absorbance changes at the λ_{\max} for each compound at 25 °C for 120 min. In all cases, no change in absorbance of the phenolic solutions due to precipitation or auto-oxidation was observed.

2.2. Hybrid xerogel preparation

2.2.1. Sol stock solutions

Four homogenous sol stock solutions of TMOS, TEOS, MeTPS, and PrTMS were made by acid hydrolysis of each silane precursor separately according to the following procedure. The starting materials (Silane, H₂O, and HCl with mole ratio of 1:4:0.0015, respectively) were mixed in a glass container and sonicated in a water bath at room temperature for 30–45 min until a clear one-phase solution was obtained.

2.2.2. Hybrid sol–gel preparation

Three different hybrid sol–gels of TMOS + Me-TPS, TMOS + Pr-TMS, and TEOS + Pr-TMS were made by mixing the desired tetraalkoxysilane sol (20–100%, v/v) with the desired *n*-alkyltrialkoxysilane sol (0–80%, v/v) in a test tube. To this volume of silane mixture, an equivalent volume of phosphate buffer solution (0.1 M, pH 7) was added and mixed. The final mixture was cast in a disposable aluminum cap at room temperature.

2.2.3. Xerogel formation

Following gelation, the casts were allowed to stand at room temperature for 3 h and were divided into two similar groups. One group was left at room temperature and the other group stored at 4 °C for further aging. Samples were weighed intermittently until no further weight loss was observed. The final xerogels were ground to fine powders and sized through a 50 μ m sieve.

2.3. Pore size analysis

Pore size analysis was performed on a Micromeritics Gemini III 2375 Surface Area Analyzer. Fine powder xerogels (30 mg) were used for this analysis with no extra treatment or preconditioning to remove possible bound air or water. The pressure was measured

as nitrogen was adsorbed or desorbed at a constant temperature controlled by liquid nitrogen. Surface areas were determined automatically by the StarDriver V2.03. The software employs the isotherm data using the multipoint BET (Brunauer–Emmett–Teller) method [13].

2.4. Spectrophotometric measurements

All the spectrophotometric determinations and UV–vis spectra were recorded at 25 °C using a double-beam Carry 1-Bio UV–vis Spectrophotometer. In this work, the λ_{\max} values employed were 269, 275, 295, 288, 350, 360, 375 and 444 nm, for phenol, CP, dHN, *p*-coumaric acid, MePAPh, NAPh, MMPAPh and APA, respectively. The optical density of dCP solutions were recorded at 279 and 297 nm. Extinction coefficients of 76,000 and 20,800 $\text{cm}^{-1} \text{M}^{-1}$ were used for MB and MePAPh, respectively [14,15].

2.5. Equilibrium isothermal adsorption experiments

To assess the adsorption characteristics of different compounds by the xerogels, 25 \pm 1 mg of the xerogel powder was added to a glass bottle containing 6 ml of the desired compound solution (20 ppm) and the resulting mixture was agitated (200 rpm) for 1 h at 25 °C which based on preliminary experiments indicated a sufficient period to allow the achievement of equilibrium. The solutions were then allowed to sit at the same temperature for another hour to allow the particles to gravity settle. The spectra of the solutions for the compounds were also recorded before and after the experiments at 25 °C. All the reported data are the average of triplicate measurements.

To obtain the equilibrium isothermal adsorption curves for the selected compounds, a constant amount of the xerogel powder (20 \pm 1 mg) was added to 6 ml of the selected compound solution at varying concentrations (2.5, 5, 10, 12.5, 15 and 20 ppm). Absorbance data was collected as described above. A blank consisting of 6 ml of the compound solution and no xerogel was tested for each sample under identical conditions. The concentration of MePAPh for a saturated solution was 0.1 mM at 25 °C.

3. Results and discussion

3.1. Materials selection

The chemical structures of the selected compounds are given in Fig. 1. Although the phenolic compounds chosen cannot be considered as representatives of all classes of phenols, they do represent popular members of this group. Phenol itself does not contain an additional substituent so it is the best representative of the amphiphilic members of this group. Chlorophenols are notorious and widespread water pollutants [10,16] and the presence of chloro-substitutes on the aromatic ring enhances the strength of Van der Waals interactions while at the same time increasing the acidity of the hydroxy functional group. Examples in this study are CP and dCP. MePAPh, dHN and *p*-coumaric acid were chosen as representatives of the diazo derivatives, polyaromatic and phenolic acids, respectively.

