The competitive adsorption of basic yellow 28 and humic acids (BY28/HA) in single and binary mixtures onto hydrophobic modified pillared montmorillonite

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Abstract

The ability of inorganic-organic pillared clays to adsorb basic yellow (BY28) and humic acids (HA) from wastewater was investigated at 20 °C. Adsorption rate data in single systems indicated that BY 28 was adsorbed more rapidly than HA. The pseudo-second-order kinetic model was found to correspond to the kinetic curves with regression coefficients greater than 0.99. The obtained results of the modeling of adsorption isotherms in single-component systems at the different considered pH using nonlinear regression showed that the best fit was obtained with the Freundlich isotherm (R2 > 0.96). In binary systems (BY28/HA), the adsorption at three molar ratio (r = BY28 / HA = 1/3, 1/1 and 3/1) showed that BY28 and HA solute retention rates were improved through a synergistic effect compared to those obtained in single-component single-solute systems. The Sheindorf-Rebhun-Sheintuch (SRS) model was used to predict isothermal data from binary systems using single-component data. The correlation between theoretical and experimental data had limited success due to the competitive and interactive effects between dye and humic acids.

Keywords: *Clays, Humic acids, Basic yellow, Freundlich, Sheindorf-Rebhun-Sheintuch*

I. Introduction

Industrial plants such as textiles, plastics, food and paper generate large quantities of wastewaters containing organic pollutants which may have negative impacts on humans, animals and ecosystems. This is the motivating factor of many studies that have been devoted to the development of new processes for the removal of colour and organic load from these contaminated effluents, over the last decade. Among various methods, adsorption techniques produce high quality treated effluents and sorption processes have been studied as a method for removing dyes from wastewater. In this field, activated carbon is widely used as an adsorbent because of its large surface area, its microporous structure and its high adsorption capacity [1]. But its current high cost and difficulties encountered both during the regeneration process and its reuse make are limiting factors. Over the past decade natural and/or modified clay minerals as adsorbents had been widely used to treat organic and/or inorganic pollutants. The choice was justified basing on economical considerations, their abundance and their great availability [2-4].

These solids are obtained by introducing large molecules of metal alkoxides, organic precursors of (inorganic) polyoxycations into their interlamellar spaces. These organo-inorganic clay materials have been extensively studied in recent years [2-6] because of their high efficiency in removing organic compounds and their good thermal stability. In the same way, several other previous studies have clearly shown that hydrophobic organo-inorganic clays can effectively remove organic compounds, especially dyes, from aqueous solutions [4, 7]. In general, organo-inorganic-clay minerals called also surfactant-modified pillared montmorillonite (Al-SMPM) are produced in powder form and are characterized by few physical properties such as particle size and porosity.

The objective of the present work is therefore to study the adsorption capacities of this new generation of prepared Al-SMPM in the removal of basic yellow acids (BY28) and/or humic acids (HA) from aqueous solutions. The performance of Al-SMPM has been evaluated under different operating conditions. The effects of contact time, initial pH and adsorbent were investigated.

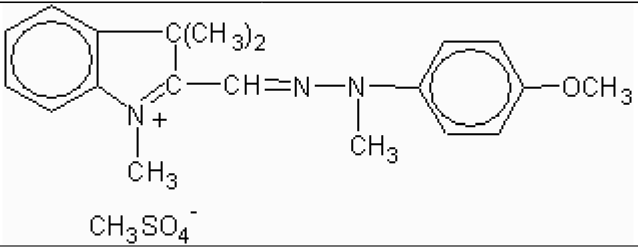
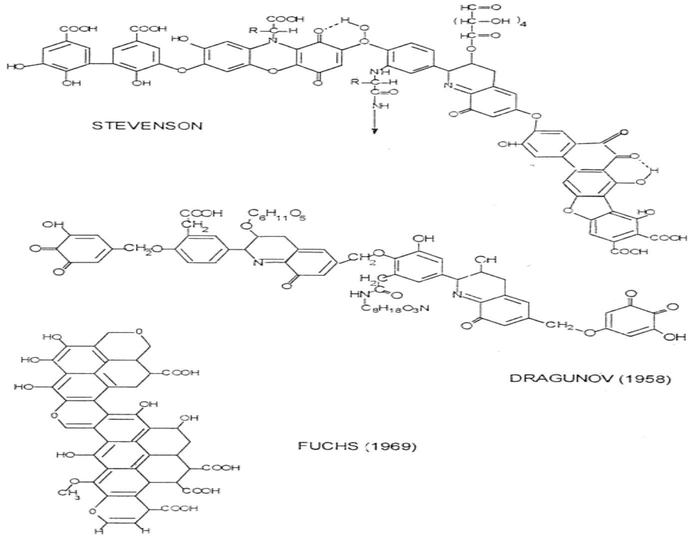
II. Materials and methods

