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Interaction of colloidal particles of NH_4^+-montmorillonite with activated carbon

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Abstract

The interaction between negative colloidal particles of NH_4^+-montmorillonite and particles of activated carbon was studied as a function of particle concentration, pH, and time of contact. The results show that carbon particles act as a support/bridge for clay particles, the type of resulting clay/carbon/clay associations depending on the pH and the clay/carbon ratio in the system. The relation between clay and carbon particles can be described by equations of the Langmuir type. For the same carbon particle concentration in the system, the relation varies from 6820 to 36,100 and is dependent on pH. The interaction coefficients at pH 6.5 correspond to reaction of pseudo-first ($k_1 = 4.14 \times 10^{-3}$ to $1.93 \times 10^{-3}\ \text{s}^{-1}$) and pseudo-second order ($k_2 = 9.36 \times 10^{-14}$ to $2.47 \times 10^{-14}\ \text{cm}^3\ \text{s}^{-1}$) for different clay/carbon ratios. By using the Dubinin–Radushkevich equation, the interaction energy (±22.42, ±685.0, and ±14.63 J mol^{-1}) was obtained for three different pH values (5, 6.7, and 7.6), demonstrating that the reaction is mainly physical.

Keywords: Activated carbon; Adsorption; Kinetics of interaction; Montmorillonite; Particle interaction

1. Introduction

The interaction of colloidal particles with opposite charges and/or of different sizes, leading to adhesion, adsorption, or other association types, is a phenomenon of interest in many natural and practical processes, such as flocculation, filtration, water treatment, flotation of minerals, and migration of the clay in silts.

Interactions between particles can generally be described by the Langmuir adsorption model [1] and could also be studied by other equations such as the Freundlich and Dubinin–Radushkevich [2–8] adsorption models and the Smoluchowski flocculation model [9–12]. In all cases the repellent and attractive interactions between similar and different particles are considered and evaluated.

Montmorillonite is a clay mineral present in most soils, where it plays an important role in retaining humidity and in binding particles. It is also much used in industry to lubricate perforations, to bind foundry sand, and in pelleting, filters, sorbents, etc. Montmorillonite particles are negatively charged by isomorphic substitution, the charge being independent of the pH [13] and generally compensated for by cationic exchange processes. The exchange cations are removed by the presence of H^+ when the pH is low, and some change in the behavior of the clay in the suspension (generally flocculation) can therefore be expected. Activated carbon is used to clarify soil suspensions in chemical analysis (determination of phosphorous, boron, etc.) and of course in industry. Negatively charged clay colloids and the positively and negatively charged particles of activated carbon (depending on the pH of the system) are very well characterized, thus opening up interesting avenues of research and study of the interactions between different-sized particles with opposite charges.

The aim of this study was to analyze the interaction of suspensions of NH_4^+-montmorillonite (particle diameter = 0.1 μm) and activated carbon (particle diameter = 10 μm) as a function of particle concentration, pH, and interaction time of

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these charged colloidal particles in terms of the Langmuir and Dubinin–Radushkevich models.

2. Theoretical background

2.1. Interaction of particles

2.1.1. Langmuir isotherm

Assuming that the interaction of particles of opposite charges and different sizes responds to treatment in a manner similar to that of the Langmuir adsorption, we have

$$\frac{N_t}{(N_0 - N_t)/N_C} = \frac{[(N_0 - N_E)/N_C]k_I N_t}{1 + k_I N_t}, \tag{1}$$

where N_0 is the initial number (particle cm^{-3}, mg dm^{-3}, etc.) of small positively or negatively charged particles (in our case negatively charged montmorillonite), N_t is the number of the same particles at a given time, N_E is the number of small particles at equilibrium, N_C is the number of large particles (particle cm^{-3}, mg dm^{-3}, etc.) of opposite charges (these can be dependent on the pH—e.g., activated carbon) present in the system, and k_I (cm^3 particle^{-1}, dm^3 g^{-1}, etc.) is a proportional coefficient of interaction of these particles in the system.

2.1.2. Dubinin–Radushkevich isotherm

To determine the interaction energy, we can use the Dubinin–Radushkevich (D–R) equation [1–7,14,15]. Assuming that the interaction occurs by adsorption of the small particles and that these form a single layer on the surfaces of larger particles, we have

$$\ln q = \ln Q - k\varepsilon^2, \tag{2}$$

where q is the quantity (mol g^{-1}) of small particles (clay) that interact with 1 g of large particles (carbon) for a given concentration of small particles (C, in mol dm^{-3}), Q is the maximum adsorbed quantity (mol g^{-1}) of small particles, k is the proportionality coefficient of the energy interaction (mol^2 kJ^{-2}), and ε is the Polanyi potential (kJ mol^{-1}) (see Appendix A) [1–7],

$$\varepsilon = RT \ln\left[1 + (C_A/C_E)\right], \tag{3}$$

where R is the gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T is the absolute temperature, C_A is the quantity of the extracted adsorptive of the dispersion (g adsorptive dm^{-3}), and C_E is the adsorptive equilibrium concentration (g adsorptive dm^{-3}).

Knowing the value of the proportionality coefficient k of interaction obtained from the D–R equation, one can obtain the adsorption median energy E (kJ mol^{-1}) $= \pm(2k)^{-0.5}$ (see Appendix B) [16].

2.2. Kinetics of the interaction

Chemical kinetics studies the velocity and mechanisms of chemical reactions. Since the reactions of adsorption and/or interaction between particles can be considered as pseudo-chemical [3], we can consider the coefficients as corresponding to reactions of pseudo-first and -second order.

