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Studying competitive retention of phthalate esters by humic acid under multi-variable experimental design optimization: interaction between experimental factors

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ABSTRACT

Retention of phthalic acid esters (dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), and benzylbutyl phthalate (BBP)) by humic acid (HA) was addressed. The influence of experimental conditions: mass of HA, solution pH, temperature, and contact time on competitive uptake of esters were investigated and optimized under the frame of multi-variable experimental design. Conducting multi-factor process using appropriate design of experiment reduce the size of experimental work. Based on a proper experimental design, 11tests were required to investigate the uptake of phthalic esters from solution over the experimental conditions including HA mass (10, 25, and 50 mg/L), pH (6.0, 7.0, and 8.0), contact time (1.0, 5.0 and 16.0 h), and temperature (25.0°C, 35.0°C and 45.0°C). Mathematical relationships between independent variables (HA mass, pH, contact time, and temperature) and dependent variables (PAE uptake) were derived for each ester. For example, the DMP interaction by HA was presented as: DMP Retention (mg/kg) = 95.43 – 44.52 HA – 0.30 pH – 6.89 Time + 11.41 Temp + 0.97HA × Time – 1.31HA × Temp – 4.74 pH × Time – 5.05 Time × Temp. The above equation indicated a strong influence of single factors (HA mass, pH, contact time, and temperature) and the interaction terms (HA × Time, HA × Temp, pH × Time, and Time × Temp) on DMP uptake. Based on the outputs of the design, the average uptake of DMP was 95.43 mg/kg and better removal was achieved at lower HA dosages (10 mg/L) and higher temperature (45.0°C). Moreover, raising pH from 6.0 to 8.0 had a small influence on DMP uptake (the coefficient has a small and negative value –0.3). Although, contact time showed a negative influence on DMP removal (coefficient – 6.89), this factor has a positive influence but at longer contact time (HA × Time coefficient + 0.97). The negative influence of interaction terms (pH × Time and Time × Temp) expected the better DMP removal when these factors set at their opposite values. The adopted design of experiment has better performance to predict the influence of experimental factors compared with the classical signal-factor analysis.

Keywords: Design of experiments; Competitive interaction; Phthalate plasticizers; Humic acid

1. Introduction

Phthalic acid esters (PAEs) are often used as plasticizers to increase the flexibility of plastic materials [1,2]. PAEs are also used in a large variety of products including cosmetics, personal care products, perfume, hair spray, soap, shampoo, and skin moisturizers [3]. Moreover, PAEs were heavily used in flexible plastic, vinyl toys, shower curtains, wallpaper,

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food packaging, and plastic wrap [3]. High-molecular-weight PAEs (C7–C11) are primarily used as plasticizers in polyvinyl chloride-based plastic products [4,5]. Based on animal-scale studies, the long exposure to PAEs resulted in serious changes in fetal development of the reproductive system [6–8]. Due to their intense applications, PAEs have been detected in many matrices including, foodstuff, consumer products, indoor air/dust, and inside public vehicles [9]. Unfortunately, conventional treatments units were not effective to remove PAEs, then, there is raising concerns on their unwanted health effects on living organisms.

Numerous studies have been addressed PAEs removal of from environmental matrices [4,6]. Physical, chemical, and biological treatment procedures were proposed to eliminate PAEs from the environment [5]. Among tested cleaning methods, oxidation-based methods were found practical to eliminate PAEs [5]. Recently, retention of PAEs by humic acid and other surfaces was also critically addressed [2,8].

HA is making a large fraction of organic matter that present in soil or aquatic environments [10]. HA has a large molecular structure with diversity of functional groups including phenolic and carboxylic groups [10]. In fact, HA was tested as a selective surface (due to the presence of many functional groups) to retain wide selection of pollutants [11–17]. Additionally, HA have two extra options to attract pollutants including partial atomic charges and high aromaticity [18]. The movement of organic pollutants in the environment is simulated through interaction with HA. Accordingly, HA had attracted environmentalists due to its mutual interaction with soil and water and its ability to transport pollutants to different environments [14,16]. Among common pollutants, polychlorinated biphenyls PCBs and pesticides were received high attention and many researchers addressed their movement in the environment via interaction with HA [15,17,19].

Very limited research was reported on the interaction of PAEs by humic acid. Schulten et al. [20] 2001 studied interaction of diethyl phthalate by HM. In a recent study, Gao and co-workers [8] have investigated the effect of temperature and pH on interaction of dibutyl phthalate by HA. In the same line, the effect of HA on phthalate ester (Di-(2-ethylhexyl) phthalate) uptake by vermiculite was systematically investigated [21].

Interaction of pollutants by HA is a multi-factor process and the most common factors affecting the process are: HA mass, concentration of analyte, solution pH, agitation time, and temperature [8,14,20,21].

In general, the effect of a certain factor on solute interaction is studied while keeping other factors at certain limits which are known as univariate optimization. Recently, there is an attention to apply optimized design of experimental (DoE) to run few numbers of tests to investigate the effect of all factors in a short time [22–25]. The most common designs are full-factorial, fractional-factorial, Plackett-Burman, central composite, and simplex centroid designs [22–26]. In 1997, Brereton and based on Plackett-Burman design had formulated new designs that can investigate many factors while running few number of experimental tests. For example, nine tests are needed to investigate the effect of eight factors [26]. In any experimental design, it is necessary include the most dominating factors and the total number of tests is dependent on the number of the levels of the selected factors. In Brereton`s method, nine tests are needed to run three-level factorial design [26]. Dehghani and co-workers [23] have applied an optimized design along with surface response methodology (total 26 tests) to determine the best conditions for malathion uptake by nano-size activated carbon. Based on four-level central composite design (total 30 tests), effect of pH, contact time, solute concentration, and mass of adsorbent on uptake of Hg and As ions was reported [22]. Al-Degs and co-workers [27,28] have applied principal component analysis to address the significance of certain operational factors on solute uptake from solution.

To the best of our knowledge, there is no published document specifically devoted to study the competitive interaction of five phthalates (dimethyl phthalate, diethyl phthalate, dibutyl phthalate, diisobutyl phthalate, *n*-butylbenzyl phthalate) by HA which is rather significant to simulate movement of phthalate esters in the environment. Moreover, application of a suitable design of experiment to explore the optimum operational conditions toward phthalates uptake will be addressed. The aims of the current works are: (a) investigating the influence of HA mass, solution pH, contact time, and temperature on interaction of five phthalate esters; and (b) evaluating the optimal operational conditions for PAEs uptake following a three-level-four-factor design based on Brereton’s method along with advanced regression analysis.