II.1 Adsorbates characterization

A. ***Basic yellow (BY28):*** All reagents were of an analytical grade. Stock solutions of the basic yellow dye were prepared by dissolving Basic yellow 28 (BY28, Fluka AG) in distilled water at the desired initial concentration. The molecular structures and main characteristics of these dyes are listed in Table 1. A stock aqueous solution (1g L^{-1}) of the BY28 was prepared in deionised MilliQ water. Experimental solutions of the desired concentration (15 mg L^{-1}) were obtained by successive dilutions.

B. ***Humix acids (HA):*** The used synthetic humic acids were commercial products provided by the company (Acros). Their molecular structures are shown in Table 1. They were regularly prepared by dissolving 1g of humic acid in 62.5 mL of NaOH (2 N) and then supplementing up to 1 L with distilled water

Table 1. Basic Yellow 28 and humic acids structures

	Chemical structure	Commecial Name	λ_{max} (nm)
BY28		Sandocryl Gold Yellow	455
HA		Humic acids	254

This solution was stirred during 24 H and kept at a temperature of 4°C away from light. Solutions of 10 mg L^{-1} were prepared by successive dilutions of the base solution.

II.2 Preparation of the adsorbent

The aluminium surfactant-modified pillared montmorillonite (Al-SMPM) was synthesized according to previously reported methods [2]. The crude bentonite (Maghnia deposit in the west of Algeria) was supplied by the ENOF Company (Algeria), and transformed to sodic homoionic montmorillonite noted Na-Mt. The intercalation of Na-Mt by the pillaring solution was obtained using the following parameters: Final concentration of aluminium $[Al]_f = 0.1$ M; molar ratio OH/Al = 1.8; ratio Al/Na-Mt = 5 mmol g^{-1}. The protocol of the preparation consisted to dropwise adding a solution of aluminium polycation (pillaring solution) to a suspension of Na-Mt (0.5% (w/w)). The obtained solution was filtered and washed several times with distilled water and then dried at 40°C at least for 72 h. The obtained aluminium pillared montmorillonite was then modified by adding CTAB (cetyl trimethyl-ammonium bromide), a cationic surfactant, in order to increase the hydrophobicity of the solid. The CTAB was added by direct mixing (co-adsorption) to a suspension of aluminium pillared montmorillonite noted $Al_x(OH)_y$-Mt (0.5% w/w) at room temperature and molar ratio CTAB/ $Al_x(OH)_y$-Mt= 1 mmol g^{-1}. The resulting solid (named CTA-$Al_x(OH)_y$-Mt or Al-SMPM) was washed several times with distilled water, centrifuged and dried at 40°C for 72h. All prepared adsorbents were sieved and stored in glass flasks for further use [2]$Al_x(OH)_y$-Mt= 1 mmol g^{-1}. The resulting solid (named CTA-$Al_x(OH)_y$-Mt or Al-SMPM) was washed several times with distilled water, centrifuged and dried at 40°C for 72h. All prepared adsorbents were sieved and stored in glass flasks for further use [2].