For a reaction and/or interaction of pseudo-first order (Lagergreen equation), the velocity of change of concentration of clay/carbon particles is dq/dt and therefore the differential form is [3,17]:

$$\frac{dq}{dt} = k_1(q_E - q_t), \tag{4}$$

and the integral form is

$$\ln(q_E - q_t) = \ln q_E - k_1 t. \tag{5}$$

For a reaction of pseudo-second order the differential form will generally be

$$\frac{dq}{dt} = k_2(q_E - q_t)^2 \tag{6}$$

and the integral form

$$\frac{t}{q_t} = \frac{1}{k_2 q_E^2} + \frac{t}{q_E}, \tag{7}$$

where q_E is the quantity (particle cm^{-3}) of small particles interacting with larger particles when equilibrium is reached, and q_t is the quantity (particle cm^{-3}) of the same particles interacting at time t (s). In our case we define $q_E = (N_0 - N_E)$ and $q_t = (N_0 - N_t)$, where N_t is the number of small particles per cm^3 after interaction with the other particles at time t. Equation (5) is thus

$$\ln(N_t - N_E) = \ln(N_0 - N_E) - k_1 t, \tag{8}$$

and Eq. (7) is

$$\frac{t}{(N_0 - N_t)} = \frac{1}{k_2(N_0 - N_E)^2} + \frac{t}{(N_0 - N_E)}. \tag{9}$$

The interaction coefficients k_1 (pseudo-first-order) and k_2 (pseudo-second-order) are expressed in s^{-1}, min^{-1}, and cm^3 particle^{-1} s^{-1}, dm^3 g^{-1} min^{-1}, etc., respectively.

3. Materials and methods

The clay used was a montmorillonite from Cerro Bandera (Neuquén, Argentina) with a specific surface area of 799.6 m^2 g^{-1}, as determined by orthophenanthroline adsorption [18,19]; a cationic exchange capacity (CEC) of 80.2 cmol$_c$ kg^{-1}; and a molecular weight of 735.48 g [20,21]. The clay was saturated with NH_4^+ ions by repeated washing with NH_4Cl 0.1 M, washing with distilled water, and centrifugation until elimination of Cl^- [22]. The suspension was then dispersed by ultrasound and centrifuged at 12,000 rpm for 15 min to eliminate particles with radius >0.05 µm. The resulting suspension has a particle concentration of 4.16 g dm^{-3}, pH 7.8, a specific surface area of particles of 498.7 m^2 g^{-1}, obtained by orthophenanthroline adsorption [19], and an electric conductivity of 11.35 mS m^{-1}.

The powdered activated carbon provided by Mallinckrodt Chemical Works (USA) had a density of 1.80 g cm^{-3} and a specific surface area of 899.7 m^2 g^{-1}, determined by orthophenanthroline adsorption [23]. The activated carbon was washed with distilled water, the particles were dispersed by ultrasound, and particles with radius >5 μm were eliminated by centrifugation, giving a sufficiently stable suspension for 24 h with a concentration of 18.753 $\mathrm{g\,dm^{-3}}$. After prior shaking for 10 min, aliquots of the suspension were taken to prepare more diluted suspensions for the different experiments.

Data from a previous paper [1] show that in the range pH 3.7–8, absorbance of a sol of 0.693 $\mathrm{g\,dm^{-3}}$ of NH_4^+-montmorillonite is independent of the pH, allowing one to obtain absorbance data and hence clay particle concentration with a safety margin.

The volumes of clay particles and activated carbon were calculated on the basis of the absorbance determinations in diluted suspensions. Assuming the validity of the Raleigh equation for the dispersion of light, this can be written in combination with the Lambert and Beer law [1,22,24] as

$$2.303A = k_0 N V^2 l = k_0 m V l/\rho, \tag{10}$$

where A is the absorbance, N is the number of particles per $\mathrm{cm^3}$, m is the mass of particles ($\mathrm{g\,cm^{-3}}$), V is the particle volume ($\mathrm{cm^3}$), l is the optical path length (1 cm), and ρ is the density of the clay (2.71 $\mathrm{g\,cm^{-3}}$) and/or of the carbon particle (1.80 $\mathrm{g\,cm^{-3}}$), and

$$k_0 = \left(24\pi^3 n_0^4/\lambda^4\right)\left[\left(n^2 - n_0^2\right)/\left(n^2 + n_0^2\right)\right]^2, \tag{11}$$

where n_0 is the refractive index of the water (1.333), n is that of the clay (1.60) and/or of the carbon (unknown value), and λ is the wavelength in nm (360 nm for clay and 560 nm for carbon).

The particle volume was calculated as a function of it's the half radius (a), obtained by centrifugation of the suspension, based on [25]

$$\ln\frac{x_2}{x_1} = \frac{2}{9}a^2(\rho - \rho_0)\frac{\varpi^2}{\eta}t. \tag{12}$$

Replacing the angular speed (ω) with $2\pi n$, where n is the number of revolutions per second (rps), we have

$$a = \frac{0.5124}{\mathrm{rps}}\sqrt{\frac{\eta\log(x_2/x_1)}{t(\rho - \rho_0)}},$$

where a is the radius (cm) of the particle (supposedly spherical), η is the viscosity of the water ($\mathrm{g\,cm^{-1}\,s^{-1}}$), x_1 and x_2 are the smallest and largest radii (cm), respectively, of the centrifuge head, t is the time of centrifugation in seconds, ρ and ρ_0 are the densities ($\mathrm{g\,cm^{-3}}$) of the particle and the water, respectively, and $0.5124 = \sqrt{(9 \times 2.303)/(2 \times 4\pi^2)}$.

Knowing the value of the particle radii, their volume can be calculated, assuming them to be spherical. The particle half radius can be calculated from the mean volume of the montmorillonite particles, obtained by Eq. (10), and the slope in Fig. 1, which is equal to $k_0 V l/\rho$ [1]. The resulting estimate is in reasonable agreement with that obtained by Eq. (12).

To study the interaction between carbon particles and negatively charged clay particles, 5 ml of a carbon suspension with a given particle concentration (1.0 $\mathrm{g\,dm^{-3}}$) was adjusted to pH 5 ± 0.2 and placed in centrifuge tubes. To each tube was added 5 ml of clay suspension with particle concentrations varying from 0.2 to 1.4 $\mathrm{g\,dm^{-3}}$ and having the same pH as the carbon suspension. The mixtures were agitated for 5 min, left in contact at 28 °C for 60 min, and then centrifuged at 3000 rpm for 5 min. The clay particle concentrations were determined in the supernatant liquid from the absorbance measurements at a wavelength (λ) of 360 nm using a standard curve obtained by measuring the absorbance of suspensions with known concentrations of clay ($\lambda = 360$ nm) and carbon ($\lambda = 560$ nm) particles (Fig. 1). The pH of the suspensions was also measured. The experiment was repeated at pH 6.7 and 7.6.