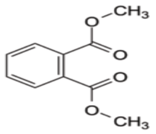
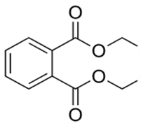
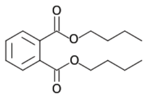
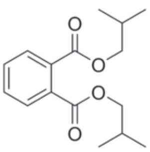
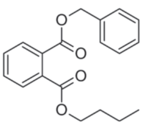
2. Experimental setup

2.1. Humic acid, characterization tests, reagents, and standard solutions

Humic acid was purchased from Sigma-Aldrich® (USA) in powder form. Contents of surface functional groups were quantified using Bohem`s technique [29,30]. The specific surface area and total cation exchange capacity were simply measured following methylene blue adsorption test at 25ºC. Elemental analysis was made using elemental analyzer (CHN Auto analyzer, PerkinElmer, USA). pH-drift method was adopted to measure pH of zero point of charge pH_{PZC} [31]. The surface of HA was examined by recording infrared (IR) spectra before and after removal of PAEs from solution (PerkinElmer Dynascan Interferometer, USA). Samples were placed in a small crystal cup (50 mm in diameter and 10 mm in depth) and sealed before scanning and the temperature was controlled at 25°C. The degree of aromatization of HA was estimated based on the Wang`s method which accomplished by recording absorbance values at 465 and 665 nm [32]. Phthalate esters were purchased from Sigma-Aldrich®(USA). All solvents were purchased from Fisher® and Sigma-Aldrich® (USA). Structural formulae along with some significant parameters of PAEs are provided in Table 1.

Standard stock solutions of phthalates were individually prepared in methanol at concentration of 1,000 µg/mL. To maintain constant ionic strength and to prevent biodegradation of esters, all diluted dilutions were made by a solution containing 0.01 M $CaCl_2$ and 0.004 M NaN_3 [8,21]. Mobile phase was freshly prepped before chromatographic analysis.

Table 1
Chemical structures of PAEs[a]

Phthalate ester	Abbreviation	Structural formula	Solubility (mg/L)	log$P$
Dimethyl phthalate	DMP		4,200	1.61
Diethyl phthalate	DEP		1,100	2.38
Dibutyl phthalate	DBP		11.2	4.45
Diisobutyl phthalate	DIBP		20.0	4.46
Benzylbutyl phthalate	BBP		2.7	4.59

[a] The provided parameters were collected from (Staples et al. 1997).

2.2. Dominating experimental factors on PAEs interaction: a screening study

The tested experimental factors on esters uptake are mass of HA, pH, contact time, and temperature. Adsorption testes were carried out over the concentration range 10–50.0 mg/L. Solution pH was varied over the range 6.0–8.0 to avoid any serious changes in the HA structure or hydrolysis of esters. Effect of temperature was changed over the range 25°C–45°C. Uptake of phthalates was investigated over period 1.0–16.0 h. In all optimization tests, the concentration of phthalates was maintained at 20.0 mg/L to get equal competition chance among solutes toward HA.

2.3. Adsorption isotherms: single and multi-solute systems

Initial studies indicated higher uptake of esters at lower HA content, moderate pH and short contact time. Accordingly, concentration-variation isotherms were conducted at pH 7.0, temperature 45°C, and over the concentration range 5.0–35.0 mg/L to study removal affinity of PAEs by HA. A freshly isolated HA was dissolved in small volume of 0.1 M NaOH and added to phthalate solutions to give a final content of 10.0 mg/L. Then, the final pH was adjusted to 7.0. The mixtures were sealed and agitated for 1.0 h at 45°C using a thermostated shaker. The outlined procedure (precision < 5%) was repeated for each phthalate. After completion of agitation, a 50 ml of the mixture was extracted 25.0 mL ethyl acetate and the organic layer was separated and added to 5.0 g anhydrous sodium sulphate to remove moisture. The organic layer was then passed through Al_2O_3 column and eluted with 20 mL n-hexane. The collected mixture was evaporated to dryness at 45°C and 12 mbr. The residue was re-dissolved in 2.0 ml n-hexane and analyzed by liquid chromatography. All PAEs were quantified using liquid chromatography-DAD at detection wavelength 226.0 nm (Shimadzu LC1100, Japan) using C_{18} column (250 mm × 4.6 mm × 5 μm). Injection volume was 20.0 μL. The mobile phase was acetonitrile/water (70:30 v/v) and the flow rate was set at 1.0 mL/min. Separation of phthalates was accomplished within 18.0 min. Five calibration graphs were created by plotting peak area against concentration (1.0–10.0 mg/L) for each phthalate. For multi-solute system, the earlier procedure was repeated using mixture of PAEs and over the same range 5.0–35.0 mg/L. The amount of retained phthalate was estimated as:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_o, C_e, V, and m are the initial phthalate content (mg/L), equilibrium phthalate content (mg/L), volume of solution (L), and HA is the mass (g or kg).

2.3.1. Modeling adsorption data and competition factors

Adsorption isotherms were plotted and different models were tested including Langmuir, Freundlich, and competitive-Langmuir isotherms. Langmuir equation which assumes monolayer surface coverage, equal-energy active sites and no solute-solute interactions is represented as [33–35]:

$$q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \tag{2}$$

where $Q_{\max}$ (mg/g) is the amount adsorbed at complete monolayer coverage and K_L (L/mg) is Langmuir parameter taken as equilibrium constant. Freundlich model which assumed a heterogeneous surface has the general form [33,34]

$$q_e = K_F C_e^{\,n} \tag{3}$$

where K_F ($mg^{1-n}\,L^{-n}\,g^{-1}$) and n are equilibrium constant indicative of relative adsorption capacity and model exponent which characterize qusai-Gaussian energetic heterogeneity of the surface. A favorable uptake of phthalate is confirmed by higher n value (1–10). For multi-solute adsorption, the competitive-Langmuir model of n solutes is presented as [33,35]:

$$q_{e,i} = \frac{Q_{\max,i} K_{L.i} C_{e,i}}{1 + \left(\sum_{i=1}^{n} K_{L,i} C_{e,i}\right)} \tag{4}$$