II.3. Experimental studies in single and binary systems

II.3.1. Adsorption kinetics

Adsorption experiments for BY28 and/or HA onto Al-SMPM were carried out in brown flasks at room temperature by shaking 0.1 g of adsorbent with 100 mL of the dye solution having an initial concentration of 15 mg L^{-1} for BY28 and 10 mg L^{-1} for AH, by means of a mechanical shaker (EDMUND BUHLER GmbH SM-30) at a constant agitation speed of 200 rpm. The samples were withdrawn from the shaker at intervals from 0 to 1440 min then filtered through a 0.45 µm membrane and analysed spectrophotometrically using a SHIMADZU 1700 PHARMASPEC spectro-photometer. For single component systems, residual concentrations of BY28 and/or HA in all solutions were determined at 458 nm and 254 nm, respectively.

II.3.2. Adsorption isotherms

Isotherm studies were conducted by shaking different quantities of adsorbent (varying from 0.005 to 0.1 g) in 100 mL of adsorbate solutions with an initial concentration of 15 mg L^{-1} for BY28 and 10 mg L^{-1} for HA. The pH of the medium was varied from 3 to 9 by adding few drops of 0.01N NaOH or 0.01N HNO_3 accordingly. The samples were shaken at constant speed of 200 rpm for 24h in order to achieve the equilibrium state. Samples were taken after 24h then filtered through 0.45µm membrane. The residual concentrations of BY28 and/or HA all solutions were determined at the appropriate wavelengths. The adsorbed amounts of BY28 and HA onto Al-SMPM were calculated using the following equation:

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

Where q_e is the amount of adsorption dye (mg g^{-1}) at equilibrium, C_0 and C_e are the initial and equilibrium concentration of dye solution (mg L^{-1}), respectively, V is the volume of the dye solution (L) and m is the mass of Al-SMPM (g).

The isotherm procedure mentioned above was also used for the binary solute systems (BY28/HA). Five concentrations of the used dye were chosen in order to obtain BY28/HA molar ratio of 1/3, 1 and 3.

The individual concentration of the residual dye in binary component systems was corrected using the optical densities of the solutes at the specified wavelengths.

The isotherm procedure mentioned above was also used for the binary solute systems (BY28/HA). Also, five concentrations of the adsorbate or co-adsorbate were chosen in order to obtain BY28/HA molar ratios of 1/3, 1 and 3.

$$C_{BY} = \frac{k_{BY1} d_{\lambda 1} - k_{BY2} d_{\lambda 2}}{k_{BY1} k_{HA} - k_{BY2} k_{HA1}} \qquad (2)$$

$$C_{HA} = \frac{k_{HA2} d_{\lambda 2} - k_{HA1} d_{\lambda 1}}{k_{BY1} k_{HA2} - k_{BY2} k_{HA1}} \qquad (3)$$

In such conditions and when several components are mixed in aqueous media, interferences and competition phenomena for sorption sites occur and lead to more complex mathematical formulations of equilibrium. Various researchers had developed models in binary systems such as the Sheindorf model:

$$q_{e.1} = K_1 C_1 \left(C_1 + a_{12} C_2\right)^{n_1 - 1} \quad (4)$$

$$q_{e.2} = K_2 C_2 \left(C_2 + a_{21} C_1\right)^{n_2 - 1} \quad (5)$$

Where, a_{12} , a_{21} are the competition coefficients of BY28 and HA respectively K_1, K_2 n_1 and n_2 are constants of the model which can be determined from single systems.

III. Results and discussion

III.1. Adsorption kinetics

The obtained results of the BY28 and HA adsorption kinetics onto the used Al-SMPM at medium pH in single systems are illustrated in Fig 1.

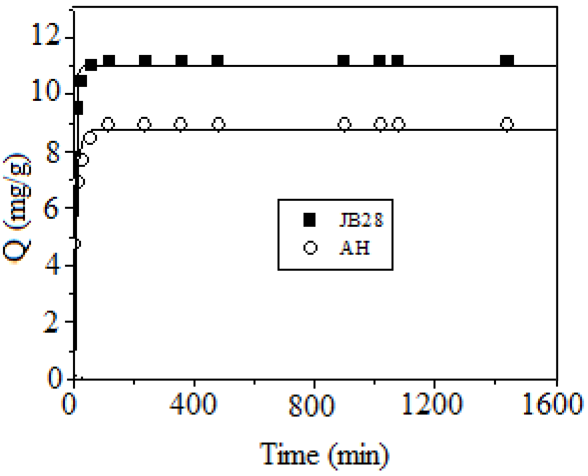


Figure1. Adsorption kinetics of BY28 and HA onto Al-SMPM at medium pH

They suggest the presence of two steps. A first step where the binding of both BY28 and HA is very fast with a 45 minute time followed by a second step after about 3h for 4h where a steady state is reached.

