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Toluene and naphthalene sorption by iron oxide/clay composites

Part II. Sorption experiments

Marilda M. G. R. Vianna · Jo Dweck ·
Frank H. Quina · Flavio M. S. Carvalho ·
Claudio A. O. Nascimento

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Abstract This study investigates the sorption of toluene and naphthalene by a sodium bentonite (BFN), an organoclay (WS35) and by their respective iron oxide hydrate composites Mag_BFN and Mag_S35. The organic matter content of WS35 and Mag_S35, determined by thermogravimetry, was used to obtain their organic matter sorption coefficients, which show that they are effective sorbents to remove organic contaminants from water, with a higher selectivity for naphthalene than for toluene sorption. The main iron oxide phase present in Mag_BFN and Mag_S35 is maghemite (γ-Fe_2O_3), which allows these sorbents to be separated from the effluent by a magnetic separation process after use.

Keywords Clay · Organoclay · Iron oxide/clay composites · Characterization · Toluene sorption · Naphthalene sorption · Thermal analysis

M. M. G. R. Vianna (✉) · C. A. O. Nascimento
Chemical Engineering Department, Polytechnic School,
University of São Paulo, Sao Paulo, SP, Brazil
e-mail: marilda@pqi.ep.usp.br

J. Dweck
School of Chemistry, Rio de Janeiro Federal University,
Rio de Janeiro, RJ, Brazil

F. H. Quina
Chemical Institute, University of São Paulo,
Sao Paulo, SP, Brazil

F. M. S. Carvalho
Geosciences Institute, University of São Paulo,
Sao Paulo, SP, Brazil

Introduction

The contamination of the surface, subsurface soils, and groundwater with biorefractory organic chemicals is a widespread problem. Aromatic components of gasoline are considered to be more hazardous than the aliphatic fractions due to their higher mobility in the subsurface and their acute and chronic toxicities.

One of the most common sorbents used in water remediation is granular activated carbon (GAC), a porous material that adsorbs organic compounds such as polycyclic aromatic hydrocarbons (PAHs). If the PAH is larger than the diameter of the pores, it simply blocks the pore, drastically decreasing the adsorption rate. This problem can be greatly reduced by placing an organoclay layer in front of the activated carbon vessel [1]. Generally, sorption of larger organic molecules by GAC is less effective than by organoclays. Thus, while competitive sorption of cosolute results in depressed sorption on GAC, in the case of organoclays, sorption of one contaminant can have synergistic effects on the sorption of cosolutes [2]. When smectite or other clays are modified with quaternary ammonium cations (QUATs), they become organophilic, and are referred to as organoclays. Sorption studies on organoclays from aqueous solution have been conducted with a variety of nonpolar, nonionic organic compounds (NOCs) including many common groundwater contaminants [2–4]. Applications of organoclays in the synthesis of nanocomposites [5, 6], in pollution prevention as sorbents for NOCs from aqueous solution include the treatment of waste effluents, as extenders for activated carbon and as components of clay barriers around waste disposal reservoirs and oil or gasoline tanks [7–9]. The magnetic composites are different types of adsorbents, which have been prepared by three methods. In the first, the magnetic clay is prepared by the adsorption of magnetic particles stabilized on a water-soluble polymer onto its external surface [10]. In the second, the magnetic particles are formed in situ by precipitation of iron oxide hydrates onto materials like clay [11, 12] or activated carbon [12]. In both cases, a calcination step is necessary. According to Bourlinos et al. [11], the magnetic clay maintains the properties of the original clay like swelling and cation exchange capacities and can be converted to a magnetic organoclay by simple exchange of the interlayer Na^+ ions by other organic cations. In the third case, the magnetic clay composites are obtained by the adsorption of magnetite and Co ferrite particles onto the external surfaces of sodium clay, which can be converted to magnetic organoclay by a simple cation exchange reaction [13]. One of the advantages of these materials is that they can be separated from the effluent by a magnetic separation process [12].