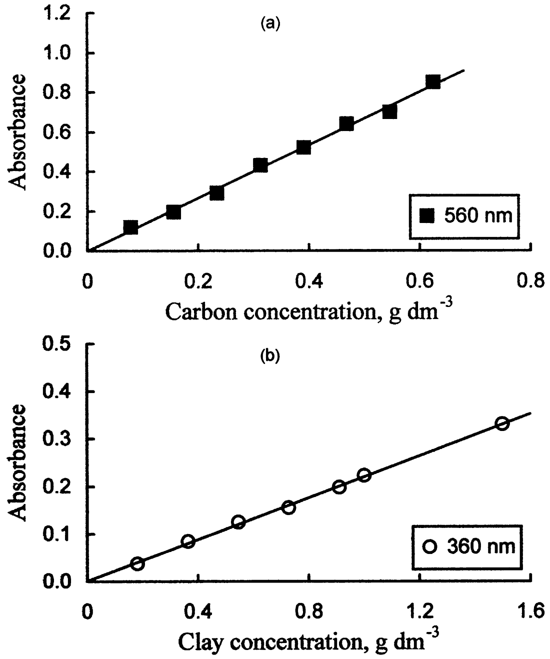

Fig. 1. Absorbance dependence on the concentration of carbon (a) and montmorillonite (b) particles in aqueous suspension. The error is within a 95% confidence interval of the mean, and the lines are the corresponding fit.

The acid–base titration of activated carbon was carried out by taking a 10-ml sample of the stock carbon suspension in 50 ml (3.75 $\mathrm{g\,dm^{-3}}$) of $NaNO_3$ 0.1 and 0.001 M as electrolyte supports and HNO_3 and NaOH 0.2 M as titration solutions; the pH was measured in each case. Blank tests were also carried out using titrations of $NaNO_3$ solutions without carbon particles in order to calculate the net sum of reception or discharge of the protons [26]. The adsorption of Na^+ and/or Cl^- was determined as a function of pH in carbon suspensions prepared as in the previous paragraph, but containing NaCl 0.01 M at different pH values (3 to 11). Sodium was determined with an absorption spectrophotometer and Cl by titration with $AgNO_3$ 0.010 M according to the Mohr method [27].

To obtain the interaction kinetics between carbon and clay particles, a 5-ml aliquot of the carbon suspension (0.0063 to 0.250 $\mathrm{g\,dm^{-3}}$) at pH 6.5 was placed in a centrifuge tube and a 5-ml aliquot of given concentrations of clay suspension (with the same pH as the carbon suspension) was added to reach final volumes of 0.511 to 0.128 $\mathrm{g\,dm^{-3}}$. The mixture was agitated for 10 s and centrifuged at 5000 rpm for 2 min, the supernatant was placed in a quartz cuvette (of 4 ml), and absorbance was determined ($\lambda = 360$ nm) at 2.5 min. The experiment was re-

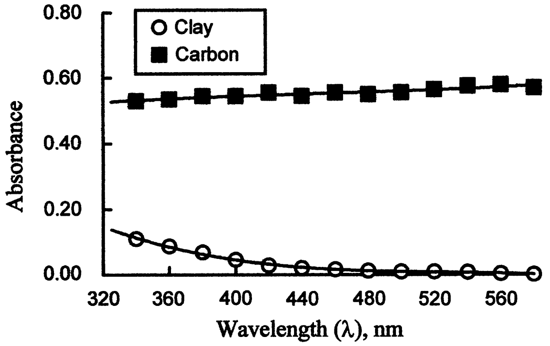

Fig. 2. Absorbance dependence on wavelength (λ, nm) in aqueous suspension at pH 7.5, a carbon particle concentration of 0.432 $g\,dm^{-3}$ (■), and a montmorillonite particle concentration of 0.525 $g\,dm^{-3}$ (○).

peated to measure absorbance at 5 and 10 min and then every 10 min until 60 min was reached, after which the pH of the suspensions was measured (pH 6.5 ± 0.2).

4. Results and discussion

Absorbance of the clay suspension was very low compared with that of the carbon suspension (Fig. 2). Furthermore, the clay suspension proved to be very stable, showing the same level of absorbance before and after centrifugation at 3000 rpm for 5 min; at this same speed and centrifugation time, decantation of the carbon particles was complete. These two factors, the low level of absorbance and the stability of the clay suspension, speak for the reliability of the experimental procedures used in this study. However, the concentration of clay particles could not be determined in the presence of carbon particles without centrifugation.

Using Eq. (10), we obtained a volume of $V_M = 5.47 \times 10^{-16}\ cm^3\,particle^{-1}$, a radius of 5×10^{-6} cm, and a number of particles per gram of $N_M = 6.75 \times 10^{14}$ for montmorillonite.

The radius of carbon particles obtained using Eq. (12) is 4.1×10^{-4} cm, giving a volume of $V_C = 4\pi a^3/3 = 2.89 \times 10^{-10}\ cm^3$ and a number of particles per g $N_C = 1.92 \times 10^9$.

4.1. Surface charge characteristics of the particles

The mixture of 0.492 $g\,dm^{-3}$ of montmorillonite particles with 0.960 $g\,dm^{-3}$ of activated carbon after 18 h of contact has a pH that varies with respect to the initial value in all cases (except when close to pH 7), as shown in Fig. 3a. The initial pH values of between 6 and 7 practically reach a plateau at a final pH of 6.75, possibly owing to the proximity of the value to the point of zero charge (pzc) of the carbon (7.5). The final pH of the suspension is higher than the initial pH, probably because at pH $<$ 6 a carbon/clay/carbon system forms (favored by the replacement of NH_4^+ by H^+ and by the positively charged carbon particles) that offers a slightly positive exposed surface. At pH values $>$7, the level of interaction between the clay and carbon particles is low, since both tend to be highly negative (clay–water and carbon–water systems), and in the absence of OH^- adsorption the final pH value increases more rapidly with respect to the initial value, as indicated by the steepest section of the slope at these pH values (Fig. 3a).