In single systems, the BY28 abatement efficiency is about 80% onto Al-SMPM. It is also shown that humic acids (HA) present a good affinity toward Al-SMPM (85%). This phenomenon could be attributed to hydrophobic interactions between HA molecules which is very hydrophobic (presence of olefins, a long carbonic chain and aromatic functional group) and organophilic and hydrophobic Al-SMPM matrix.

In order to investigate the mechanism of adsorption, the pseudo-first– and pseudo-second-order equations are applied to model the BY28 and HA kinetics. The pseudo-first– rate expression of Langergren [8] is presented as

$$q = q_e(1 - e^{k_1 t}) \quad (6)$$

Where qe and qt are the adsorbed amount (mg g^{-1}) at equilibrium and time t (min), respectively; and k_1 is the pseudo-first-order rate constant of pollutant. The k_1 value was calculated from the slope of linear plot of log (qe-qt) versus time.

The pseudo-second-order kinetic model is presented as follow [9]:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where q_2 is the maximum adsorption capacity (mg g^{-1}), k_2 is the rate constant of the pseudo-second-order equation mg g^{-1}, and qt (mg g^{-1}) is the amount of pollutant at a time t. K_2 can be obtained from the slope of plot of 1/(qe-qt) versus time (t). The intercept of this linear relation is 1/qe.

The values of k_1, k_2 and the correlation coefficients (R^2) of the pseudo-first- and pseudo-second—order are summarized in table 3.

Table2. Kinetic constants of the two used pollutants with the two models pseudo-first and second order.

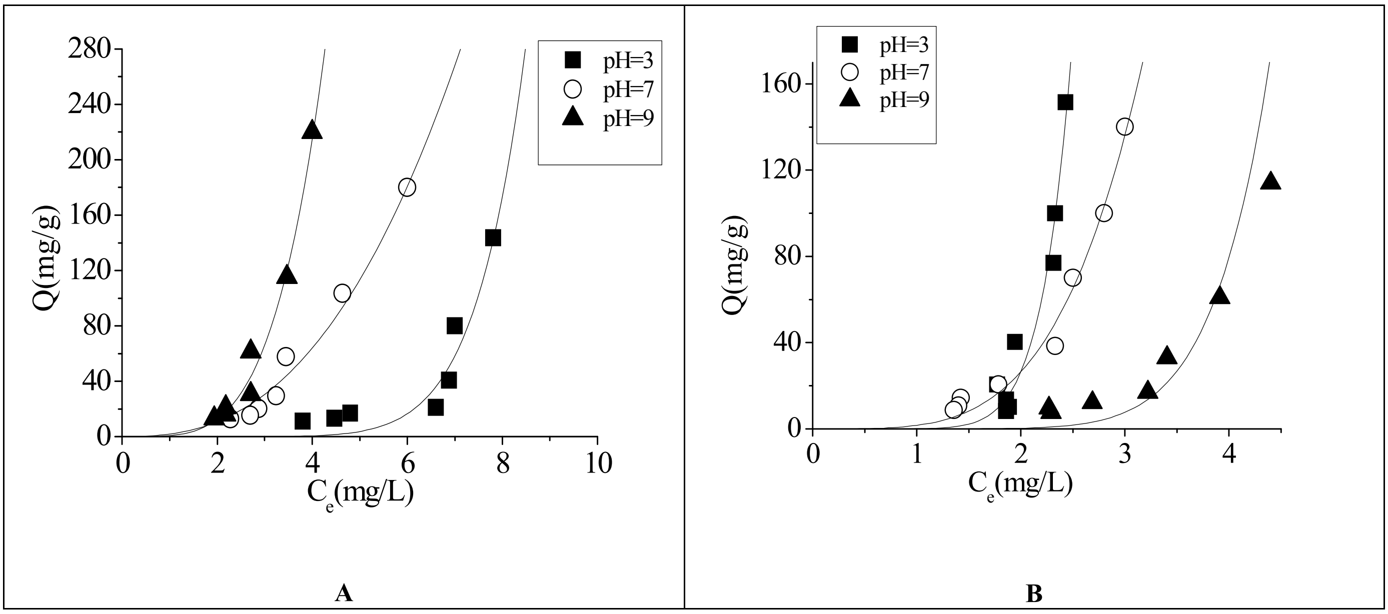
	Pseudo-first-order Model						Pseudo second-order Model					
Adsorbent	JB 28			HA			JB 28			HA		
parameters	K_1 min^{-1}	Q $mg.g^{-1}$	R^2	K_1 min^{-1}	Q $mg.g^{-1}$	R^2	K_2 $g.mg^{-1}.min^{-1}$	Q $mg.g^{-1}$	R^2	K_2 $g.mg^{-1}.min^{-1}$	Q $mg.g^{-1}$	R^2
Al-SMPM	0.22	10.99	0.98	0.02	0.91	0.96	0.0396	11. 23	0.99	0.02	8.99	0.99