where $q_{e,i}$, $q_{e,i}$, $Q_{\max,i}$, and $K_{L,i}$ are the surface concentration of ith phthalate, equilibrium concentration of ith ester, maximum adsorption capacity for i^{th} phthalate, and the equilibrium constant for the i^{th} phthalate, respectively. The model parameters were estimated as outlined elsewhere [33]. The parameters of the above models were estimated following a non-linear fitting methodology. The chi-square value, X^2, was then estimated to assess the performance of the model [36]:

$$X^2 = \sum_{i=1}^{n} \frac{(q_{\text{pred}} - q_{\text{exp}})^2}{q_{\text{pred}}} \tag{5}$$

where q_{pred} and q_{exp} are the predicted and measured adsorption values of phthalates, respectively, while n presented number of experimental points. Higher X^2 values reflected the poor performance of the model to present adsorption data. The competition between phthalates was measured by estimating competition factor (CF) [37]:

$$\text{CF} = \frac{\text{Q}_{\max}(\text{Mixture} - \text{PAEs})}{\text{Q}_{\max}(\text{Single} - \text{PAE})} \tag{6}$$

where $Q_{\max}$ (mixture-PAEs) and $Q_{\max}$ (Single-PAE) are the maximum retention capacities estimated from single and multi-solute isotherm for the phthalate, respectively. In case of positive competition, CF should be higher than unity and adsorption is enhanced by other solutes. For CF = 1, adsorption is proceeded with no competition. The general case is CF < 1 which proved that solute's affinity is reduced due to negative competition with other solutes [35,37].

2.3.2. Factorial analysis: design of experiments, factors coding, and optimization the process

The large number of adsorption tests would be reasonably reduced following appropriate design of experiments DoE [22–26]. Factorial design is necessary to save time while studying the influence of all factors on PAEs retention by running limited number of tests. Moreover, factorial design can detect the possible interaction among factors. In factorial analysis, the proper selection of the levels of factors and coding of these levels is necessary to end up with informative results. Initially, three levels of each factor were selected and coded as –1, 0, and +1. The selected levels along with codes for the factors are provided in Table 2.

As indicated in Table 2, the selected levels reflected the lower, middle and higher limits of the factor and this is necessary to uncover the possible interaction between factors. Brereton`s tables were adopted to build the design [26] as shown in Table 3.

Eleven adsorption tests were carried out as depicted in Table 3 to locate the best combination of factors leading to

Table 2
Coding of the levels of different factors (independent variables)[a]

Factor	Level	Code
Mass (mg/L)	Low 10.0	–1
	Middle 25.0	0
	High 50.0	+1
pH	Low 6.0	–1
	Middle 7.0	0
	High 8.0	+1
Contact time (hour)	Low 1.0	–1
	Middle 5.0	0
	High 16.0	+1
Temperature (°C)	Low 25.0	–1
	Middle 35.0	0
	High 45.0	+1

[a]For each experimental factor, the levels were coded to balance the numerical variations between levels and to get accurate influence of factors on retention of each PAE

Table 3
Experimental design matrix and retention values of PAEs based on Brereton's method[a]

Test	Independent variables				Dependent variables				
	HA (code)	pH (code)	Contact Time (code)	Temperature (code)	Retention value (mg/kg)				
					DMP	DEP	DBP	DIBP	BBP
1	25 (0)	7 (0)	5 (0)	35 (0)	111.6	39.2	42.5	37.1	23.1
2	10 (–1)	8 (+1)	16 (+1)	35 (0)	126.3	111.4	99.2	91.6	106.2
3	50 (+1)	8 (+1)	5 (0)	45 (+1)	62.5	12.6	19.8	22.3	9.7
4	50 (+1)	7 (0)	16 (+1)	25 (–1)	39.2	11.2	12.6	12.7	14.3
5	25 (0)	8 (+1)	1 (–1)	25 (–1)	87.0	35.6	35.2	28.1	22.5
6	50 (+1)	6 (–1)	1 (–1)	35 (0)	49.1	16.7	15.6	25.2	18.6
7	10 (–1)	6 (1)	5 (0)	25 (–1)	121.7	117.0	96.0	99.1	91.2
8	10 (–1)	7 (0)	1 (–1)	45 (+1)	162.3	134.2	122.4	63.8	115.4
9	25 (0)	6 (–1)	16 (+1)	45 (+1)	99.2	47.2	45.6	45.2	44.6
10	50 (+1)	8 (+1)	16 (+1)	45 (+1)	41.2	13.6	19.0	20.3	25.0
11	10 (–1)	6 (–1)	1 (–1)	25 (–1)	129.4	126.3	93.2	105.7	102.2

[a]Tests 1–9 were designed based Brereton's method (Brereton 1997) while tests 10 and 11 were added to the design to account for the factors when set at their extremes. Test 1 (which represents the middle of the design) was repeated five times to assess the overall precision of the experimental procedure

maximum retention of phthalates. Test 1 was repeated five times and in this test the factors were set at their middle values (Table 3). It is common in factorial analysis to model experimental data by building a relationship between the factors or x-independent variables (HA mass, pH, temperature and contact time) and y-dependent variables (PAEs retention). The relationship between independent and dependent variables is presented as [26]:

$$y = b_0 + b_1\text{HA} + b_2\text{pH} + b_3\text{Temp} + b_4\text{Time} + b_{12}\text{HA} \times \text{pH} + b_{13}\text{HA} \times \text{Temp} + b_{14}\text{HA} \times \text{Time} + b_{23}\text{pH} \times \text{Temp} + b_{24}\text{pH} \times \text{Time} + b_{34}\text{Temp} \times \text{Time} \tag{7}$$

The value of intercept b_0 is indicated the average retention value of the solute in the tests. Linear terms (b_1–b_4) allow for a direct relationship between phthalate retention and the studied factors. The factor of higher coefficient has higher linear effect on solute uptake. If $b_1 >>> b_2$ then solute retention is strongly dependent on mass HA compared with pH. Moreover, positive coefficient reflected a direct relation of the factor with retention value and vice versa. Interaction terms b_{12}–b_{34} (which often significant when modeling adsorption systems) are necessary to uncover the nature of interaction between factors on PAEs retention. For example, ester retention at low pH and high HA mass may be better at the same mass but at higher pH. In fact, the influence of two factors (pH and temperature for example) on solutes retention is rarely independent. For example, if $b_{12} >> b_{13}$ (positive coefficients) then interaction between HA-pH is more significant than HA-Temp toward ester retention. Moreover, the negative coefficients indicated better retention if both factors fixed at their opposite limits [22,25,26]. Initial analysis indicate that non-linear terms (HA × HA, pH × pH, Time × Time, and Temp × Temp) were not significant for modeling Eq. (7) and hence eliminated from the relation. Analysis of variance (ANOVA) was adopted to test the significance of all terms on PAEs uptake. Regression analysis and ANOVA test were performed using statistical packages available in Excel®. Assessment of models were assessed at (α) at 95% confidence level ($p = 0.05$). The factor or term is significant to the model at high F value and p value < 0.05 [24,25]. Moreover, coefficient of determination (R^2) and Fisher's statistical test (F test) were estimate to assess the significance of the model [24,25].