In the first part of the work, which was presented in Part I, the BFN, WS35, S35, Mag_BFN, and Mag_S35 materials were characterized by powder X-ray diffraction (XRD), X-ray fluorescence (XRF), and simultaneous thermogravimetric (TG) and differential thermal analysis (DTA).

In this second part, we evaluate and compare the capacities of BFN clay, WS35 organoclay, Mag_BFN iron oxide/clay, and Mag_S35 iron oxide/organoclay composites to remove organic compounds from water by sorption. Toluene was used as a model solute to represent BTEX compounds, as it exhibits intermediate physical and chemical characteristics of the other BTEX compounds, and naphthalene was chosen to represent PAH compounds. The materials were characterized by chemical analysis, N_2 adsorption–desorption isotherms and carbon, hydrogen, and nitrogen (CHN) analysis.

Materials and methods

Surface areas and pore diameters were measured with a Micrometrics ASAP 2010 volumetric analyzer using N_2 as adsorbate. Organic CHN contents were performed in replicate using a Perkin Elmer 2400 CHN Elemental Analyzer.

The uptake of toluene and naphthalene from water was measured by batch equilibrium sorption. Samples of the materials (BFN, Mag_BFN, WS35, and Mag_S35) (0.2 g) were weighed into 22 mL Shimadzu vials. For toluene experiments, 16 mL of distilled water were added into the vials. Gilson positive displacement pipettes were used to deliver toluene into the vials, in replicate, at various amounts (1–6 μL) to yield a range of different initial concentrations. Aqueous solutions of naphthalene were prepared by dilution of aliquots (1–6 μL) of a stock naphthalene solution in methanol (26.93 g L^{-1}) in 16 mL distilled water. The concentration range used for the toluene experiments was 112.27–324.75 mg L^{-1} and for the naphthalene was 1.68–10.17 mg L^{-1}. The vials were sealed immediately with Teflon-lined septa (ref. 221-29084-91). All samples, plus blank solutions containing only toluene or naphthalene or only adsorbent materials (BFN, Mag_BFN, WS35, or Mag_S35) were shaken at 250 rpm for 24 h at 30 °C (Tecnal Incubator Shaker, Model TE 424). Initial experiments demonstrated that sorption equilibrium is reached in less than 20 h. After reaching equilibrium, the vials were transferred to an automatic headspace sampler (Shimadzu Model HSS-4A Headspace sampler) coupled to a Shimadzu Model GC—17 A gas chromatograph equipped with flame ionization detector (FID). The GC separation column was a 30 m × 0.25 mm i.d. DB-5 (equivalent to a 5% phenyl, 95% metilpolysiloxane) fused silica capillary column (J&W Scientific, Folsom, CA) with Helium as carrier gas. The injector and detector port temperatures were, respectively, 150 and 200 °C; oven temperature was programmed to maintain 45 °C for 4.5 min, heating rate at 30 min^{-1} to 80 °C (hold 5 min), heating rate 60 min^{-1} to 150 °C (hold 7 min) [14]. Peak areas were compared to external standards to determine the concentrations of toluene and naphthalene.

The amount of sorbed organic compound was calculated from the difference between the added amount and that remaining in the final solutions. All measurements were performed in triplicate, and the difference was generally <5%. The isotherms were obtained by plotting the average sorbed amount versus the final equilibrium concentration of the solution. Sorption was analyzed using linear and Freundlich equilibrium isotherm models. In order to compare all the organoclays, sorption coefficients (K_d) were determined as the ratio between the sorbed amount and the equilibrium concentration. In order to normalize toluene and naphthalene sorption on organic-matter-basis, corrected sorption coefficients on this basis (K_{om}) were calculated from K_d values and respective organic matter (OM) contents obtained from thermal analysis characterization data in Part I, as shown in the next item.

Results and discussion

Chemical composition

The chemical composition of BFN, Mag_BFN, WS35, and Mag_S35 samples was presented in Part I. The Fe_2O_3 contents of Mag_BFN and Mag_S35 are higher than those of the clays used to obtain them, due to the added iron oxide during each formation process. From thermal analysis [15] and XRF data shown and discussed in Part I, the contents of respective main phases were estimated for each of the original clays and composites used in the following sorption experiments. The obtained values are shown in Table 1.