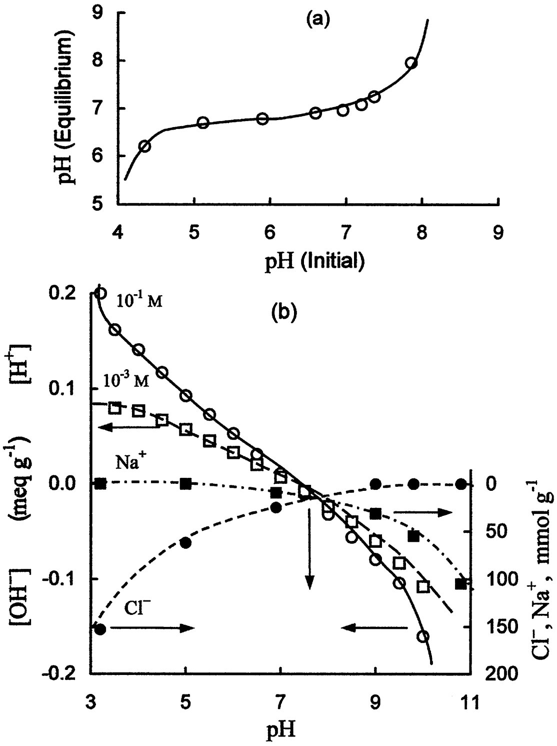

Fig. 3. (a) Variation from initial pH in a suspension containing 0.432 $g\,dm^{-3}$ montmorillonite and 0.960 $g\,dm^{-3}$ of activated carbon. (b) Acid/base titration data of a suspension of activated carbon of concentration 3.75 $g\,dm^{-3}$ in $NaNO_3$ 10^{-1} M (○) and 10^{-3} M (□) and adsorption of Na^+ (■) and/or Cl^- (●) in a similar suspension in NaCl 10^{-1} M.

Carbon particle charge is dependent on pH, as confirmed by the data relating to the acid–base titrations shown in Fig. 3b, which also show that carbon particles reach the pzc at pH 7.5. The adsorption of Na^+ and Cl^- as a function of pH is also shown; the position of the pzc is corroborated by the intersection of the adsorption data of Na^+ with that of Cl^-.

4.2. Interaction isotherms

Fig. 4 presents the interaction isotherms of clay particles with carbon particles at pH 5, 6.7, and 7.6 in accordance with Eq. (1), where $(N_0 - N_t)/N_C = q$. The concentration of the clay suspensions varies until a value of 1.4 $g\,dm^{-3}$ is reached. The isotherms at pH 5 and 6.7 are of the L type [28], showing high affinity of clay particles for those of carbon, whereas at pH 7.6 (a value close to the pzc) there is low affinity.

The higher level of interaction between particles whose charges depend on the pH of the system is in agreement with the fact that carbon particles have higher positive charges at lower pH values (Fig. 3), whereas at higher pH the negative charges prevail on the surface of the carbon. This observation demonstrates the importance of electrostatic phenomena in the studied interactions.

The data in all the interactions shown in Fig. 4 can be adjusted to the usual Langmuir isotherm, as evidenced by the straight lines observed in the figure. The maximum quantity of

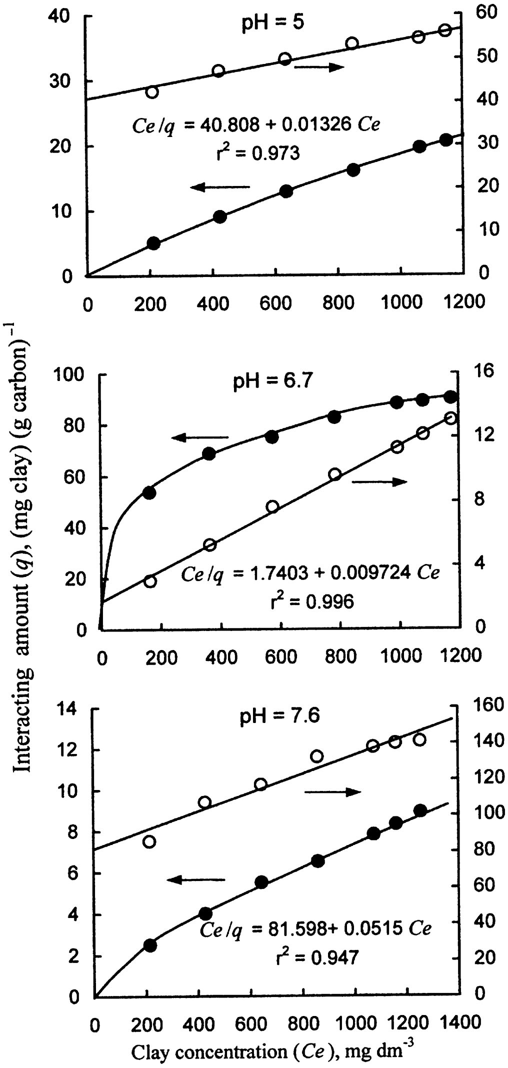

Fig. 4. Adsorption isotherms of montmorillonite particles on activated carbon at different clay concentrations and pH values. Full and open circles correspond to adsorption according to the Langmuir equation and Eq. (1), respectively. The error is within a 95% confidence interval of the mean, and the lines are the corresponding fit.