3. Results and discussion

3.1. Chromatographic separation and polarity of PAEs

Based on the proposed chromatographic procedure, PAEs were separated within 20.0 min a typical chromatogram is shown in Fig. 1.

As indicated in Fig. 1, optimum separation of dimethyl phthalate (DMP), diethyl phthalate (DEP), and benzylbutyl phthalate (BBP) while a small peak-overlap was obtained for diisobutyl phthalate (DIBP) and dibutyl phthalate (DBP). The solutes were eluted according to the trend: DMP (4.12 min), DEP (5.78 min), BBP (15.47 min), DIBP (17.11 min), DBP (17.74 min). Detection and quantification limits were estimated according to signal-to-noise ratio of 3 and 10, respectively. PAEs were detected in solution down to 0.35, 0.26, 0.15, 0.10, and 0.05 mg/L for DBP, DIBP, BBP, DEP, and DMP, respectively. Quantification limits were 1.17, 0.87, 0.50, 0.33, and 0.17 mg/L, respectively. The polarity of PAEs would be predicted from the elution trend, the faster eluted is the more polar. Accordingly, DMP and DEP exhibited higher polarity compared to the rest of phthalates. The polarity of solutes deceased in the following trend: DMP > DEP >> BBP > DIBP > DBP. The earlier trend was in agreement with the solubilities and hydrophobicities of the solutes, both DMP and DEP were highly solubility in water and had lower hydrophobic natures compared with the rest of phthalates (Table 1).

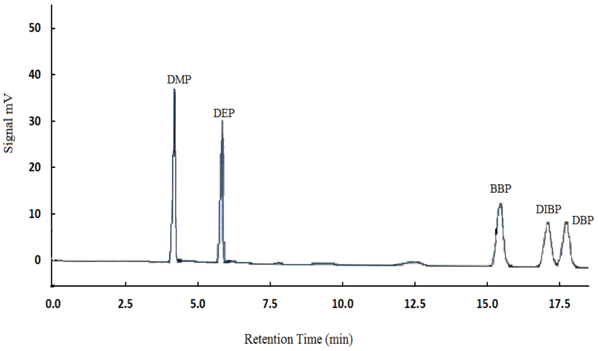


Fig. 1. Chromatographic separation of phthalates (3.0 mg/L) according to the proposed procedure.

3.2. Retention of PAEs from solution: single and multi-solute isotherms

Removal of organic pollutants by HA and sediments containing HA was investigated in the literature [38], however, few studies addressed the uptake of PAEs by HA. Retention of PAEs from single and multi-solute systems were measured at the following conditions: concentration range 5.0–35 mg/L, pH 6.0, Temperature 45°C, Contact Time 1.0 hr, Volume 100 mL and mass 1.0 mg. Isotherms are shown in Fig. 2.

For single-solute isotherms (Fig. 2(a)), L2-shape isotherms were obtained for the five phthalates according to the Giles and Smith classification [39]. This isotherm indicated that PAEs interaction by HA was attained by forming one layer only [39]. In fact, L2-type indicated the high affinity between PAEs and HA at lower concentrations and at higher concentrations the surface becomes more saturated. As shown in Fig. 2(b), the L2-isotherm for competitive system was also observed [40] and this behavior is not commonly reported in the literature. In this study, the typical L2-isotherm was attributed to modest competition among PAEs toward active sites. The competition among solutes should increase at higher concentrations and this affect the typical shape of L2 isotherm. To measure the maximum retention of PAEs and study the mechanism of interaction, the data were further handled by different isotherms and the results are provided in Table 4.

3.2.1. Langmuir isotherm

This model was workable for presenting retention of all PAEs from both single and multi-solute systems. For single solute-solution, acceptable X^2 (12–28) values were obtained for this model. On the other hand, Q_{max} values predicted by Langmuir isotherms (142.6–221.3 mg/kg) were measurably larger than experimental ones which observed from isotherms (Fig. 2(a)). The same behavior was also noted in multi-solute isotherm where higher retentions values (82.0–171.3 mg/kg) than those noted experimentally particularly for DIBP (Fig. 2(b)). In fact, retention values confirm a significant reduction in PAEs uptake in multi-solute system and obviously due to solute competition for active sites. Although, the individual retention of each single phthalate was reduced, the final performance of HA was excellent with a combined uptake value of 615.2 mg/kg (sum of the maximum retentions estimated by competitive Langmuir model). For both systems, similar removal trends were observed: DMP > DEP > DBP > BBP > DIBP. The good applicability of this model reflected the homogenous distribution of active sites on HA, as the model assumed homogenous distribution of active sites [26]. Although, the model was workable for presenting PAEs retention from solution, consideration of other isotherms is still necessary.

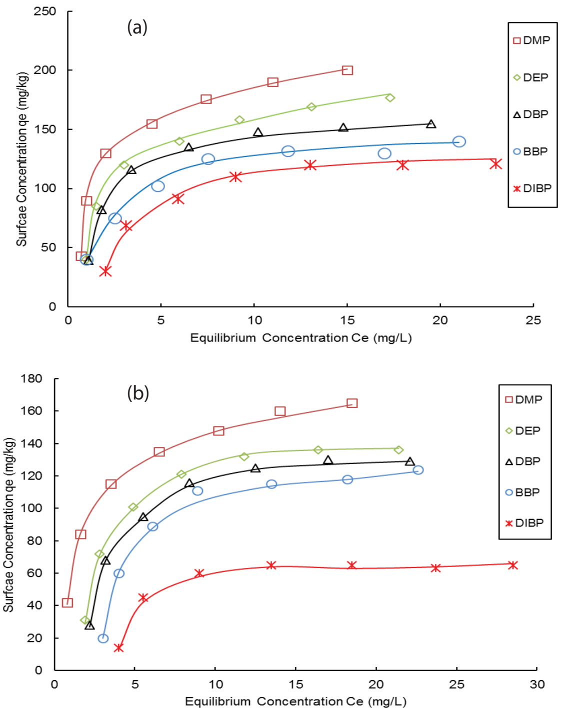


Fig. 2. Single-solute and competitive adsorption isotherms of PAEs by HA. Conditions: concentration range = 5.0–35 mg/L, pH = 6.0.0, Temperature = 45°C, Contact time = 1.0 h, Volume = 100 mL and mass = 1.0 mg.