The adsorbents examined in this study are the well studied xerogels of TMOS, TEOS and their corresponding HyXs containing 10–80% (v/v) ormosils. As previously discussed, HyXs containing ormosils are expected to show more pronounced hydrophobic character than xerogels prepared exclusively from TMOS and TEOS. There are some problems associated with using 100% ormosils such as aging time, mechanical, and physical properties of the final product [5,9]. Therefore, the HyXs designed here used TMOS, TEOS, and two popular *n*-alkyltrialkoxysilane precursors, MeTPS, PrTMS. The pendant groups in the resulting materials are expected to be

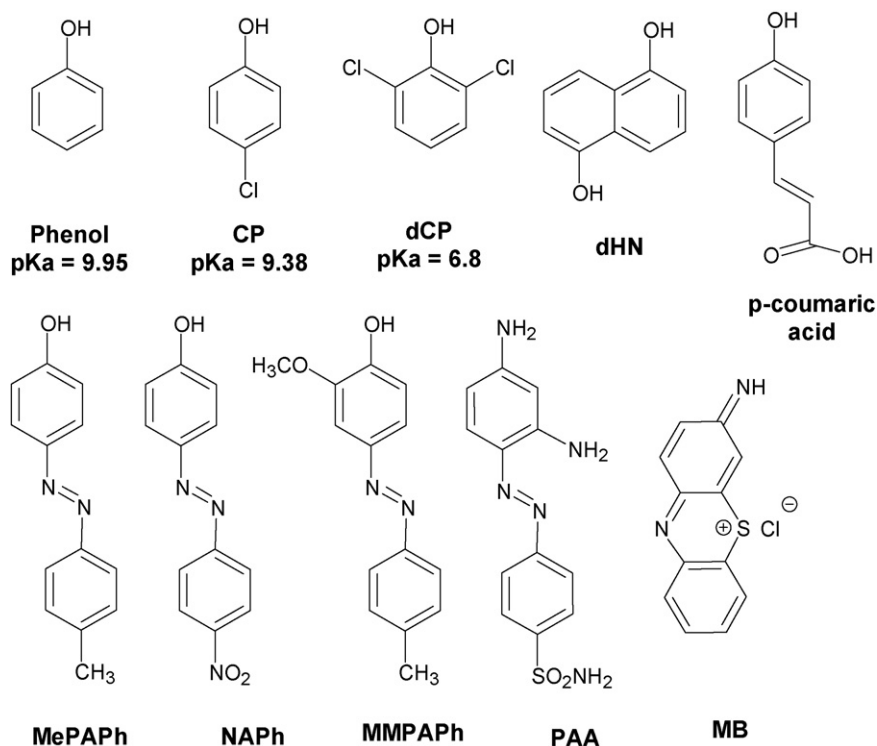


Fig. 1. Chemical structures of the phenolic compounds investigated in this study. pK_a values are according to Han et al. [17].

stable and give higher hydrophobicity enhancing possible intermolecular physical interactions between the HyX and the phenolic compounds.

3.2. Adsorption of phenolic compounds

A series of adsorption experiments were run testing the selected phenolic compounds against three different HyXs with various aging regimes. Three distinct patterns of adsorption as illustrated in Fig. 2 were observed for the optical density changes for the phenolic solutions tested. The patterns of the absorbance changes for the phenolic solutions were similar in the presence of HyXs aged at room temperature and 4 °C indicating that the aging regime had no effect on the adsorption of the compounds tested. In contrast to dCP and MePAPh, there was little change in the absorbance levels for phenol, CP, dNH, and p-coumaric acid in the presence of all the

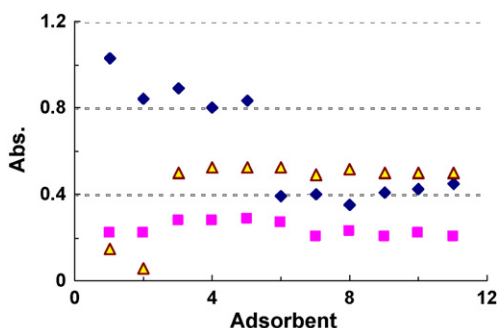


Fig. 2. Results of CP (■), dCP (▲), and MePAPh (◆) adsorption on TMOS + PrTMS HyXs aged at ambient temperature. The first and second points represent the absorbance values of the blank samples of the phenolic solutions before and after the experiment. Points 3–11 represent the absorbance of the phenolic solution in the presence of the HyXs containing 0, 10, 20, 30, 40, 50, 60, 70, and 80% (v/v) ormosil, respectively, at the end of the experiment.

tested HyXs suggesting that the HyXs in this study had no tendency to adsorb these compounds (Table 1).