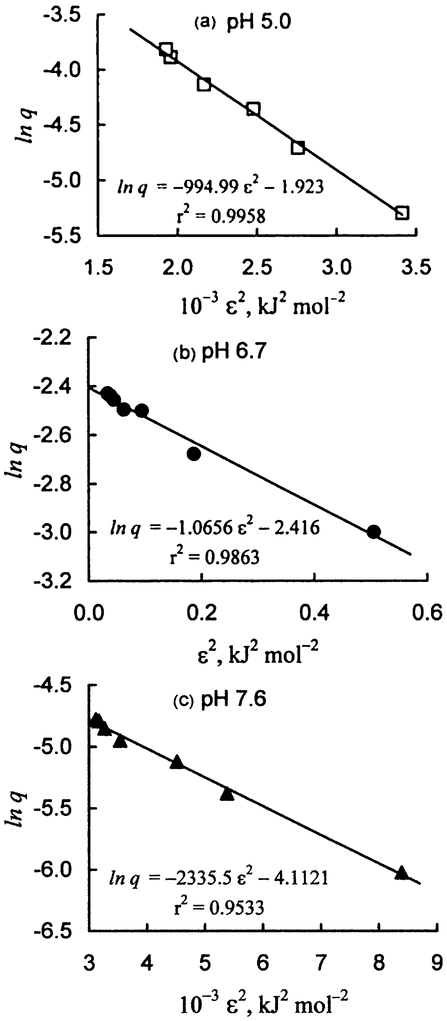

Fig. 5. Interaction isotherms of activated carbon with montmorillonite particles in agreement with Dubinin–Radushkevich equation for three pH values: (a) pH 5, (b) pH 6.7, and (c) pH 7.6.

clay acting reciprocally with carbon [$Q_i = (N_0 - N_E)/N_C$] can be calculated from the slopes of the lines as a proportion of clay particles with carbon particles expressed in mg/g or in particles numbers per g (see Table 1).

The data in Fig. 4 can be interpreted as follows: the carbon particles are sufficiently large in size ($V_C/V_M = 528{,}000$) and specific surface ($A_C/A_M = 1.80$) to act as a support/bridge between clay particles that form associations at these pH values. The quantities of clay per gram of carbon and/or number of clay particles ($N_M/N_C = 26{,}500$, 36,100, and 6820 clay particles/carbon particle, respectively) involved at pH 5, 6.7, and 7.6 indicate that interaction is favored at pH 6.7. Furthermore, it is a process involving a different interaction, as can be appreciated from the different values of the coefficients $k_5 = 0.3251\ \mathrm{dm^3\,g^{-1}}$ clay and $k_{6.7} = 5.591\ \mathrm{dm^3\,g^{-1}}$ clay and the different form of the two isotherms. This could be due to the fact that at low pH values the quantity of positively charged sites on the carbon particles increases significantly but the number of protons H^+ also increases in the system, causing competition between these and the positive carbon particles. At pH 7.6, the negative and positive charges of the surface carbon particles

Table 1
Ratio of montmorillonite particles (small) to carbon particles (large) $(N_0 - N_E)/N_C$ and interaction coefficients at equilibrium (according to Eq. (1))

Carbon concentration		$(N_0 - N_E)/N_C$		Interaction coefficient (k_I)		r^2
($\mathrm{g\,dm^{-3}}$)	pH	((mg clay)(g carbon)$^{-1}$)	(particle particle^{-1})	(dm^3 (g clay)$^{-1}$)	(cm^3 particle^{-1})	
1.0	5.0	75.41	26,500	0.325	0.482×10^{-12}	0.973
1.0	6.7	102.9	36,100	5.628	8.34×10^{-12}	0.996
1.0	7.6	19.41	6820	0.6315	0.935×10^{-12}	0.947

are the same (pzc = 7.5), causing a phenomenon of repulsion between these and the clay particles. This effect is manifested in low adsorption and/or interaction ($N_M/N_C = 6{,}820$ clay particles/carbon particle) and in the value of the coefficient $k_{7.6} = 0.7795\ \text{dm}^3\ \text{g}^{-1}$ clay.

Tracing $\ln q$ (q, clay particles adsorbed on those of carbon, in $\text{mol}\ \text{g}^{-1}$) as a function of ε^2 ($\text{kJ}^2\ \text{mol}^{-2}$) obtains Q ($\text{mol}\ \text{g}^{-1}$) and k ($\text{mol}^2\ \text{kJ}^{-2}$) for the intercept and the slope of the line, respectively (see Fig. 5). The results of Q in $\text{mg}\ \text{g}^{-1}$ and k in $\text{mol}^2\ \text{kJ}^{-2}$ are presented in Table 2. As can be observed, with the D–R isotherm, values of Q are obtained that are inversely proportional at the pH of the equilibrium and are also higher than those obtained with the Langmuir isotherm. This can only be explained by the fact that the linear Langmuir equation (for a homogeneous surface) at pH 5 fits a lower correlation coefficient ($r^2 = 0.973$) than that of the D–R equation ($r^2 = 0.995$) (see Tables 1 and 2) for this same isotherm, and also by the fact that the empirical equation of D–R is based on a model of gas adsorption by microporous sorbents [14,29].

From the physicochemical point of view, the clay/carbon/clay aggregates formed at pH 5 and 6.7 are adequate for the association, as are agglomerates with a clay–water interface, forming a more stable equilibrium condition than carbon–water and clay–water interfaces together in a system at pH $\geqslant 7.6$.

4.3. The interaction energy

The median adsorption energy and/or interaction, defined as the energy required to transfer one mol of the adsorptive (clay) from the solution to the adsorbent surface (carbon), was obtained from the relationship $E = \pm(2k)^{-0.5}$ given by Hobson [2,5–8,16] (see Appendix B). The E values for pH 5 and 7.6 are of the same order of sign and magnitude (± 22.42 and $\pm 14.63\ \text{J}\ \text{mol}^{-1}$, respectively), whereas at pH 6.7 a value of $\pm 685.0\ \text{J}\ \text{mol}^{-1}$ is obtained. In all cases the interaction is a completely physical process since the value lies within the range in which physical processes develop: 8–20 $\text{kJ}\ \text{mol}^{-1}$ [5,25]. The E values and the parameters of the D–R equation are given in Table 2.