3.2.2. Freundlich isotherm

This common model was not as effective as the previous one as indicated from X^2 value (55–78) and (49–68) for single and multi-solute systems, respectively. Although, was not highly applicable, the corresponding n values indicated the favorable uptake of PAEs in both cases. This model predicted the same removal trend as before: DMP > DEP > DBP > BBP > DIBP as confirmed from K_F values. The poor performance of this model supported the fact that retention of PAEs was not favorable at higher concentration. The competition between PAEs in multi-solute solution would retard the formation of a multilayer on the surface.

3.3. Competitive-Langmuir isotherm

Among the tested models, competitive-Langmuir model generated the best prediction for solute retention in the mixture. The model has good performance for presenting retention of PAEs from the mixture as confirmed from statistical indicator (8–11). As indicated in Table 4, maximum values were 165.7, 139.4, 128.4, 114.3, and 67.4 mg/kg for DMP, DEP, DBP, BBP, and DIBP, respectively. Compared with other phthalates, DIBP was highly affected as the retention value was reduced from 142.6 to 67.4 mg/kg.

Table 4
Parameters of the tested adsorption models and competition factors for PAEs interaction by HA

Model	DMP		DEP		DBP		BBP		DIBP	
	Parameter	X^2	Parameter	X^2	Parameter	X^2	Parameter	X^2	Parameter	X^2
Single-Solute system										
LM	Q_m 221.3 K_L 0.57	27	Q_m 202.4 K_L 0.40	25	Q_m 179.5 K_L 0.42	16	Q_m 156.2 K_L 0.38	12	Q_m 142.6 K_L 0.23	28
FM	K_F 87.0 n 0.33	62	K_F 67.1 n 0.36	70	K_F 63.4 n 0.31	73	K_F 57.6 n 0.31	55	K_F 43.1 n 0.36	78
Five-Solute system										
LM	Q_m 171.3 K_L 0.54	21	Q_m 142.2 K_L 0.42	27	Q_m 139.5 K_L 0.39	19	Q_m 128.5 K_L 0.35	16	Q_m 82.0 K_L 0.20	24
CLM	Q_m 165.7 K_{CL} 0.52	11	Q_m 139.4 K_{CL} 0.39	10	Q_m 128.4 K_{CL} 0.41	9	Q_m 114.3 K_{CL} 0.37	11	Q_m 67.4 K_{CL} 0.24	8
FM	K_F 65.8 n 0.32	52	K_F 52.8 n 0.33	63	K_F 48.1 n 0.29	49	K_F 41.4 n 0.36	57	K_F 38.5 n 0.27	68
CF	0.75		0.69		0.72		0.73		0.47	

3.3.1. Competition factors

The competition among phthalates was finally assessed by estimating CF from retention values of single and multi-solute systems. Retention values needed to calculate competition factor CF were obtained from competitive Langmuir model (CLM) due to its better performance for modeling isotherms. As shown in Table 4, competition values were 0.75, 0.73, 0.72, 0.69, and 0.47 for DMP, BBP, DBP, DEP, and DIBP, respectively. For all esters, CF values were less than unity, confirming a negative competition among solutes. The least affected solute was DMP with a value of 0.75 and the most affected was DIBP with a CF value 0.47. HA has high specific surface area and many functional groups, therefore, it was able to interact with the five solutes with different mechanisms including H-bonding and dipole–dipole forces.

3.4. Mechanism of phthalates interaction by HA

In fact, degree of aromatization, molecular weight, and degree of condensation of the aromatic rings available in HA would be investigated using simple UV-analysis [8,32]. A higher A_{465nm}/A_{665nm} ratio reflected a lower humic degree and hence simpler molecular structure. The spectral analysis indicated that the ratio A_{465nm}/A_{665nm} was equal to 1.1 which confirmed the higher aromatization and more complex structure with many functional groups capable for attracting PAEs [8,16,19,32]. The physicochemical properties of isolate humic acid are presented in Table 5.

The provided analysis indicated the surface of isolated HA is high (623 m^2/g) and this is necessary for physical removal of organic pollutants from solution. Moreover, a high cation exchange capacity (CEC) was reported and this would improve interaction of positively-charged pollutants form solution. In the same time, titration outputs also confirm the presence of high concentration of acidic groups (carboxylic, phenolic, and alcoholic) compared with basic ones (lactonic) and this was in agreement with published results [19]. The acidic pH$_{ZPC}$ (5.2) was expected and also close to commercial HAs. In fact, all retention tests were reported at mild conditions (6.0–8.0) and at this environment the net surface change of the substrate is negative and can improve retention of positively charged PAEs molecules. Moreover, at this mild range of pH the hydrolysis of phthalate esters is not possible. As already known, hydrolysis of esters by water is highly accelerated at acidic and basic solutions [8]. On the other hand, IR analysis of HA before and after PAEs uptake was useful to elucidate the nature of interaction between HA and PAEs. The collected IR spectra are presented in Fig. 3.