The plots of the optical density for dCP solutions at 297 nm revealed an increase in absorbance that occurred and were independent of the HyX composition. Spectra for dCP in the absence and present of HyX are given in Fig. 3a. The spectrum of dCP in deionized water ($pH\ 6.1 \pm 1$) has a peak at 279 nm which is very close to its λ_{max} in neutral water. This peak also shows a shoulder at 297 nm which is assigned to the anionic form of dCP. Considering the relatively high pK_a of dCP [17], it is assumed that the equilibrium between dCP and its corresponding anion shifts largely toward the anion in the presence of the HyXs which, in turn, causes the observed blue shift in its UV–vis spectrum that would explain the increase in absorbance observed. This would suggest that there is an acid–base interaction between the xerogels and dCP supporting the idea that the prepared xerogels and HyXs bear negative charges [4,18].

In contrast to dCP, data for MePAPh shows a decrease in the absorbance values when contacted with the HyXs (Fig. 2 and Table 1). This decrease in the absorbance, which is relatively large (40–60%), is seen when the MePAPh solutions were contacted with HyXs containing 30–50% ormosils. Based on the spectra for MePAPh (Fig. 3b) before and after adsorption and the color of the HyXs at the end of the experiments, the observed decrease in the optical density is attributed to adsorption of the phenolic diazo dye by the HyXs. The HyXs, which contained more than 50% ormosils, did not produce any significant increase in the MePAPh adsorption.

3.3. Adsorption of diazo dyes

To better understand the adsorption behavior of the HyXs and phenolic diazo dyes, three more dyes, NAPh, MMPAPh, and PAA were identified and tested and results are given in Table 2. The absorbance changes for all the three dyes follow similar patterns in the presence of both of the HyXs examined suggesting that the

Table 1

Optical density changes (%) for the given phenolic solutions at the end of isotherm adsorption experiments in the presence of the given HyXs containing different amounts of ormosils and aged at RT or 4 °C. N = no change.

Temperature	Ormosil content %(v/v)	Phenol, CP, dHN, p-coumaric acid	MePAPh
TMOS + PrTMS			
RT	0	N	0
	10	N	-4.8
	20	N	0
	30	N	-53
	40	N	-53
	50	N	-58
	60	N	-52
	70	N	-50
4 °C	0	N	0
	10	N	0
	30	N	-46
	50	N	-56
	70	N	-50
TMOS + MeTPS			
RT	0	N	0
	10	N	-15.4
	30	N	-61.8
	50	N	-47.2
	70	N	-48.1
4 °C	0	N	0
	10	N	-12.7
	30	N	-41.6
	50	N	-67.8
	70	N	-43.7
TEOS + PrTMS			
RT	0	N	0
	10	N	-29.6
	30	N	-60.8
	50	N	-48.7
	70	N	-47.8

affinity of the HyXs for MMPAPh and APA is clearly higher than that for NAPh.

To understand the importance of hydrogen bonding in the observed adsorption, MMPAPh was tested first. In comparison with MePAPh, MMPAPh has a methoxy substituent at the *ortho* position of the hydroxy group which apparently does not affect the affinity of the phenolic diazo derivative for the HyXs tested. The methoxy group of MMPAPh was expected to hinder hydrogen bonding between the phenolic dye and the xerogel surface through two mechanisms. First, the *ortho* methoxy group could hinder the hydrogen bonding of the adjacent phenolic terminal group through steric hindrance. Second, the methoxy group of MMPAPh could be used for *intra*-molecular hydrogen bonding by the phenolic termi-

Table 2

Optical density changes (%) for the diazo dyes solutions at the end of isotherm adsorption experiments in the presence of the HyXs containing different concentrations of ormosils and aged at RT.

