Adsorption of *p*-xylene in dry and moist clay

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Abstract: It is well known that volatile organic compound (VOC) adsorption on dry soils decreases as relative humidity increases causing water to adsorb and displace VOC. The objective of the current study is to suggest a quantitative explanation for the dependence on relative humidity of *p*-xylene adsorption isotherms between the limiting case of zero relative humidity and super-saturation. Adsorption of *p*-xylene on Na-montmorillonite clay was studied at different relative humidity (0, 27, 48 and 76 %) by using the dynamic pulse technique. Adsorption behaviours at dry condition can be explained by the BET isotherm. *p*-Xylene was successfully adsorbed on the surface of the Na-montmorillonite in dry condition. It was observed when surface is covered by water patches *p*-xylene adsorption decreases. The adsorption isotherm of *p*-xylene at moist clay surface was also obtained from a mathematical model. Based on the limiting cases of adsorption on a totally dry mineral surface and at an air-water interface, a mathematical model is provided for the nonlinear adsorption isotherm for *p*-xylene onto moist clay. The mathematical model correctly describes significant features of experimental VOC adsorption on moist clay. The experimental data and results of the mathematical model for the same humidity values are matches, mainly. The amount of water and *p*-xylene to cover the mineral surface by monolayer were found as; 2.0265, 21.314 mg/g, respectively.

Keywords: *Adsorption, montmorillonite, volatile organic compounds.*

Symbols and Abbreviations

C_{gs}	Adsorbed contaminant amount on the solid surface, mg/g
C_{gs}^m	Required contaminant amount to form a layer on the surface, mg/g
C_{ws}	Adsorbed water amount on the solid surface, mg/g
C_{ws}^m	Required water amount to form a layer on the surface, mg/g
C_i	Inlet concentration to the column, mol/m^3
k	BET energy constant
M	Contaminant molecular weight, g/mol
$m_{accumulation}$	Adsorbed mass, g
m_{out}	Output mass from the column, g
m_{in}	Inlet mass to the column, g
n	BET energy constant
r	BET energy constant
t_{fa}	Residence time, s
v	Volumetric flow rate of the inlet gas, m^3/s
y	Contaminant concentration
δ	Layer number on the surface
ε	Void ratio
a, b, c	Empirical constants for surface contaminant

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Introduction

Volatile organic compounds (VOCs) can keep their properties for long periods and easily relocate by atmospheric effects. These compounds may accumulate in human body and cause some health problems. Leaking petroleum storage tanks, using excessive amount of agricultural chemicals, combustion gases, products of recycling processes and some violating ethical/environmental standards may result in VOCs emission. These emissions can be held in air, water and soil. Besides, VOCs move from one phase to the other. VOCs properties show huge differences if their structures include halogens. In addition, VOCs may turn into seconder more harmful compounds depending on environment in which they are released (Dursun *et al*. 1996). Thus it is necessary to investigate soil properties and VOC characteristics in the soil.

The environmental fates of volatile and semivolatile organic pollutants strongly depend on their partitioning between the gas phase and condensed phases. This partitioning includes absorption in bulk phases like water or organic matter and adsorption on ambient surfaces. Adsorption properties depend on the surface and adsorption properties, temperature and relative humidity (Goss, 2004).

Removing of gas phase hydrocarbons in unsaturated conditions is important for environmental processes. Karbiwnyk *et al*. (2002) indicate that water vapor can be a significant interference in the analysis of air for non-methane VOCs using solid-adsorbent sampling techniques. Humidity of adsorbent material must be controlled for the efficiency of the process. Marginal changes of the adsorbent temperature cause huge differences in humidity level. Investigation of Rutherford and Chiou (1992) shows the importance of humidity on VOC transfer. While humidity increases, retardation factor and adsorption go down. Moreover, irreversible adsorption is obtained in the dry soil. In the nature, all soils contain humidity. There must be an interaction between water and VOC molecules which compete to adsorb to the soil surface. It is offered that adsorption under 25 % humidity obeys BET II isotherm. But when the humidity goes higher, isotherms change because entire surface is covered with a water layer (Hu *et al*., 1995; Thibaud *et al*., 1992). Zou *et al*. (2003) studied to characterize the ambient air VOCs. The amount and number of VOCs show seasonal chances. Also it is important where they are searched in landfill or urban area. p-xylene and carbon tetrachloride are decided not to be seasonal and locational dependent contaminants.