Table 5
Physiochemical analysis of HA

Test	Parameter and value			
Elemental	C%	H%	N%	S%
analysis	55.8 (±0.4)	6.5 (±0.2)	4.4 (±0.2)	0.9 (±0.1)
Functionality	Carboxylic	Phenolic	Alcoholic	Lactonic
(mmol/g)	6.5 (±0.2)	1.4 (±0.1)	0.8 (±0.2)	1.4 (±0.1)
SSA (m^2/g)	623			
CEC (cmol/kg)	210			
pH$_{ZPC}$	5.2			

IR studies are often applied to elucidate nature of interaction between HA and target solutes including PAEs [8]. The mechanism of interaction would be deduced from the shift in the position or intensity of a certain peak. Therefore, the IR spectra of HA, adsorbate, and HA-adsorbate is necessary for identification of the nature of interaction in the solution. The IR spectra of DMP (favorably removed by HA), HA, and HA-DMP are depicted in Figs. 3(a) and (b). For DMP (Fig. 3(a)), the major IR peaks were 3,001, 1,721, 1,433, 1,383, 1,275, 1,119, 1,073, 773, and 742 cm^{-1}. The peaks 3,001 were attributed to symmetric and asymmetric stretching vibrations of saturated C–H in the molecule. The strong peak 1,721 cm^{-1} was attributed to the C=O stretching vibration in the ester molecule, while, 1,275 and 1,119 cm^{-1} were accounted for C–O stretching in ester. The peaks appeared at 1,433, 1,073, and 1,038 cm^{-1} were attributed to the stretching vibrations of the aromatic C–C bond and CH_3 group. Finally, the band positioned at 773 and 743 cm^{-1} was both attributed to ortho-substituted benzene stretching vibrations [8]. IR spectra of HA indicated the following main peaks: 3,379, 2,921, 1,582, 1,371, 1,043, and 461 cm^{-1}. The peak positioned at 3,379 cm^{-1} was mainly attributed to the vibrations of alcoholic and carboxylic functional groups. The peak at 1,371 cm^{-1} indicated O–H bending vibration of carboxylic or C–O stretching vibration of phenolic groups. However, the peak positioned at 1,043 cm^{-1} was attributed to C–O stretching vibration of the carboxylic group. IR analysis was in agreement with Bohem`s results which indicated the presence of carboxylic group in HA. The sharp IR peak observed at 2,921 cm^{-1} attributed to aliphatic C–H stretching vibrations. The large absorption peak at 1,582 cm^{-1} would reflect

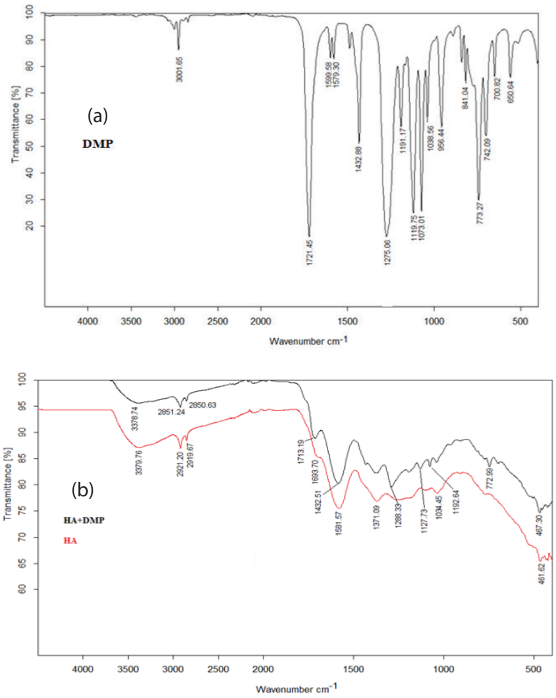


Fig. 3. FTIR spectra HA, DMP, and HA-DMP.

the high aromatisation degree in HA which was consistent with low spectral ratio A_{465nm}/A_{665nm} [32]. Finally, the spectra of DMP+HA do indicate the interaction of ester molecule and HA. The main characteristics IR bands of the ester molecule (1,721, 1,275, 773 cm^{-1}) were detected in the IR spectrum of the complex. The band detected at 1,713 cm^{-1} evidenced the presence ester molecule which has an intense IR peak at 1,721 cm^{-1} with a shift of 8 cm^{-1}. In the same time, the band positioned at 1,288 cm^{-1} was attributed to the detection of ester molecule which has a strong IR band at 1,275 cm^{-1} with a shift of 13 cm^{-1}. The IR analysis supported the formation a complex between ester molecules and the surface of HA.

3.5. Interaction behavior of PAEs with HA: multivariate analysis

Following Brereton`s procedure (Table 3), 11 experiments were conducted to account for the influence of experimental factors on retention of PAEs by HA. The analysis of the optimized design lead to building a second-order polynomial model and the parameters needed to validate the derived equations were *P*-value (95% confidence level), *F*-value, lack of fit P-value, R^2 and adjusted R^2 [23–25]. The quality parameters of the final regression are provided in Table 6

Statically, larger *F*-value and smaller *p*-value are the most significant coefficients. The provided results in Table 6 showed that final multivariate regression was statistically significant with *F*-values of 5.3, 11.4, 12.3, 14.95, and 19.20 for BBP, DMP, DIBP, DEP, and DBP. The *p* values (not provided) were lower than (0.05) for most of the terms in the models and this ensure their importance to model PAEs retention. Moreover, analysis indicated that the quadratic terms (i.e., HA × HA, pH × pH, Time × Time and Temp × Temp) were not significant to model the process and *p*-values were > 0.05. Among Statistical parameter, the coefficient of determination (R^2 and Adj-R^2) is the most informative one as it measures the closeness between measure and predicted retention values [24,25]. For all PAEs, both R^2 (0.9754–0.9948) and Adj-R^2 (0.9662–0.9922) were comparable and this will confirm the high performance of model for presenting experimental data. The high R^2 values indicated this closeness between experimental and predicted results and confirm the workability of the regression model and also the effectiveness of the design.

Table 6
Outputs of ANOVA and regression analysis for the significance of factors and other terms on PAEs retention

Statistical parameter	DMP	DEP	DBP	BBP	DIBP
Degrees of freedom	10	10	10	10	10
F-value	11.4	14.95	19.20	5.30	12.30
R-Squared (R^2)	0.9948	0.9875	0.9871	0.9754	0.9835
Adjusted R-squared (Adj-R^2)	0.9922	0.9812	0.9754	0.9662	0.9808
Relative error of prediction (REP%)	8.2	6.5	7.7	5.4	7.8

The values of REP% were lower than 10% for all PAEs and this also confirmed the suitability of the adopted model. The significant terms that controlling PAEs retention was used to investigate retention behavior for each single solute.