Other characterization data

Table 2 reports the d_{001} basal spacing, BET surface areas, micropore volumes, and CHN analysis of BFN, Mag_BFN, WS35, and Mag_S35 samples. As shown in Part 1, from XRD data, basal spacings (d_{001}) of the raw material (BFN), and Mag_BFN were 1.56 and 1.30 nm, respectively. The value of the d_{001}-spacings of WS35 and Mag_S35 were almost the same (2.68 and 2.64 nm), so the addition of iron does not decrease the basal spacing of the Mag_S35 [9, 10]. The measured surface area of the WS35 is very small, comparable to the particle external surface only, because no internal surface area was accessible to the nitrogen gas. According to Jaynes and Vance [3], no consistent relationship was found between the surface area of the natural clay and the corresponding organoclay. As indicated in Table 1, the precipitated iron oxide hydrates contribute to the high iron content of Mag_BFN and Mag_S35. These composites also showed much higher surface areas and micropore volumes compared to BFN and WS35, presumably due to the added iron oxides on the clay (Tables 1, 2) [12].

Table 2 shows the total carbon content of each sample, and Table 1 shows the total OM contents estimated from Part I thermal analysis data. From these data, which are based on respective dry-mass-basis, the mass ratio between WS35 total OM content and total carbon content (from only OM in this case) is equal to 31.86/26.19 = 1.216. As this mass ratio is the same to that between total OM and organic carbon contents of Mag_S35, it can be estimated that Mag_S35 organic carbon content is equal to 16.67/1.216 = 13.70%. As from Table 2, the total carbon content of Mag_S35 is 14.88, the difference (1.18%) comes from inorganic carbon, due to some carbonation of the present iron hydroxides by ambient CO_2 during the composite formation process. The unmodified base clay BFN and the synthesized Mag_BFN have, respectively, total carbon contents of 0.17 and 0.37%. This indicates that some ambient CO_2 carbonation process has also occurred during Mag_BFN composite preparation, but in a lower degree than in Mag_S35 case.

Table 1 Main phase contents of BFN, WS35, Mag_BFN, and Mag_S35 estimated on respective dried-mass-basis, from thermal analysis and XRF data shown on Part I

Sample	Clay matrix/m%	Organic matter/m%	Iron compounds/m%
BFN	100.00	–	–
WS35	68.14	31.86	–
Mag_BFN	56.17	–	43.83
Mag_S35	35.42	16.67	47.91

Table 2 Characterization data of the samples and CHN analysis on dried basis

Sample	d_{001}/nm	S_{BET} /m^2 g^{-1}	$V_{micropore}$/ cm^3 g^{-1}	C/%	H/%	N/%
BFN	1.56	13.56	0.04	0.17	1.29	0.11
Mag_BFN	1.30	96.57	0.24	0.37	1.33	0.04
WS35	2.68	3.60	0.01	26.19	4.87	0.70
Mag_S35	2.64	26.60	0.14	14.88	3.01	0.36

Sorption experiments

Two equilibrium isotherm models, linear and Freundlich, were used to analyze toluene and naphthalene sorption from aqueous solutions by the BFN, Mag_BFN, WS35, and Mag_S35 materials. Linear isotherms [16] were obtained by plotting the average sorbed amount versus the equilibrium concentration remaining in solution, according to the equation: $X/M = K_d \cdot C_e$, where X is the mass of sorbate removed from solution (mg), M the mass of sorbent (g), C_e the solution equilibrium concentration (mg L^{-1}), K_d the distribution coefficient [(mg g^{-1})/(mg L^{-1})].