Existence of water also decreases material pore sizes. Sometimes all pores are filled with water, entirely. Thibaud *et al*. (1993) considered the pore diameter decrease with water adsorption in the pores. The adsorption decreases with increasing humidify. Tetrachloro ethylene adsorption is found very sensitive if the adsorbent is affected from water and has Brønsted or Lewis acid sites. These sites are highly selectivity for water molecules if adsorbed amounts are compared (Guillemot *et al*., 2007). As the water content in the soil goes up, gas-solid interaction decrease and BET II type isotherms are obtained. The effect of partial vapor pressure of VOC and water in the soil, whose organic matter amount is negligible, is investigated by McCoy and Cabbar (1996). Adsorptions at gas-solid and gas-liquid interfaces are set as boundary conditions and a model is developed for the nonlinear adsorption rate of VOC on humid soils. It is observed that gas-solid interaction decrease exponentially with water (McCoy & Cabbar, 1996; Goss & Eisenreich, 1996). Rise in the humidity amount causes reduction in the gas-solid interface area. If the humidity reaches to a certain level, gas-liquid interfaces area also reduces. These effects reduce the adsorption amount (Bradford *et al*., 1997; Costanza & Brusseau, 2000).

In this study, Na-montmorillonite was used for *p*-xylene adsorption. Movements of the molecules during the adsorption were investigated with various contaminant concentrations and humidity amount. Experimental adsorption data were investigated using a mathematical model.

Materials and Method

In this study, Na-montmorillonite natural clay obtained from Hançılı-Çankırı. Clay sample was dried at 105 °C in an oven. Dried clay particulates of size 0.25 mm diameter were separated for the further use. Physical characteristics of clay were measured with He-piknometer, sorptometer and porosimeter. Solid density and surface area of Na-montmorillonite were found as 2.655 g/cm^3

and 56.8 m^2g^{-1}, respectively. Chemical and physical properties of the clay and *p*-xylene are listed respectively in Table 1 and 2.

Table 1. Physical and chemical properties of Na-montmorillonite

Compound	%, Weight
SiO_2	73.62
Na_2O	2.08
Al_2O_3	17.35
CaO	0.36
K_2O	0.29
Fe_2O_3	2.62
MgO	3.06
Combustible parts	0.62

Table 2. Basic properties of *p*-xylene

Molecular weight, g/mol	106.16
Boiling point (1 atm), K	411.51
Freezing point (1 atm), K	286.43
Liquid density, g/ml	0.86
Dipol moment, debye	0.10
Henry constant, $kPa.m^3.mol^{-1}$	0.58
Water solubility	0

In our experiments, p-xylene was used as contaminant. This compound is commonly used in the industry. It is harmful to human health and has long half-live. It can evaporate easily due to their high partial pressure. Once in the gas form, it diffuses to far away locations. *p*-Xylene used in the experiments have purity of 99% and were provided by Merck.

Experiments use the set up depicted in Figure 1. Adsorption of VOCs to clay samples with humidity of 0%, 27%, 48% and 76% were studied. The samples were humidified with N_2 gas which previously has passed through bottles containing water. Contaminant was introduced to the N_2 gas in the contamination bottle. The same bottles were used to introduce water to N_2 gas. Various relative humidity levels were obtained by mixing pure N_2 gas at various proportions with humidified N_2 gas coming from the contamination bottles. The same process was used to regulate the concentration of the contaminant. Running gas contaminant and humidity values were calculated by weight changes of active carbon and magnesium perchloride.