Ormosil content %(v/v)	MMPAPh	NAPh	APA
TMOS + PrTMS			
0	0	0	-16.0
20	-16.5	0	-59.3
40	-64.4	-7.9	-65.6
60	-63.1	-3.8	-61.7
TEOS + PrTMS			
0	0	-1.2	-18.8
20	-70.1	-7.5	-68.14
40	-63.2	-16.6	-64.6
60	-51.5	0	-64.6

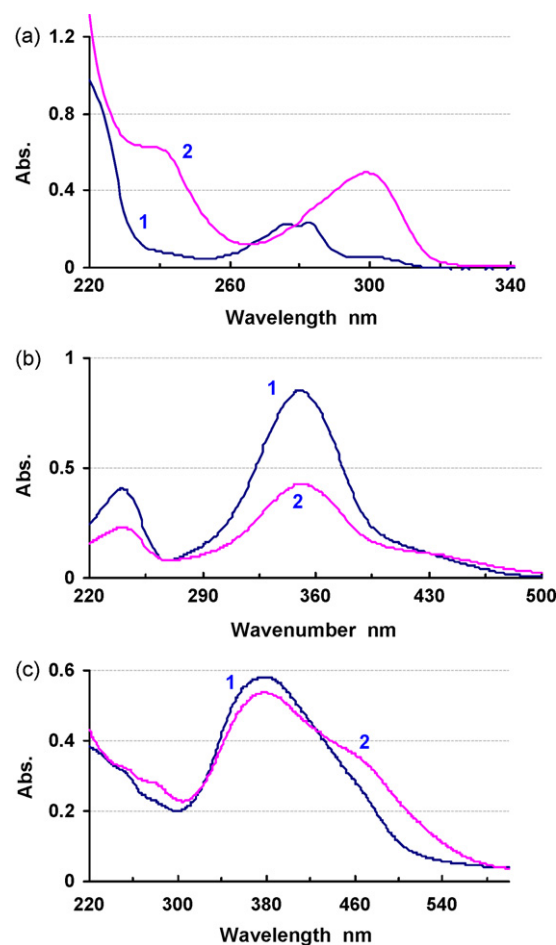


Fig. 3. Overlaid UV-vis spectra of: (a) dCP, (b) MePAPh, and (c) NAPh at the beginning (1), and at the end (2) of the adsorption experiments.

nal and reduce the chance of hydrogen bonding between the dye and the xerogel surface. In contrast, APA is a diazo derivative of aniline carrying two amino groups and no hydroxyl substituent and still shows a similar pattern of adsorption onto the HyXs. Considering these observations, it can be concluded that the hydroxyl moiety of the phenolic compounds is not an essential structural feature for adsorption to occur. Apparently, the functional groups which can participate in hydrogen bonding between the solute and HyX surface is counterbalanced by their possible hydrogen bonding with the solvent molecules.

Comparing the chemical structures of MePAPh and NAPh reveals that these two compounds are similar except for the nature of the substituent on the second aromatic ring. MePAPh carries an electron donating methyl group while NAPh bears an electron withdrawing nitro group. Since the electron withdrawing group stabilizes the conjugated base of NAPh, its acidity is increased [19]. The net effect of this would be that the acid-base equilibrium should shift to some extent towards the NAPh anion in the presence of HyXs which is substantiated based on the shift in the absorbance spectrum of NAPh in the presence of HyXs (Fig. 3c).

It is also important to acknowledge the absorbance changes of the dyes at the end of the experiment in the presence of the xerogels containing 0% (v/v) ormosil (Tables 1 and 2). It is clear that the classic xerogels of TMOS and TEOS have no tendency for adsorbing the dye molecules but, increasing the ormosil content (up to 50%, v/v) in the HyXs enhances the adsorption ability of the corresponding surfaces, possibly through a physical intermolecular interaction.

Table 3

Adsorption equations discussed in this paper. C_e = the concentration (mg/l or M) of solute remaining in solution at equilibrium, C_s = the concentration (M or mg/l) of solute at saturation, $X = C_e/C_s$, q_e = the amount (mol or mg) of solute adsorbed per gram of the adsorbent at equilibrium, Q^0 = the maximum mass of solute adsorbed per mass of adsorbent for complete monolayer, q_m = saturation capacity (mol/g) of adsorbent for solute, b ($l\ mg^{-1}$), $1/n$ (dimensionless), K_F ($l\ g^{-1}$), K'_F ($l\ g^{-1}$), B (dimensionless) are constants, ε = Polanyi constant. See Section 3 for the details.