Among the results giving in this table, it appear clearly that the pseudo second-order fit very well the obtained results with correlation coefficient around 0.99.

III.2. Adsorption isotherms in single component systems

The adsorption equilibrium experiments for BY28 and HA at three values of pH (3, 7 and 9), from the differences between the initial C_0 and equilibrium concentrations C_e, the amounts of BY28 and HA adsorbed q_e on Al-SMPM were calculated. The corresponding experimental adsorption equilibrium data were drawn as Q_e versus C_e plots in Fig. 2.

The sorption isotherms of BY28 on the Al-SMPM sorbents at the tree pH values (Fig. 2) showed that the sorbed amount increased with increasing pH. At pH 9, the Al-SMPM is more favourable for binding BY28 with adsorption capacity of 240 mg g^{-1} at residual concentration of 4 mg L^{-1}



A

B

Figure 2. Adsorption isotherms of the used pollutants onto Al-SMPM at different pH values
A: BY28 and B: HA

In the other hand, the amount of HA is very important in acidic medium with quantity Q of about 140 mg g^{-1} at residual concentration of only 2 mg L^{-1}.

The phenomenon of steric exclusion can play an important role during the sorption of the HA macromolecules. In this study, we investigated also the behaviour of both the prepared $Al_x(OH)_y$-Mt and Al-SMPM materials towards HA.

Results clearly shown a notable retention of HA on Al-SMPM which seems to have a good affinity towards HA, particularly at acid pH.

In another hand, the BY28 is a hydrophobic basic dye which becomes cationic in aqueous solution. At the used conditions, BY28 is adsorbed onto inorgano-pillared montmorillonite $Al_x(OH)_y$-Mt by hydrophobic interactions (non-polar interactions between alkyl groups of pillared montmorillonite with the dye molecules).

Adsorption isotherms of two adsorbates onto the prepared sorbent clays at the different pH values were analyzed by the Langmuir and Freundlich models using non-linear regression technique.

The Langmuir isotherm [10] based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent is represented by Eq. (8):

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \qquad (8)$$

Where q_e is the solid phase concentration of adssorbate at equilibrium (mg g^{-1}), C_e is the equilibrium concentration in solution (mg L^{-1}), q_{max} is the monolayer of the adsorbent (mg g^{-1}) and K_L (mg^{-1}) is the Langmuir adsorption constants.

The Freundlich isotherm model [11] takes the multi-layer and heterogeneous adsorption. Its non-linear form can be represented as:

$$q_e = K_F C_e^n \qquad (9)$$

Where q_e and C_e are the dye concentrations on adsorbent (mg g^{-1}) and in solution (mg L^{-1}) and K_f is the Freundlich constant (mg^{1-n} L^{3n} g^{-1}), respectively.