4.4. Interaction kinetics

The interaction isotherms between carbon and montmorillonite particles show high affinity and the straight line in the graph of the experimental data C_e/q against C_e (Fig. 4) suggests the possible application of a Langmuir-type treatment of the reaction data shown in Fig. 6 [1].

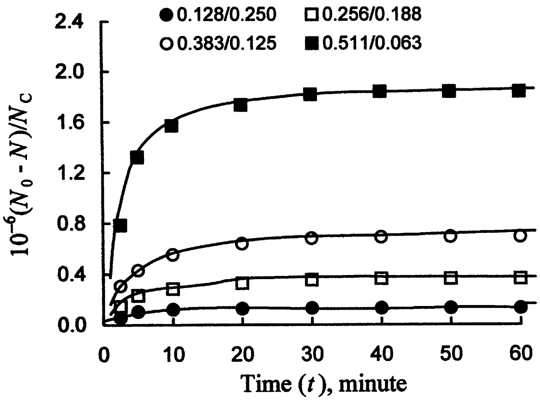

Fig. 6. Variation of the proportion $(N_0 - N_t)/N_C$ with the time for systems of different proportions of concentrations in $\text{g}\ \text{dm}^{-3}$ of clay particles and carbon to pH 6.5: 0.188/0.250, 0.256/0.188, 0.383/0.125, and 0.511/0.063.

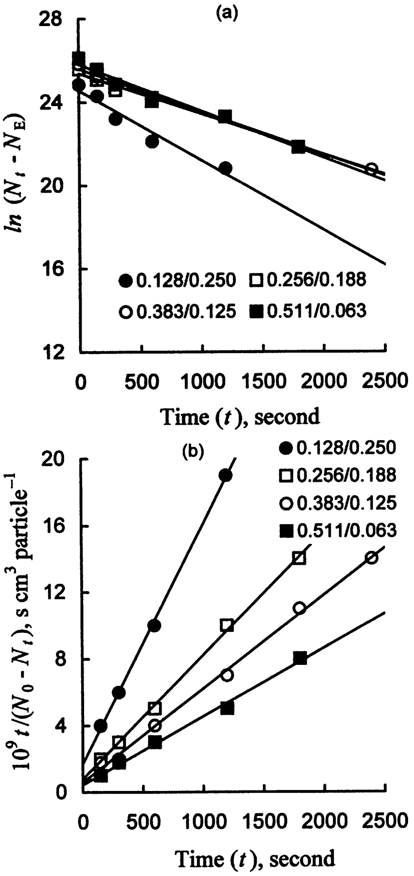

Fig. 7. Kinetics data of interaction in agreement with the Dubinin–Radushkevich model, Eqs. (7) (a) and (9) (b), for the clay/carbon ratios (●) 0.128/0.250, (□) 0.256/0.188, (○) 0.383/0.125, and (■) 0.511/0.063 $(\text{g clay})(\text{g carbon})^{-1}$.

Table 2

Parameters of the Dubinin–Radushkevich isotherm of the montmorillonite/carbon interaction for different pH values

Parameters	pH		
	5.0	6.7	7.6
Maximum interaction (Q) ($(\text{mg clay})(\text{g carbon})^{-1}$)	146.2	89.24	16.37
Proportional coefficient of energy interaction (k) ($\text{mol}^2\ \text{kJ}^{-2}$)	994.8	1.066	2335
Correlation coefficient (r^2) of Eq. (2)	0.995	0.931	0.953
Mean interaction energy (E) ($\text{J}\ \text{mol}^{-1}$)	±22.42	±685.0	±14.63

Table 3
Data of the interaction kinetics at pH 6.5 for different montmorillonite/carbon ratios

Parameters	Clay/carbon ratio ((mg clay)(mg carbon)$^{-1}$)			
	128/250	256/188	383/125	511/63
Number of carbon particles per cm^3, (N_C) × 10^{-5}	4.80	3.61	2.40	1.21
Number of clay particles per cm^3, (N_0) × 10^{-10}	8.64	17.28	25.85	34.49
Number of clay particles at equilibrium per cm^3, (N_E) × 10^{-10}	2.45	4.20	9.20	12.20
Clay/carbon interaction, $(N_0 - N_E)/N_C$, (particle particle^{-1}) × 10^{-5}	1.29	3.62	6.94	18.42
Interaction coefficient (k_1) of Eq. (8), s^{-1} × 10^3	3.36	1.94	2.06	2.25
Correlation coefficient (r^2) of Eq. (8)	0.950	0.981	0.994	0.978
Interaction coefficient (k_2) of Eq. (9), (cm^3 particle^{-1} s^{-1}) × 10^{14}	9.36	2.47	5.12	3.77
Correlation coefficient (r^2) of Eq. (9)	0.992	0.973	0.997	0.994

In equilibrium, all small clay particles should interact with all large carbon particles. This condition was not observed in the present study, as can be seen from the data shown in Tables 1 and 3 and in Fig. 7, where equilibrium was reached in between 30 and 40 min.

It is clear from Eqs. (8) and (9) that a graphic representation of $\ln(N_t - N_E)$ and/or $t/(N_0 - N_t)$ as a function of t (s) will give straight lines, from whose slope can be calculated the coefficients of pseudo-first (k_1) and pseudo-second (k_2) order of the clay/carbon interaction. Graphs of this type are shown in Fig. 7a. The data obtained from these graphs have a high correlation coefficient and are valid within the time range it takes for the interaction to reach equilibrium (30 to 40 min). The straight lines obtained confirm the concept expressed above through Eq. (8) and indicate that the level of interaction is directly proportional to the concentration of clay particles. In other words, the interaction is of pseudo-first order in terms of clay particle concentration.

Table 3 gives the interaction coefficients obtained from Eq. (8), corresponding to a reaction of pseudo-first order. The values for the coefficients are of the order of $k_1 \approx 10^{-3}\ \mathrm{s}^{-1}$. The fact that the clay/carbon ratio is >1:1, a value that normally applies to the factor of bimolecular collision, may be responsible for the high interaction coefficients.