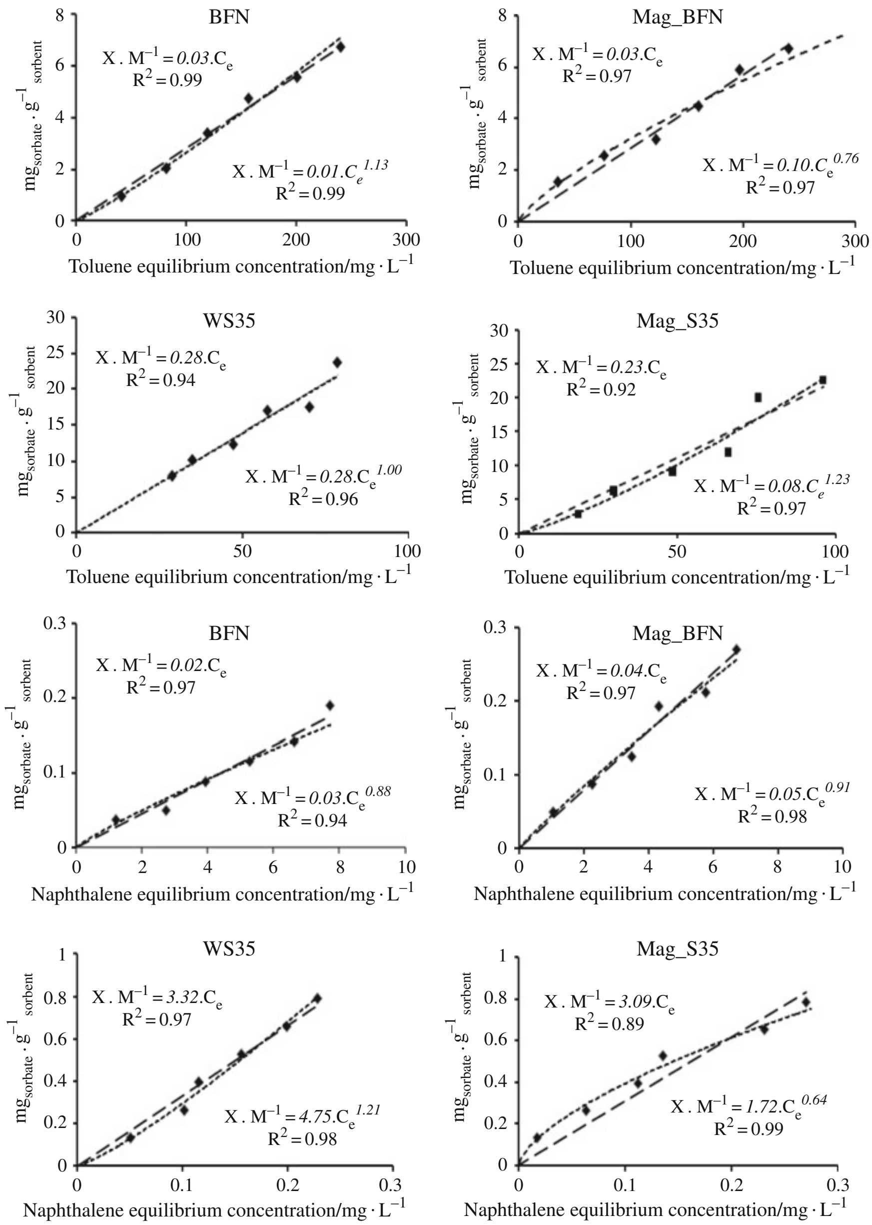
The Freundlich equation can be expressed by: $X/M = K_f \cdot C_e^{1/n}$, where K_f (L kg^{-1}) and n (dimensionless) are, respectively, the sorbate binding constant and a conditional index, which describes the shape of the isotherm [17]. Values of n less than 1 and greater than 1 represent, respectively, sorption results having upwardly concave or upwardly convex curvatures.

The equilibrium isotherms of toluene and naphthalene on BFN, Mag_BFN, WS35, and Mag_S35 are shown in Fig. 1. The applicability of the sorption model to experimental data is supported by the high correlation coefficients noticed in all cases.

The Freundlich parameters (n) were less than 1 for toluene sorption by BFN and Mag_S35 and for naphthalene sorption by WS35. The Freundlich parameters (n) were greater than 1 for toluene sorption by Mag_BFN and for naphthalene sorption by BFN, Mag_BFN, and Mag_S35. The value of n was equal to one for toluene sorption isotherm by WS35 (Fig. 1).