The analysis of adsorption isotherms in single component systems were analyzed and best fits were obtained with the Freundlich model (Table 3). The sorption was not supported (n > 1) and the binding was weak. In this case, favourable sorbate/surface interactions may increase the affinity of the sorbent surface. It can be revealed by its hydrophobic character and isotherm upwardly shape curves.

Table 3. Constants of Freundlich model

	Freundlich Model			
	pH	**K** **$mg^{1-n} L^n g^{-1}$**	**1/n**	**R^2**
HA	**3**	0.067	8.62	0.94
	7	1.37	4.19	0.98
	9	0.00126	8.145	0.88
JB_{28}	**3**	7.10^{-6}	8.16	0.91
	7	1.85	2.56	0.97
	9	0.74	4.09	0.98

The parameters values of Freundlich model indicate favourable conditions for adsorption and correlation coefficients (R^2) values are higher than 0.94. In the used conditions, Langmuir model do not fit well our results (results not shown).

III.3. Effect of HA on BY28 sorption

A. Kinetic study in the binary mixtures

The kinetic study of the two pollutants in binary mixtures (BY28/AH) are given in Fig. 3 which gives adsorbed amount versus residual concentration.

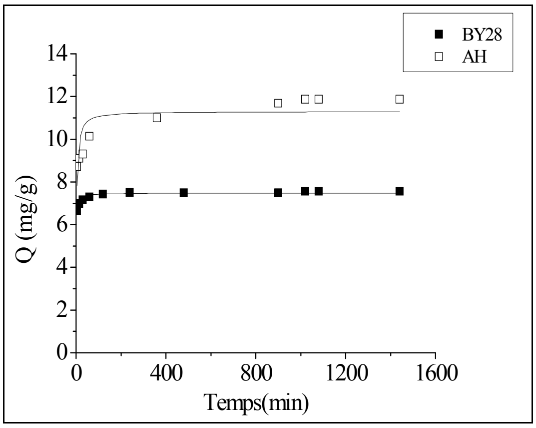
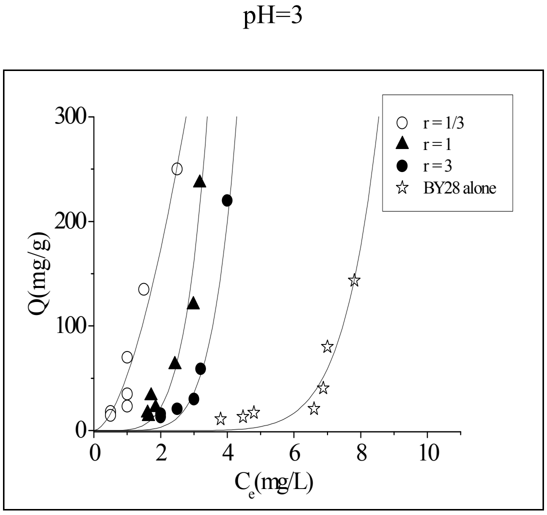


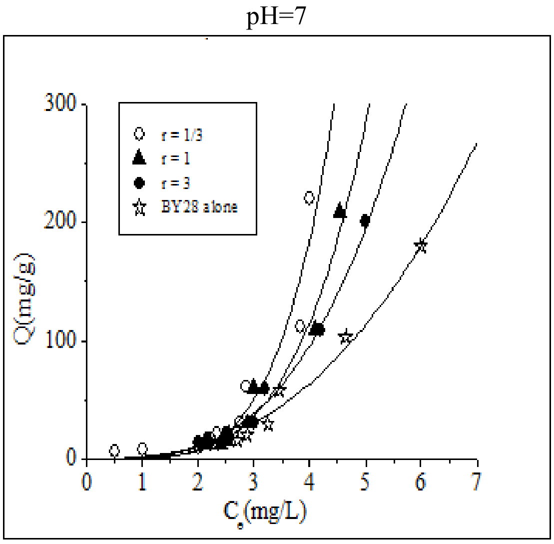
Figure 3. Kinetic study of BY28 and HA in binary mixtures at medium pH and ratio of adsorbate/co-adsorbate r = BY28/HA = 1

In binary systems, the results obtained clearly show that the presence of HA species in BY28 mixtures increases their retention and decreased their equilibrium time.