3.5.1. Retention behavior of DMP

Earlier retention tests, confirmed that DMP showed the best affinity to HA and strongly compete with other esters. The influence of experimental factors on DMP retention by HA is presented as:

$$y = 95.43 - 44.52\,\text{HA} - 0.30\text{pH} + 11.41\,\text{Temp} - 6.89\,\text{Time} - 1.31\text{HA} \times \text{Temp} + 0.97\text{HA} \times \text{Time} - 4.74\text{pH} \times \text{Time} - 5.05\text{Temp} \times \text{Time} \quad (8)$$

The above correlation predicted DMP uptake in all tests with high accuracy (REP 8.2%). In fact, this solute has high affinity and preferably removed from solution as indicated from adsorption tests. Another indication of the workability of the model is the accurate prediction of average ester retention on the design (94 mg/kg) which was very close to the intercept in Eq. 8 (95.43). As indicated in Table 3, the retention of DMP was highly variable and ranged from 39.2 (test 1) to 162.3 mg/kg (test 8) with average retention of 94 mg/kg. As indicated in Eq 8, mass of and HA, temperature and contact time have a strong and direct influence on solute uptake with coefficients of –44.52, 11.41 and –6.89, respectively. Solution temperature has a significant influence on solute uptake where the final retention was improved by 11.41% as temperature increased from 25°C to 45°C. The earlier observation indicated the endothermic nature of the process. In fact, the size of the coefficient can determine the overall effect of the factor (or interaction of factors) on solute retention. For example, changing mass from 10 to 50 mg/L has been reduced DMP retention by 44%. However, changing pH from 6.0 to 7.0 did not significantly DMP (reduction by –0.3%). Linear terms indicated that DMP has better retention at low HA mass and short contact time and higher temperatures while pH has no effect over the selected range (6.0–8.0). In fact, HA particles tended to aggregate at pH ≤ 7.0 and this would explain the poor interaction at higher dosages where the particles aggregated in the solution [15]. However, at 10 mg/L the aggregation rate was lower and particles homogenously distributed and this would afford more sites for phthalates interaction. The negative coefficient of contact time (–6.89) may be attributed to competition of other phthalates with DMP which would reduce the final retention. Discussing the results in the frame of liner terms may be misleading, interaction terms indicated a negative interaction between pH and contact time with a value of –4.74. Accordingly, better DMP retention would be achieved if both factors set at their opposite limits. In test 9, good DMP retention (99.2 mg/kg) was observed at low pH and long time while the mass of HA was maintained at the lower limit. Another interesting point obtained from multivariate regression was the interactions between pH–HA mass and pH – temperature were not involved. Although, the mass was 50 mg/L in test 3, DMP retention was high (62.5 mg/kg) and this attributed to the negative interaction between temperature and contact time (–5.05). For DMP retention, interaction between factors was not significant as long as mass HA was maintained at 10 mg/L. Finally, the influence of interaction terms of factors on modeling DMP retention by HA is presented in Fig. 4.

In Fig 4, prediction of DMP retention values was carried using Eq. (8) with and without including interaction terms (HA × Temp, HA × Time, pH × Time, and Temp × Time). As indicated in Fig 4, a poor performance was observed (R^2 = 0.6914) when interaction terms were excluded from the regression model. However, a high predictive power was observed for DMP when interaction terms were added with R^2 value of 0.9986. This was also observed for the rest of solutes confirming the significance of interaction terms for modeling retention of PAEs from solution.

3.5.2. Retention behavior of DEP

As indicated from single and multi-solute isotherms, DEP has a high retention value (202.4 mg/kg) with a reasonable completion with other solutes. Based on the results of adopted design (Table 3), DEP solute was also favorably removed against other solutes with maximum retention of 134.2 (test 8) down to 11.2 mg/kg (test 4) and this confirmed the influence of experimental factors on solute retention. The retention behavior of DEP by HA and the final influence of experimental factors can be presented as following:

$$y = 58.46 - 53.78\,\text{HA} - 3.56\text{pH} + 4.93\text{Temp} - 3.05\text{Time} + 4.44\text{HA} \times \text{Temp} + 6.72\text{HA} \times \text{Time} + 9.90\text{pH} \times \text{Time} - 9.56\text{Temp} \times \text{Time} \tag{9}$$

The empirical formula was workable to predict DEP retention as the intercept (58.46) was very close to the average retention in the design (60.45 mg/kg). The estimated coefficients of the main factors indicated a negative influence of HA mass on solute retention, increasing the mass from 10 to 50 mg/kg has notably reduced solute retention by 53.78%. Moreover, both pH and contact time have a negative influence on solute uptake but with lower magnitudes compared with mass of HA. Unlike the other factors, temperature has a positive influence on DEP with a coefficient of 4.93 which indicated the endothermic nature of the retention process. The earlier observations were supported in Table 3 as very modest retentions for DEP reported in tests 3, 4, 6, and 10. For example, in test 4, the poor retention would be attributed to higher mass of HA, lower temperature, and longer time. On the other hand, the high retention in test 8 was notably attributed to the lower mass, higher temperature and shorter contact time. As longer contact time, competition between molecules toward the surface increases, hence reducing the adsorption ability for of certain molecules. The negative effect of contact time on DMP and DEP can be explained by the strong ability of the other three esters to release DMP and DEP from the surface. For the studied esters, the coefficients of pH indicated that this factor has a negative influence on retention process. DEP and DIBP were the most affected with coefficients of –3.56 and 4.34, respectively. Solution pH can control the hydrolysis of esters. In general, organic esters can hydrolyze to phthalic acid in acidic solutions. The rate of the reaction increase by acidity and protonation of phthalic acid is possible. On the other hand, esters undergo hydrolysis reaction at basic environment to give phthalic acid and its basic form [1,8,32]. With pK_a values of 5.0–5.5, most HA were negatively charged at pH 7 due to ionization carboxylic groups. In fact, hydrolysis rate of organic esters is much higher in basic medium. In the current study, pH was controlled over the range (6.0–8.0) and at this condition HA is mainly negatively charged while esters should be partially hydrolyzed and may reduce their retention by HA. At pH 7.0, HA exhibited fibrous-polymer-like structure and gradually changed to sheet-like structural at higher pHs [15,41]. Hence at pH ≤ 7.0, the possibility of aggregation of HA particle is highly possible. In general, the most dominant retention mechanisms with HA were electrostatic interaction with positively charged solutes, H–bonding with, and hydrophobic-hydrophobic forces [42]. Numerical regression indicated the significant interaction between factors on DEP interaction. pH has no interaction with mass and temperature while a positive interaction with time, mass with time and mass with temperature with coefficients of 9.9, 6.72, and 4.44 respectively. Although, coefficient of linear terms indicated negative influence of pH and contact time on DEP retention, both actors were positively interacted with a value of 9.9. Hence, better DEP retention is possible when pH and contact time were set at their higher limits. The factors time and temperature were negatively interacted (–9.56) and hence between retention is expected both factors set at their opposite limits. Accordingly, the modest retention observed in test 10 (13.6 mg/kg) would be attributed to the fact that both temperature and contact time were being at their upper limits (16 h and 45°C).