Steel pipe in 4 mm diameter and 50 mm length was used as adsorption column and filled with Na-montmorillonite. In order to have a suitable void fraction value, amount of clay was carefully calculated based on the clay densities; full detail is given by Çakanyıldırım (2003). Carrier gas with the desired relative humidity was passed through the clay packed column. In the experiment, a positive step change in the concentration *p*-xylene was produced at the inlet of the clay packed column. The concentration boundary travels through the column and breaks through at the outlet of the column. The effluent stream was analysed using a gas chromatograph (Gow-Mac Series 350) until it reached a constant stable value equal to the inlet concentration.

The effluent concentration was monitored by using a recorder. The VOC amount adsorbed by 1 g clay was computed by measuring the area below the curve which relates the time to the contamination concentration. Each dot on the sorption isotherm was found from the analysis of a breakthrough curve.
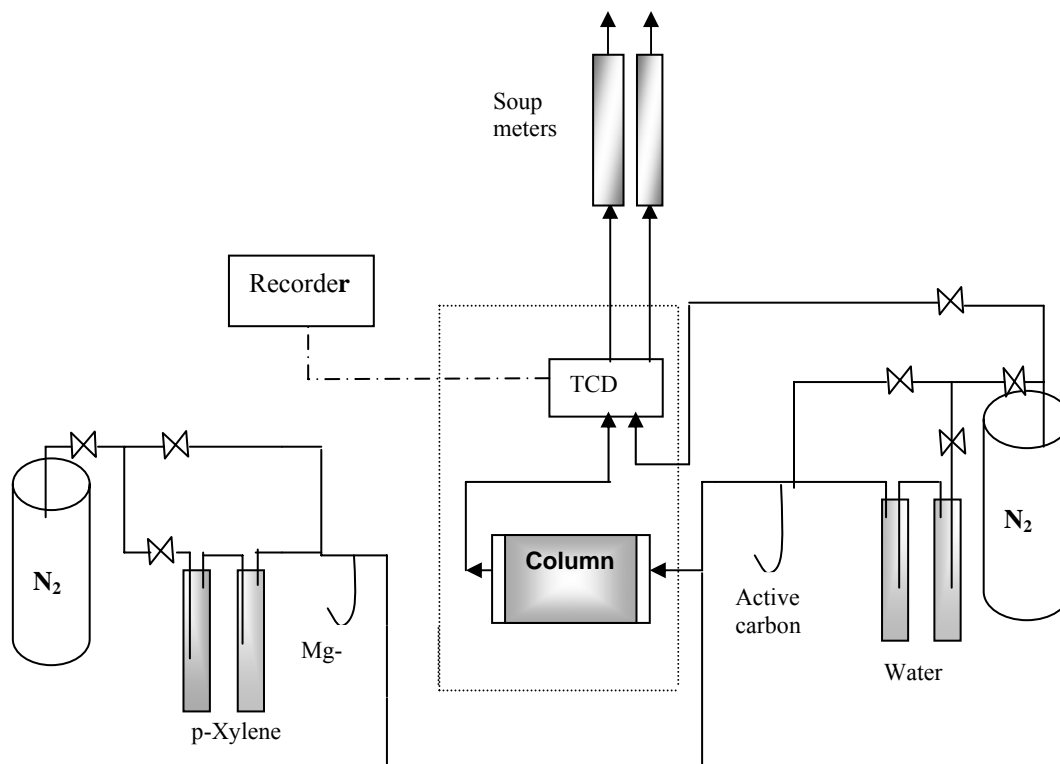
Figure 1. Experimental set-up

Theory

In order to calculate the contaminant amount on the surface, for all adsorption process it is assumed that; there is equilibrium in gas and solid phase and VOC concentration at the entrance is equal to the gas phase concentration. By these knowledge and assumption mass balance for the packed bed can be written as:

$$m_{in} - m_{out} = m_{accumulation} \qquad (1)$$

Equation 2 and 3 represent the entering and outlet amounts. Entering gas concentration (C_i) is kept constant while experiment is performed.

$$m_{in} = \left[\int_0^{t_{fa}} C_i dt \right] Mv = C_i Mv t_{fa} \qquad (2)$$

$$m_{out} = \left[\int_0^{t_{fa}} C_i(t) dt \right] Mv \qquad (3)$$

If equation 2 and 3 are settled in equation 1, contaminant accumulation amount on the clay surface can be obtained.