B. Isotherm study in the binary mixtures

Adsorption experiments were conducted at three different pH values (3, 7 and 9) in binary component (BY28/AH) systems. As mentioned above in the kinetic part, BY28 adsorption increased when BY28/HA ratio decreased as shown in Fig.4.





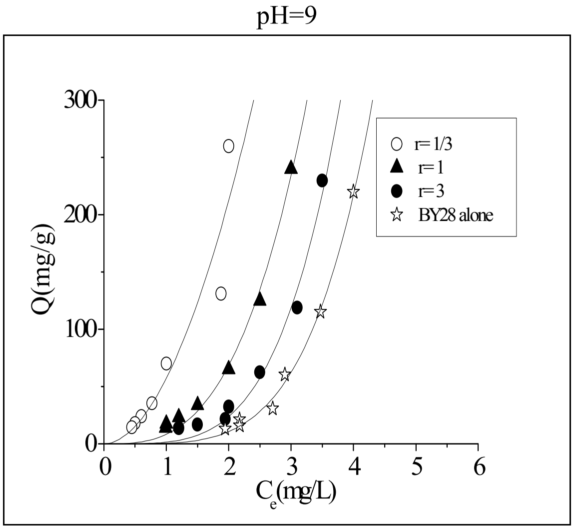


Figure 4. Adsorption isotherms in binary mixtures (JB28/HA) at three pH values.

When solute-solute interactions are strong compared to those between solute and adsorbent, a solute molecule at an adjacent position becomes more stable to other already adsorbed molecules, than at an isolated position. In the present case, the Al-SMPM sorbent was very hydrophobic according to previous studies [5].

To better understand the adsorption mechanism of BY28 molecules in the presence of HA at different concentrations, adsorption experiments were carried out at three molar ratio (r=BY28/AH: 1/3, 1, 3) and three different pH values (3, 7 and 9). Corresponding results of adsorption isotherms in binary systems are shown in Fig 4. For all the given conditions, the comparative study of the corresponding adsorption isotherms (Fig. 4) clearly show that the presence of HA molecules causes an increase in the adsorption of BY28 in comparison with performed in single-component systems. In fact, the adsorption of BY28 molecules increases with the decrease of the ratio r= BY28/AH, thus suggesting an adsorption by mechanism of cooperation between the two adsorbates BY28 and HA molecules. Also, BY28 molecules could interact with HA species to form complexes.

The modeling of the competitive results using Sheindorf (SRS) model showed that the two used solutes presented a cooperative behavior. The synergetic effect mechanism was confirmed by interaction coefficient $\mu_{BY28,HA}$ which are all higher than 1 at acidic medium

Table 4. Sheindorf model parameters and correlation coefficients

(JB28/AH)		**r=1/3**		**r=1**		**r=3**	
		$\mu_{(BY28,HA)}$	R^2	$\mu_{(BY28,HA)}$	R^2	$\mu_{(BY28,HA)}$	R^2
Al-SMPM	**pH=3**	0.68	0.80	1.44	0.90	1.83	0.98
	pH=7	0.10	0.86	0.36	0.88	0.46	0.94
	pH=9	0.08	0.92	0.20	0.99	0.17	0.98

IV. Conclusion

This present study has shown that aluminium surfactant modified pillared montmorillonite (Al-SMPM) had proven to be a good adsorbent to BY28 and HA in both single and binary systems. In the single systems, pillared clay had a greater affinity for BY28 than HA. In binary mixtures, the presence of HA improved the adsorption of BY28 with synergetic mechanism. Also, the BY28 sorption capacity onto Al-SMPM increased in the opposite direction to the BY28/HA ratios when the BY28/HA ratio decreased.

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