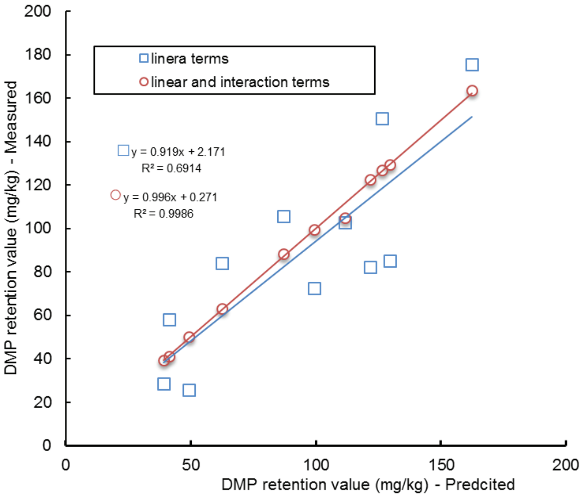


Fig. 4. Prediction of DMP with and without including interaction terms in the derived correlation.

3.5.3. Retention behavior of DBP

Retention of DBP from solution was fairly presented (REP 5.4%) using the following empirical formulae and in the frame of the studied experimental design:

$$y = 43.06 - 29.93\,\text{HA} - 2.39\text{pH} - 11.46\text{Temp} + 12.37\text{Time} + 14.8\text{HA} \times \text{Temp} - 9.19\text{HA} \times \text{Time} + 5.09\text{pH} \times \text{Time} + 2.37\text{Temp} \times \text{Time} \tag{10}$$

The predicted average-retention of DBP was 43.06 and was notably lower than the measured value (54.6 mg/kg). Among linear terms, mass of HA strongly dominated solute uptake with a coefficient of –29.93 while pH has a slight influence (–2.39). In the same time, contact time has a positive influence with a coefficient of +12.37. Unlike other solutes, temperature has a negative influence on DBP uptake with a coefficient of –11.46 and this reflected the exothermic nature of the process. Gao and co-workers [8] also reported an exothermic process for PAE uptake by HA. Another interesting point was the high coefficient of contact time (+12.37) indicating that better retention of this solute would attained even in the presence of the solutes. The maximum interaction among factors was observed between HA × Temp and HA × Time with values of 14.8 and –9.19, respectively. The earlier coefficients indicated that better DBP removal would achieved when mass and temperature fixed at their lower limits while mass and contact time fixed at their opposite limits (i.e., lower mass and longer contact time). The interaction between temperature and contact time has a small effect on DBP removal with a value of +2.37. As indicated in Table 3, the best removal of DBP was achieved in tests 2, 7, 8, and 11 (93.2–122.4 mg/kg) while modest retentions (12.6–19.8 mg/kg) were observed in tests 3, 4, 6, and 10. The poor retention reported in test 4 (12.6 mg/kg) was expected as both mass and temperature were fixed at their upper limits (not at their lower limits) while mass and contact time were also fixed at their upper limits (no at their opposite limits). The excellent performance reported in test 8 was highly attributed to the fact that both mass and temperature were set at their opposite limits while mass and contact time were set at their opposite limits which ended up with better retention even in the presence of other solutes.

3.5.4. Retention behaviors of BBP and DIBP

The competitive uptake of BBP in the presence of other solutes and under the frame of adopted experimental design was presented as follows:

$$y = 50.44 - 46.12\text{HA} - 2.36\text{pH} + 8.65\text{Temp} + 0.34\text{Time} - 3.41\text{HA} \times \text{Temp} + 6.6\text{HA} \times \text{Time} + 15.14\text{pH} \times \text{Time} - 5.17\text{Temp} \times \text{Time} \tag{11}$$

As the case with the rest of phthalates, mass of HA and pH have negative influences on solute uptake. Changing mass from 10 to 50 mg/L resulted in 46% reduction in solute uptake. The interesting point was the insignificant influence of contact time on solute retention with coefficient of +0.34 and this would reflect the poor competition with other solutes. The maximum interaction between factors was among pH × Time with a value of +15.14 and this was observed in the rest of solutes. To attain better retention for BBP, mass and temperature should be set at their upper limits while both pH and contact time should be at their upper limits to achieve maximum interaction between these factors. As indicated in Table 3, the best retention was observed in test 8 (115.4 mg/kg) in which mass and temperature were at their opposite limits while temperature was at the upper limit.

The competitive uptake of DIBP in the presence of other solutes was presented as following:

$$y = 54.67 - 43.41\text{HA} - 4.34\text{pH} + 9.98\text{Temp} - 5.56\text{Time} + 3.83\text{HA} \times \text{Temp} + 7.29\text{HA} \times \text{Time} + 8.72\text{pH} \times \text{Time} - 11.51\text{Temp} \times \text{Time} \tag{12}$$

It is important to recall that retention of this solute was highly affected with a competition factor of 0.47 (Table 5). As indicated in Eq. (12), mass has the maximum influence with a coefficient of –43.41. The maximum interaction between factors was between Temp × Time with a value of –11.51 which was not observed in other solutes. The best retention was observed in tests 2, 7, and 11 (91.6–105.7 mg/kg) and in these tests mass was fixed at the lower level and a better retention was achieved when contact time and temperature set at their lower limits (test 11).

4. Conclusion

The interaction of five phthalic acid esters with humic acid was studied using a three level factorial design to reduce number of tests. In the mixture, the esters were removed from solution with values retentions of 105.7, 115.4, 122.4, 134.2, and 162.3 mg/kg for DIBP, BBP, DBP, DEP, and DMP, respectively. In the meantime, single-solute isotherms indicated the following uptake trend: DMP > DEP > DBP > BBP > DIBP with maximum uptake of 221.3 mg/kg for DMP as estimated form Langmuir model. Retention values were decreased in the presence of all solutes and the most affected solute was DIBP with a competition factor of 0.47. The high retention values of PAEs in the mixture reflected the high affinity to HA with low competition between solutes. Compared with signal-factor analysis, studying competitive retention of phthalate under multi-variable experimental design was pertinent to determine the best combination of factors using minimum number of tests. The optimum combination of all factors to give best retention was10 mg/L HA, pH 7.0, contact time 1.0 h and temperature 45^{o}C.

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