$$m_{accumulated} = \left[\int_0^{t_{fa}} \left(1 - \frac{C_i(t)}{C_i} \right) dt \right] C_i Mv \qquad (4)$$

And the adsorbed amount on the surface is:

$$m_{adsorbed} = m_{accumulation} - \varepsilon v C_i M \tag{5}$$

$\varepsilon v C_i M$ in equation 5 shows accumulation in gas phase. This value is much smaller than the amount held on the surface. Thus adsorbed and accumulated amount can be assumed equal.

The amount of adsorption occurs on the surface of the clay depends on: composition, porosity and surface area of the clay. Thus some parameters belong to clay must be known in order to explain the adsorption properties. The adsorption isotherm which gives the adsorption on dry surface is (C_{gs}) is a function of relative partial pressure ($y=P/P_o$).

The adsorption happens on the water layer is not just effected with y value, but also the properties of the mineral surface under the water layer. Covering mineral surface by a different matter cause adsorbent-contaminant interaction decrease exponentially (Bostancı & Cabbar, 2001). If the adsorbed molecules layers are assumed to be finite and represented by n, gas-solid interface adsorption BET isotherm can be given as:

$$\frac{C_{gs}}{C_{gs}^m} = \frac{kry}{(1-y)} \tag{6}$$

the *r* value in equation 6 can be detailed:

$$r = \frac{1-(n+1)y^n + ny^{n+1}}{1+(k-1)y - ky^{n+1}} \tag{7}$$

y value means the ratio of partial vapor pressure (P), over the saturation vapor pressure (P_o). BET adsorption constants n, k and the mininum amount of VOC (C_{gs}^m) to cover the entire surface, can be calculated by the regression of the experimental data.

Water adsorption isotherm on the solid surface can be explained as it is given in equation 6 for the gas solid adsorption. If Eq. 7 is placed in Eq. 8 and saturated condition is considered ($y=1$), Eq. 9 is obtained:

$$\delta = \frac{C_{ws}}{C_{ws}^m} = \frac{kry}{(1-y)} \tag{8}$$

$$\delta_0 = \frac{kn(n+1)}{2(nk+1)} \tag{9}$$

y represents relative humidity. In equation 8, δ shows the water film number on the mineral surface. By the help of the methods which are applied to find for VOC, it will be possible to obtain the k, n and C_{ws}^m values for the water (McCoy & Cabbar, 1996).

Hauxwell and Ottowill (1968) offered that it is possible to compute gas accumulation amount on the liquid surface by Gibbs adsorption equation. In order to estimate the a, b and c coefficients, a series of non-linear regression procedure and surface tension experiment were done. Eq. 10 shows how these constant numbers are used:

$$C_{gw}^\infty = ay + by^2 + cy^3 \tag{10}$$

If the Eq. 6, 8, 9 and 10 combined in one mathematical expression as given in Eq. 11 theoretical way of calculating contaminant amount on the surface at any y values, could be possible:

$$C = C_{gw}^\infty + (C_{gs} - C_{gw}^\infty)\exp(-\frac{\delta}{\delta_o}) \tag{11}$$