Equation	
$q_e = Q^0 b C_e / (1 + b C_e)$	(1)
$C_e / q_e = (C_e / Q^0) + (1 / Q^0 b)$	(2)
$q_e = q_m K_{BET} X / (1 - X) [1 + (K_{BET} - 1) X]$	(3)
$q_e = K_F C_e^{(1/n)}$	(4)
$\ln q_e = (1/n) \ln C_e + \ln K_F$	(5)
$\ln q_e = (1/n) \ln (C_e / C_s) + \ln K'_F$	(6)
$q_e = q_m e^{-B \varepsilon^2}$	(7)
$\ln q_e = \ln q_m - B \varepsilon^2$	(8)

3.4. Isotherm equilibrium adsorption

Isotherm equilibrium adsorption experiments were carried out to identify the possible mechanisms of adsorption operating with these HyXs. The data was analyzed by various adsorption models to determine the possible nature of the adsorption phenomena. This includes the classical Langmuir model (Eq. (1)–Table 3). From Table 1, it is clear that increasing the ormosil content of the HyXs beyond 50% does not increase the adsorption of MePAPH for both type RT and 4 °C aged HyXs. Therefore, isotherm equilibrium adsorption of MePAPH was obtained in the presence of TMOS + MeTPS which contained 30% (v/v) of the ormosil. Analysis of the corresponding data by the rearranged form of the Langmuir equation (Eq. (2)–Table 3) failed to produce meaningful parameters, which was not unexpected. The presence of the pendent group in the HyX containing 30% (v/v) ormosil produces a heterogeneous surface. As a result of this heterogeneity, the adsorption constants are not expected to be the same for all the adsorbate molecules at equilibrium (K_e). In the Langmuir model all the adsorption sites on the adsorbent surface are considered equal, the interaction of the adsorbate and adsorbent does not affect the equivalence of the adsorption sites and only a monolayer of the sorbate molecules covers the sorbent surface [20].

The Freundlich empirical equation (Eq. (4)–Table 3) is the most convenient model which has been applied in numerous cases [20–23]. In contrast to Langmuir model, the Freundlich equation has the ability to adopt the heterogeneous surface adsorption data. The logarithmic form of the equation (Eq. (5)–Table 3) is usually used for determining the adsorption parameters. However, there are some controversial aspects associated with the conventional form of the Freundlich equation including that the amount of the adsorbed solute seems to increase indefinitely with the concentration of solute in the solution. In addition, the K_F value is sensitive to both the dimensions and the range of C_e . To circumvent these limitations, the modified form of the Freundlich equation (Eq. (6)–Table 3) was used to circumvent these problems [24]. Results of the analysis using the Freundlich equation are given in Fig. 4a and Table 4. The modified Freundlich constants, K'_F and $1/n$, are representatives of the factors which influence the adsorption of the sorbate on the sorbent, but generally K'_F is interpreted in terms of the capacity of the sorbent and $1/n$ is considered for describing the heterogeneity of the surface and its affinity for the adsorbate [24,25]. The results suggest that while the both TMOS + MeTPS dried at 4 °C and at RT have similar $1/n$ constants, they have different adsorption capacities for MePAPH. To gain a better understanding of the mechanism, the data was also analyzed by the Dubinin–Radushkevich (D–R) method (Eq. (7)–Table 3) [22,26]. The ε parameter is the