Toluene and naphthalene sorption by the BFN and Mag_BFN were negligible when compared to WS35 and Mag_S35 cases. The sorption isotherms of toluene by WS35 and Mag_S35 and of naphthalene by WS35 have much higher slopes, and are consistent with the concept of solute partitioning into the organic phase. According to Jaynes and Vance [3], the upwardly concave curvature ($n < 1$) can be

Fig. 1 Sorption isotherms for toluene and naphthalene by BFN, Mag_BFN, WS35, and Mag_S35



attributed to partitioning. The curvature is caused by an influence of the sorbate on the sorption medium, a cosorptive-enhanced process that results from enhanced toluene and naphthalene sorption. Note that the toluene sorption isotherm in Fig. 1 is a straight line as usually found for organoclays of this type. These results are consistent with previous observations [3, 17], and indicate that sorption involves partitioning of toluene and naphthalene between water and the OM phase formed by aggregation of the alkyl chains of the quaternary cations (DMDTA) [3, 17]. Not surprisingly, the more hydrophobic solute naphthalene (water solubility = 31 mg L^{-1}) is more strongly sorbed than toluene (water solubility = 518 mg L^{-1}). Studies using the Freundlich model to describe BTEX sorption on Wyoming organoclays (SWy-HDTMA) also indicate a partitioning process [8, 16].

Naphthalene sorption by Mag_S35 was stronger and nonlinear compared to toluene sorption. Mag_S35 has advantages and disadvantages when used as sorbent in environmental applications. As the adsorption isotherm is nonlinear, the ratio of sorbed-phase to aqueous-phase concentration decreases as the aqueous-phase solute concentration increases. WS35 and Mag_S35 exhibit strong solute uptake for toluene and naphthalene contaminants.

In all cases the Freundlich parameters (*n*) were greater than 1, corresponding to upwardly convex curvatures. This indicates that adsorption occurred on the surface and in the micropores of the samples and is consistent with the fact that the surface area and pore diameter are greater in Mag_S35 than in WS35 (Table 2). For Mag_BFN, WS35 and Mag_S35 the correlation coefficients (R^2) indicate that the data fit the Freundlich model better than the linear model, except in BFN case (Fig. 1).

From the K_d values (Fig. 1) and the OM content of the samples (OM) estimated from thermal analysis in part I (Table 2), OM corrected sorption coefficients (K_{om}) that normalize the hydrocarbon sorption on an OM basis can be calculated from the equation: $K_{om} = K_d/\mathrm{OM}$. As OM values to obtain K_{om} must be used on respective initial mass basis and Table 2 OM data are on dried basis, Fig. 2 shows TG and DTG data of WS35 and Mag_S35 samples on respective initial mass basis, to obtain the respective dried/initial mass percentages, to calculate their OM values on proper basis.

From Fig. 2, it can be seen that WS35 and Mag_S35 dried sample masses represent, respectively, 98.80 and 98.27% of their initial masses. Thus, the OM values on initial mass basis, which will be used to obtain K_{om} values, are: $\mathrm{OM}_{\mathrm{WS35}} = 31.86 \times 98.80 = 31.48\%$ and $\mathrm{OM}_{\mathrm{Mag\_S35}} = 16.67 \times 98.27 = 16.38\%$.

The value of K_{ow} for a compound is equal to the ratio of the solubility of the compound in water-saturated octanol to its solubility in octanol-saturated water. Similarly, the K_{om} value for an organic compound is a distribution ratio of the compound between an organic cation derived material and water. Thus, the adsorption efficiency of the OM in samples as a partition medium can be compared with that of octanol by dividing the K_{om} values by the K_{ow} value, as shown in Tables 3 and 4 as log ($K_{om} \cdot K_{ow}^{-1}$) [17].