Results and Discussion

The experiments in this study, Na-montmorillonite filled columns were used in order to investigate *p*-xylene adsorption isotherms. Dry and humidified conditions were used during the experiments. While dry clay studies only *p*-xylene were adsorbed on the clay surfaces. The ratio of partial vapour pressure to saturated vapour pressure (P/P_o) was adjusted to prepare different concentrations. At dry clay experiments there were no water molecules preventing *p*-xylene to reach to the surface. Thus contaminant found more area to store it self. Moreover, it was observed that adsorption amount decreased when the surface was introduced with water. Water molecules tend to be adsorbed on the surface more than the *p*-xylene molecule was done (Guillemot *et al.*, 2007; Pennel *et al.*, 1992). Especially for Na-montmorillonite on which water has been adsorbed easily, this competition effect is more sensible. Figure 2 gives negative trends of the adsorbed amount with humidty. Especially, it is more sensible when the relative humidity level is over 25% (Hu *et al.*, 1995); adsorption isotherm type also shows the changes with increasing water amount. This is an effect of decreasing interaction of surface and p-xylene molecules.
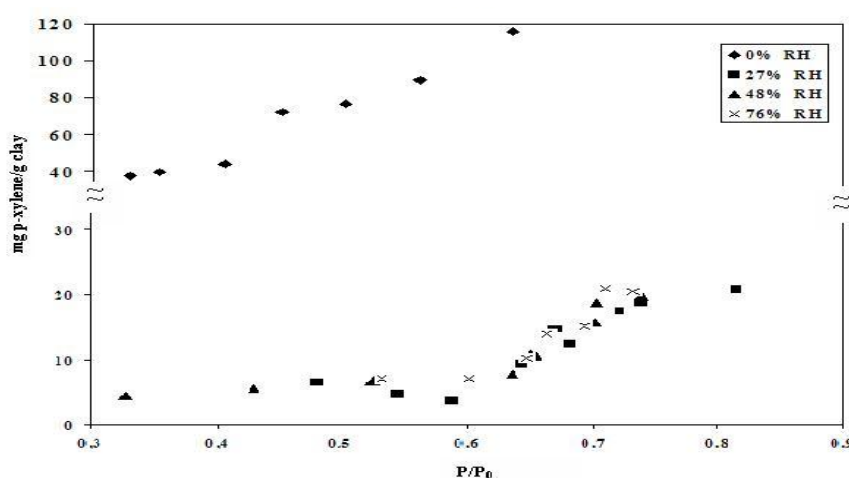
Figure 2. Adsorption isotherms of *p*-xylene sorbed on Na-montmorillonite at different relative humidity.

Na-montmorillonite is a good one for adsorption because it has micro pores and high surface area when compared to other adsorbents. These isotherms demonstrate that Na-montmorillonite has larger adsorption capacity. Even the Na-montmorillonite surface was exposed to high relative humudity value and the pores of the adsorbent were occupied by water molecules, p-xylene can still find empty places to hold onto the surface. This adsorption amount is approximately up to 30 mg *p*-xylene / g adsorbent. Furthermore, at small relative humidity levels adsorbed p-xylene amount goes higher.

It might be thought that there were more p-xylene layer on the Na-montmorillonite surface because the amount adsorbed on it is high in Table 3. The molecular weight of water is 6 times less than p-xylene. Thus, when the moles of contaminant and water are compared slightly more p-xylene is required to cover the entire area by one layer. Water layer amount does not exceed one on Na-montmorillonite unless enough humidity level is supported and Figure 2 demonstrate that this humidity level is below 27%. The value of required water amount to create one layer on Na-montmorillonite was calculated by equation 8 and can be checked from Table 3.

Table 3. Calculated BET energy constants

Clay-Contaminant	n	k	C^m_{gs}, mg g^{-1} clay
Na-Montmorillonite, p-xylene	3.812	0.313	21.314
Na-Montmorillonite, Water	7.383	5.822	2.0265

At equilibrium gas and water phase concentrations of p-xylene can be explained by Henry law. That is also explaining why p-xylene is less soluble in water. Providing that p-xylene is dissolved in the liquid, p-xylene molecules can be adsorbed in the liquid-solid interface. Solubility in the liquid is negligible if the adsorbed amount on the liquid surface is considered. Although, water molecules are blocking the p-xylene, its solubility and molecular properties result in accumulation between water and clay surfaces.