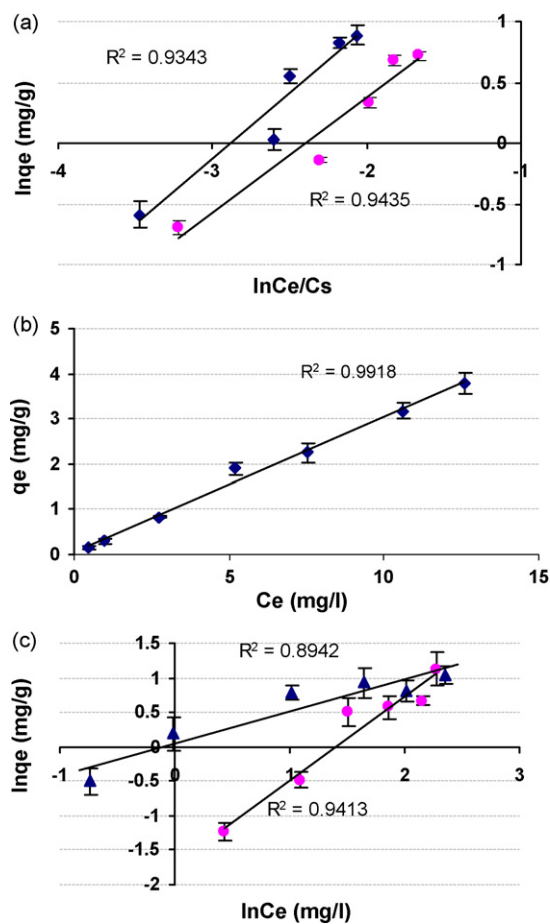


Fig. 4. Analysis results of results for: (a) MePAPH adsorption on TMOS + MeTPS containing 30% (v/v) ormosil and aged at 4 °C (■) and on its analogue aged at RT (◆) by Eq. (6) in Table 3; (b) MB adsorption on TMOS + PrTMS containing 40% (v/v) ormosil and dried at 4 °C by Eq. (2) in Table 3; (c) MB (▲) and MePAPH (■) adsorption data on the HyX introduced in (b) by Eq. (5) in Table 3.

Polyani potential which can be correlated to C_e by the following equation:

$$\varepsilon = RT \ln \left[1 + \left(\frac{1}{C_e} \right) \right] \quad (9)$$

where R is the gas constant in kJ mol^{-1} and T is the absolute temperature in Kelvin. The advantage of the D–R method is that the B constant obtained from the logarithmic form of the equation (Eq. (8)–Table 4) can be used for calculating the mean free energy (E) of sorption per mole of the solute after it is adsorbed onto the surface by the following equation:

$$E = \frac{1}{(-2B)^{1/2}} \quad (10)$$

Table 4 contains the E values and D–R parameters for the MePAPH adsorption on both TMOS + MeTPS dried at 4 °C and room temperature. In agreement with the K'_F values obtained, the q_m values also suggest higher adsorption capacity for the latter HyX. However, the E value of the former HyX is a little larger. Therefore, it is assumed that the smaller $1/n$ value of the HyX dried at 4 °C is mainly because of its more heterogeneous surface in comparison with TMOS + MeTPS dried at room temperature.

3.5. MePAPH versus Methylene blue

In contrast to MePAPH which is almost neutral at pH(s) close to 7, MB is a cationic dye usually used for assessing the accessible anionic

Table 4
The modified Freundlich analysis of the MePAPh adsorption on: (A) TMOS + MeTPS containing 30% (v/v) of the ormosil and aged at room temperature; (B) aged at 4 °C; (C) TMOS + PrTMS containing 40% (v/v) of the ormosil and aged at 4 °C; (D–F) the D–R analysis of the MePAPh adsorption on A–C, respectively; (G) the D–R analysis of the MB adsorption on C.

Compound	Fitted equation	R^2	$1/n$	K'_f (lg^{-1})	q_m (mol g^{-1})	$-B$ ($\text{mol}^2 \text{kJ}^{-2}$)	E (kJ mol^{-1})
A	$y = 1.08x + 3.12$	0.93	1.08	22.65			
B	$y = 0.94x + 2.25$	0.94	0.93	9.49			
C	$y = 1.21x + 2.014$	0.94	1.21	7.49			
D	$y = -0.0073x - 5.71$	0.93	–	–	0.0033	0.0073	8.28
E	$y = -0.0066x - 6.11$	1	–	–	0.0022	0.0066	8.7
F	$y = -0.0098x - 5.04$	0.93	–	–	0.0065	0.0098	7
G	$y = -0.0031x - 9.55$	0.92	–	–	0.00007	0.0031	12.7

surfaces like xerogels [27]. The adsorption of MB and MePAPh on TMOS + PrTMS containing 40% (v/v) ormosil and dried at 4 °C was studied. Again, the adsorption data of MePAPh on this HyX did not fit meaningfully into the Langmuir equation, but the MB adsorption data did which is shown in Fig. 4b. On the other hand, when the adsorption data was analyzed by Eq. (5) (Table 3), the MePAPh data complied with the Freundlich equation better than the MB adsorption data. These results are illustrated in Fig. 4c.