By applying Eq. (9) we obtain the coefficients of pseudo-second order ($k_2 \approx 10^{-14}\ \mathrm{cm^3\ particle^{-1}\ s^{-1}}$) shown in Table 3 (see Fig. 7b). These pseudo-second-order interaction coefficients are very similar to those obtained for the interaction between the same clay particles and positively charged Fe-oxyhydroxyde (β-FeOOH: akaganeite) particles, which have a volume ratio of $V_{\mathrm{FeOOH}}/V_{\mathrm{M}} = 2.44$ and $k_1 \approx 10^{-14}\ \mathrm{cm^3\ s^{-1}}$ [1].

5. Conclusions

Positively charged carbon particles appear to act as a support for negatively charged montmorillonite particles and form associations even at values of pH 5 and 6.7, under which conditions the presence of positive charges in the carbon does not have much effect. At pH values ⩾ 7.6 the interaction is smaller, and at pH > 9 any interaction would not be detectable, owing to the presence of negative charges in the carbon particles. At the same concentration of carbon particles, the ratio of clay particles to carbon particles was 6200 to 36,000, depending on the pH of the system. The interaction of the particles as a function of the suspension concentration gave place to isotherms of high affinity with interaction coefficients of pseudo-first order ($k_1 = 3.354 \times 10^{-3}$ to $1.94 \times 10^{-3}\ \mathrm{s}^{-1}$) and pseudo-second order ($k_2 = 9.36 \times 10^{-8}$ to $2.47 \times 10^{-8}\ \mathrm{cm^3\ particle^{-1}\ s^{-1}}$) when the data were adjusted to Eqs. (8) and (9). The energy (±14.63 to ±685.0 J mol^{-1}) data show that the reaction is mainly physical.

The values of the pseudo-first-order coefficients ($10^{-3}\ \mathrm{s}^{-1}$) are much bigger that those of the pseudo-second-order coefficients ($10^{-14}\ \mathrm{cm^3\ s^{-1}}$). These, in turn, are smaller than those obtained with the flocculation kinetics, usually on the order of $10^{-12}\ \mathrm{cm^3\ s^{-1}}$ [1]. This could indicate that the collisions between the clay and carbon particles form clay/carbon/clay aggregates at first, and later bigger aggregates are formed, which eventually produce the flocculation and sedimentation.

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Appendix A. Calculation of the Polanyi potential

The equation of the Polanyi potential (ε) given by Hobson [16] for the adsorption of gases on solid surfaces is

$$\varepsilon = -RT \ln(p/p_0), \tag{A.1}$$

where p is the gas pressure in contact with the adsorbent surface at equilibrium and p_0 corresponds to the initial pressure. To apply this equation to the adsorption of an adsorptive in aqueous media, $p_0 = C_I k_B T$ and $p = C_E k_B T$ [30] must be replaced, where C_I is the initial concentration of the adsorptive, C_E is the equilibrium concentration, k_B is the Boltzmann constant ($1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}\ molecule^{-1}}$), and T is the absolute temperature. $C_A = C_I - C_E$, where C_A is the amount adsorbed. The quantities C_A, C_I, and C_E have the same units, i.e., molecule cm^{-3}, molecule dm^{-3}, particle cm^{-3}, etc. Equation (A.1) can thus be written as

$$\varepsilon = \mathrm{RT} \ln\left(1 + \frac{C_A}{C_E}\right). \tag{A.2}$$

Table 4
Different parameters of the Dubinin–Radushkevich equation obtained by the three equations of the Polanyi potential (ε) for pH 5

Parameters	Eq. (A.2)	Eq. (A.3)	Eq. (A.4)
C_A ((g clay) dm^{-3})	0.0128	0.0128	0.0128
C_e ((g clay) dm^{-3})	0.6373	0.6373	0.6373
ε^2 (kJ^2 mol^{-2})	0.002476	5.575	7.9602
k (kJ^2 mol^{-2})	994.8	0.08618	0.09044
Q ((mg clay)(g carbon)$^{-1}$)	146.2	23.46	17.81
E (kJ mol^{-1})	±0.02242	±2.409	±2.351
Correlation coefficient r^2	0.996	0.954	0.871

This equation is written by many researchers [2–8,31–33] as

$$\varepsilon = \mathrm{RT}\ln\left(1 + \frac{1}{C_\mathrm{E}}\right), \tag{A.3}$$

$$\varepsilon = \mathrm{RT}\ln\frac{1}{C_\mathrm{E}}, \tag{A.4}$$

and also as [34,35]

$$\varepsilon = \mathrm{RT}\ln\frac{S}{C_\mathrm{W}}, \tag{A.5}$$

where S is the adsorptive solubility in water (g dm^{-3}) and C_W is the equilibrium concentration of the adsorptive in water (g dm^{-3}).

The results of Eqs. (A.3) and (A.4) are similar but differ considerably from those obtained by Eq. (A.2) proposed in the present paper (see Table 4). We are not aware of adequate support in the literature for the use of Eqs. (A.3) and (A.4), nor of any proposal for C_E units: mol L^{-1}, (g solute)(g solution)$^{-1}$, etc. In Eqs. (A.1) and (A.2) the units correspond to the pressures (dyn cm^{-2}) but these are eliminated in both, so that the units depend solely on RT (J mol^{-1}, kJ mol^{-1}, etc.).

Appendix B. The adsorption energy

According to Hobson, “the most probable energy of adsorption” [16] is given by

$$E = (2k)^{-0.5}, \tag{B.1}$$

where k is the energy constant of the equation of D–R [14,15].

In Eq. (B.1), the sign ± should be assigned, since it is the result of a square root. We obtain in this way

$$E = \pm(2k)^{-0.5}. \tag{B.2}$$

This would solve the different interpretations that various authors give to Eq. (B.1), even those who cite Hobson, giving the adsorption energy E positive [2,5–8,31–33,36–38] and/or negative [3,39–41] values. Another form of presenting the energy E is [32,33,39]

$$E = 1/\sqrt{-2k}. \tag{B.3}$$

This equation is mathematically impossible to solve with real numbers, unless the sign of k is negative; but according to the D–R equation it has a positive value. To correct this, some authors [42,43] write Eq. (B.1) as

$$E = -(2k)^{-0.5}. \tag{B.4}$$

The sign of the value of adsorption energy should be determined by the adsorption enthalpy ΔH, which will be negative in exothermic and positive in endothermic processes.