The partitioning parameters (Tables 3, 4) measured in this study agree well with values observed with other organoclays [16]. Log K_{om} values for toluene and naphthalene for WS35 were 2.95 and 4.02, respectively, which are comparable to the values of 3.05 and 4.23, respectively, reported by Jaynes and Boyd [16] for SAz-HDTMA.

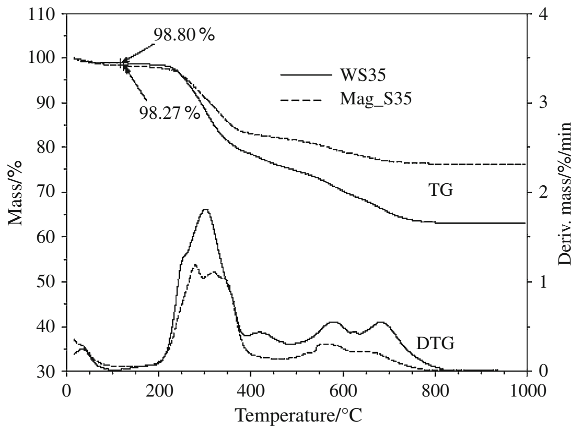


Fig. 2 TG and DTG curves of WS35 and Mag_S35 samples

Table 3 Partitioning parameters for toluene retention by organoclays

Samples	K_d/ L kg^{-1}	K_{om}/ L kg^{-1}	log K_{om}	log($K_{om} \cdot K_{ow}^{-1}$)
WS35	279.65	888.41	2.95	0.26
Mag_S35	225.31	1375.38	3.14	0.45
SAz-HDTMA [16]	319.00	1118.51	3.05	0.36
SWy-HDTMA [16]	74.00	351.04	2.55	−0.14

Octanol–water partitioning constant (log K_{ow}) value is 2.69 [18]

Table 4 Partitioning parameters for naphthalene retention by organoclays

Samples	K_d/L kg^{-1}	K_{om}/L kg^{-1}	log K_{om}	log ($K_{om} \cdot K_{ow}^{-1}$)
WS35	3,320	10547.16	4.02	0.65
Mag_S35	3,090	18862.62	4.28	0.91
SAz-HDTMA [16]	4,818	16893.41	4.23	0.86
SWy-HDTMA [16]	1,130	5360.53	3.73	0.36

Octanol–water partitioning constant (log K_{ow}) value is 3.37 [4]

Log K_{om} for toluene and naphthalene for Mag_S35 were 3.14 and 4.28, respectively, which are comparable to the values of 2.95 and 4.02 for WS35, as well as to those of SAz-HDTMA. The positive log ($K_{om} \cdot K_{ow}^{-1}$) values for WS35 and Mag_S35 correspond to a somewhat greater retention of toluene and naphthalene when compared to an octanol medium.

Conclusions

- The surface area of Mag_BFN and Mag_S35 composites are much higher than the respective BFN and WS35 precursor clays, due to the morphology of the added iron oxides on respective clays.
- The Freundlich model to evaluate the adsorption is more indicated than the Linear model for practically all the cases.
- The OM content of WS35 and Mag_S35, determined by the TG method developed by the authors, allows one to obtain the OM sorption coefficient (K_{om}).
- As WS35 and Mag_S35 have interlayer space values consistent with paraffin complexes, the positive log ($K_{om} \cdot K_{ow}^{-1}$) values obtained for sorption data indicate that they show a greater retention of toluene and naphthalene than octanol. However, these materials are much more selective for naphthalene than for toluene sorption.
- The presence of the iron oxides compounds on the external surface of Mag_BFN and Mag_S35 iron oxide–clay composite does not change their toluene

and naphthalene sorption capacity, when compared to respective BFN and WS35 sorption data.

- The results of this study show that WS35 organoclay and the iron oxide/organoclay Mag_S35 composite are effective sorbents for removing organic contaminants from water, indicating their potential use in environmental applications and technologies.
- The main iron oxide phase present in Mag_BFN and Mag_S35 is maghemite (γ-Fe_2O_3). This fact allows removing these sorbents from the effluent after use, by a magnetic separation process.

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