The adsorption data of MB and MePAPh on TMOS + PrTMS was also processed using the D–R equation. Results are summarized in Table 4. These results help to better explain the adsorption behavior of the selected HyXs. It has been shown that E values $> 8 \text{ kJ mol}^{-1}$ represent adsorption behavior characterized by ion-exchange interactions and that E values $< 8 \text{ kJ mol}^{-1}$ are representative of non-ionic intermolecular interactions [28]. Comparing the E values for MB and MePAPh, it is clear that the adsorption of MB on the HyXs is best described by an ion-exchange mechanism while the adsorption of MePAPh is characterized by weaker interactions. What is of interest is the magnitude of the q_m parameter obtained for MB and MePAPh. The q_m value extracted from the MB adsorption data is obviously smaller than the q_m value of MePAPh. Taking into account the chemistry of the HyX and the chemical structures of MB and MePAPh, it is possible to explain the observed discrepancy in the q_m values. A 40% (v/v) ormosil content in the HyXs appears to not only extend the hydrophobic surface of the material but the propyl dopants interfere sterically with the ionic interactions of the anionic surface with the cationic dye reducing the available surface for MB adsorption.

3.6. TMOS + MeTPS versus TMOS + PrTMS

The following conclusions can be made by focusing on the results of the MePAPh adsorption analysis using both the modified Freundlich and D–R methods (Table 4). First, the correlation coefficients (R^2) for the MePAPh corresponding Freundlich equations falls in the range of R^2 reported for the previously studied organic compounds by the Freundlich method on various adsorbents [20,29,30]. However, they are smaller than the R^2 reported for the adsorption of phenolic compounds on the activated carbons [31]. This indicates that the HyXs considered in this study have surfaces more heterogenous than the activated carbon surfaces. Increasing the ormosil share from 30% (v/v) in the TMOS + MeTPS to 40% (v/v) in TMOS + PrTMS decreased the heterogeneity of the corresponding HyX surface reflected in the magnitude of $1/n$ (1.21 in comparison with 1.08) Aging of the sol–gel of at lower temperatures produced HyXs with a more heterogenous surface and lower adsorption capacity.

N_2 adsorption results for TMOS HyXs are summarized in Table 5. These results are in agreement with the fact that the xerogels with larger pore sizes, the characteristic feature of ormosil incorporation, have less surface area [9]. Additional points of interest are that the N_2 adsorption data for HyXs aged at room temperature indicate almost similar pore sizes for both TMOS + MeTPS and

Table 5
Pore size analysis of the xerogels dried at room temperature as described in Section 2.3. Data in parentheses is for analogous xerogels aged at 4 °C.

Ormosil share (v/v)%	Surface area (m^2/g)	Surface area (m^2/g)
	TMOS + MeTPS	TMOS + PrTMS
0	308.29	236.52
30	172.14 (96.72)	192.35
60	70.21 (20.60)	67.92

TMOS + PrTMS. In agreement with the aforementioned results, the available surface of the HyXs dried at 4 °C is clearly smaller than the analogous gels dried at room temperature.

The E values obtained E for MePAPh reveal strong physical interactions of this molecule with the HyX surfaces studied. A small decrease in the E value of MePAPh adsorbed on the TMOS + PrTMS is observed. This decline can be ascribed to the fact that the Van der Waals interactions are geometry-dependant forces. It is assumed that the propyl dopants, in comparison with methyl dopants in TMOS + MeTPS, reduce the structural symmetry of the surface which is necessary for favorable intermolecular interaction.

Finally, it appears that there is a contradiction between the q_m and K'_f values of MePAPh adsorption on TMOS + PrTMS. While the q_m value suggests a larger surface capacity for the TMOS + PrTMS in comparison with the TMOS + MeTPS, the K'_f value would suggest an opposite conclusion. Since the results of the experiments were highly reproducible at 25 °C, the difference between the parameters obtained would seem valid. Therefore, it is assumed that the observed discrepancy is either due to the nature of the parameters or the adsorption type. The K'_f value is obtained from an empirical model which is generally considered as an index for the surface capacity but it is influenced by different factors affecting the adsorption phenomenon.

It should be noted that none of the MePAPh adsorption fitted well with the Langmuir equation while the MB data did. Although the analysis of the MePAPh adsorption data by Eq. (3) (Table 4) did not produce higher R^2 in comparison with the reported R^2 for the modified Freundlich equations shown in Table 4 (data not shown), the possibility for Type II adsorption of MePAPh on the designed HyXs cannot be ruled out.

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