References

[1] E.A. Ferreiro, A.K. Helmy, S.G. de Bussetti, Clay Miner. 30 (1995) 195.
[2] G. Akçay, M. Akçay, K. Yurdakoç, J. Colloid Interface Sci. 281 (2005) 27.
[3] M. Yurdakoç, Y. Seki, S. Karahan, K. Yurdakoç, J. Colloid Interface Sci. 286 (2005) 440.
[4] X. Yang, B. Al-Duri, J. Colloid Interface Sci. 287 (2005) 25.
[5] S.I. Lyubchik, A.I. Lyubchik, O.L. Galushko, L.P. Tikhonova, J. Vital, I.M. Fonseca, S.B. Lyubchik, Colloids Surf. A Physicochem. Eng. Aspects 242 (2004) 151.
[6] M.S. Onyango, Y. Kojima, O. Aoyi, E.C. Bernardo, H. Matsuda, J. Colloid Interface Sci. 279 (2004) 341.
[7] C.-T. Hsieh, H. Teng, J. Chem. Technol. Biotechnol. 75 (11) (2000) 1066.
[8] C.-T. Hsieh, H. Teng, J. Colloid Interface Sci. 230 (2005) 171.
[9] B. Vincent, G.A. Young, Th.F. Tadros, J. Chem. Soc. Faraday Trans. I 76 (1980) 665.
[10] B. Vincent, M. Jafelicci, P.F. Luckham, Th.F. Tadros, J. Chem. Soc. Faraday Trans. I 76 (1980) 674.
[11] S. Harley, D.W. Thompson, B. Vincent, Colloids Surf. 62 (1992) 163.
[12] Z. Adamczyk, B. Siwek, M. Zembala, Colloids Surf. 62 (1992) 119.
[13] S.L. Swartzen-Allen, E. Matijevic, J. Colloid Interface Sci. 50 (1975) 143.
[14] N.D. Hutson, R.T. Yang, Adsorption 3 (1997) 189.
[15] M. Manes, L.J.E. Hofer, J. Phys. Chem. 73 (1969) 584.
[16] J.P. Hobson, J. Phys. Chem. 73 (1969) 2720.
[17] Y.S. Ho, G. McKay, Process Biochem. 34 (1999) 451.
[18] E.A. Ferreiro, S.G. de Bussetti, Z. Phys. Chem. 217 (2003) 1143.
[19] S.G. de Bussetti, E.A. Ferreiro, A.K. Helmy, Clays Clay Miner. 28 (1980) 149.
[20] N. Peinemann, E.A. Ferreiro, A.K. Helmy, Rev. Asoc. Geol. Argentina 27 (1972) 399.
[21] S.G. de Bussetti, E.A. Ferreiro, Clays Clay Miner. 52 (2004) 334.
[22] A.K. Helmy, E.A. Ferreiro, J. Electroanal. Chem. Interface Electrochem. 57 (1974) 103.
[23] S.G. de Bussetti, E.A. Ferreiro, Z. Phys. Chem. 217 (2003) 45.
[24] E.A. Ferreiro, A.K. Helmy, Clay Miner. 10 (1974) 203.
[25] K.J. Laidler, J.H. Meiser, Fisicoquímica, Cia. Editorial Continental, S.A. de C.V., Mexico, 1997, p. 987.
[26] A.K. Helmy, E.A. Ferreiro, S.G. de Bussetti, Z. Phys. Chem. 261 (1980) 1065.
[27] The United State Department of Agricultural (USDA), Soil Survey Laboratory Method Manual, Soil Survey Investigation Report No. 42, vol. IV, 1996, p. 634.
[28] C.H. Giles, A.P. D'Silva, I.A. Easton, J. Colloid Interface Sci. 47 (1974) 766.
[29] M.M. Dubinin, Carbon 27 (1989) 457.
[30] A.K. Helmy, E.A. Ferreiro, S.G. de Bussetti, J. Colloid Interface Sci. 183 (1996) 131.
[31] A. Benhammou, A. Yaacoubi, L. Niboub, B. Tanouti, J. Colloid Interface Sci. 282 (2005) 320.
[32] R. Donat, A. Akdogan, E. Erdem, H. Cetisli, J. Colloid Interface Sci. 286 (2005) 43.
[33] S.Q. Memon, S.M. Hasany, M.I. Bhanger, M.Y. Khuhawar, J. Colloid Interface Sci. 291 (2005) 84.
[34] S. Kleineidam, C. Schüth, Environ. Sci. Technol. 35 (2002) 4689.
[35] A. Bembonowska, R. Peech, E. Milchert, J. Colloid Interface Sci. 265 (2003) 276.

[36] S.A. Dastgheib, T. Karanfil, J. Colloid Interface Sci. 292 (2006) 312.
[37] S. Kundu, A.K. Gupta, Colloids Surf. A Physicochem. Eng. Aspects 273 (2006) 121.
[38] G. Gereli, Y. Seki, İ.M. Kuşoğlu, K. Yurdakoç, J. Colloid Interface Sci. 299 (2006) 155–162.
[39] M. Akçay, J. Colloid Interface Sci. 280 (2004) 299.
[40] M. Akçay, J. Colloid Interface Sci. 296 (2006) 16.
[41] Y. Seki, K. Yurdakoç, J. Colloid Interface Sci. 287 (2005) 1.
[42] G. Akçay, M. Akçay, K. Yurdakoç, J. Colloid Interface Sci. 296 (2006) 428.
[43] S. Karahan, M. Yurdakoç, Y. Seki, K. Yurdakoç, J. Colloid Interface Sci. 293 (2006) 36.