Mathematical model described in Eq. 11 was used to predict p-xylene adsorption behaviour and it is compared in Figure 3 with experimental data while the relative humidity value is 27%. At all points contaminant concentration model and experimental results are in good agreement. Furthermore, water adsorption data are given with mathematical model results in Figure 4. Both experimental and theoretical data are close to each other to conclude, the model is successful, adequately.
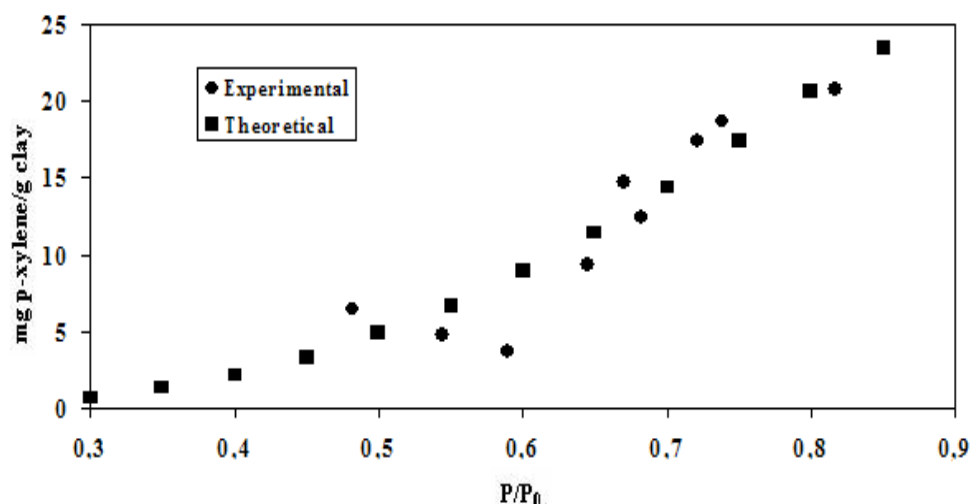
Figure 3. Theoretical and experimental data obtained for *p*-xylene adsorption on Na-montmorillonite (27% RH).
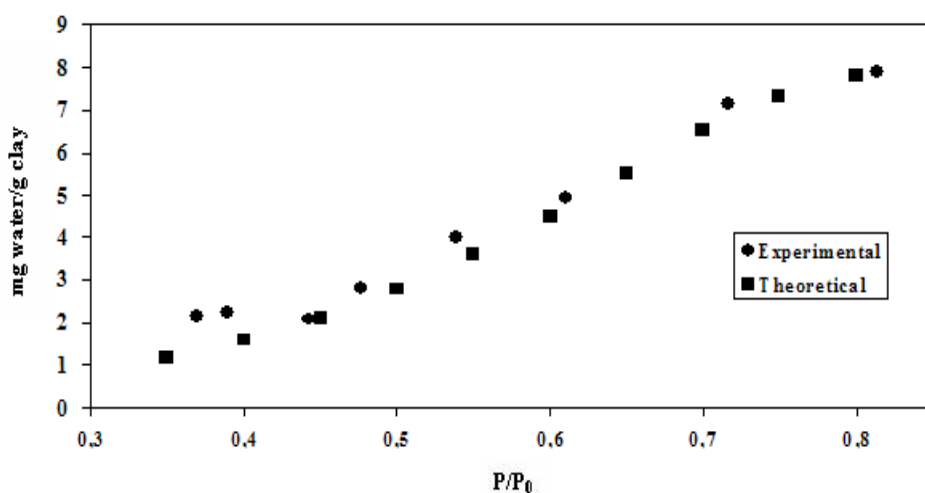
Figure 4. Theoretical and experimental data obtained for water adsorption on Na-montmorillonite

It will be helpful to investigate surface-contaminants interaction in case more than one VOCs are mixed in heterogenic clays and effect of humidity on the system. Also derivation of a model must be considered to simplify the complex surface pheneoma.

Conclusion

Na-montmorillonite clay and *p*-xylene were used in the presence of humidity, to obtain adsorption behaviours. Experiments were performed under dry and threee different relative humidity level. Competing adsorption of water and *p*-xylene happened with in humidified experiments. Water existence blocks the contaminant molecules to reach surface, thus maximum adsorption data were recorded for dry condition. However, even at the highest moisture level Na-montmorillonite was found to be successful in adsorbing *p*-xylene. This is a result of high surface area and adsorption capacity of the clay. Also, a model was applied to predict adsorption amount at any humidity value. According to the results, model and experimental dates compatibility is good, generally.

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