

Available online at www.sciencedirect.com

ScienceDirect

www.journals.elsevier.com/jes

Mechanism of Methylene Blue adsorption on hybrid laponite-multi-walled carbon nanotube particles

Maryna Manilo¹, Nikolai Lebovka^{1,*}, Sandor Barany^{2,3}

1. Institute of Biocolloidal Chemistry named after F.D. Ovcharenko, National Academy of Sciences of Ukraine, 42, Vernadsky blvd., 030142 Kyiv, Ukraine. E-mail: assol_M@i.ua

2. University of Miskolc, MTA-ME Materials Science Research Group and Institute of Chemistry, Hungary

3. The Transcarpathian II. Ferenc Rakoczi Hungarian Institute, Beregovo, Ukraine

ARTICLE INFO

Article history:

Received 7 April 2015

Revised 10 June 2015

Accepted 26 June 2015

Available online 31 August 2015

Keywords:

Multi-walled carbon nanotubes

Laponite platelets

Methylene Blue

Adsorption

Kinetics

Zeta potential

ABSTRACT

The kinetics of adsorption and parameters of equilibrium adsorption of Methylene Blue (MB) on hybrid laponite-multi-walled carbon nanotube (NT) particles in aqueous suspensions were determined. The laponite platelets were used in order to facilitate disaggregation of NTs in aqueous suspensions and enhance the adsorption capacity of hybrid particles for MB. Experiments were performed at room temperature (298 K), and the laponite/NT ratio (X_1) was varied in the range of 0–0.5. For elucidation of the mechanism of MB adsorption on hybrid particles, the electrical conductivity of the system as well as the electrokinetic potential of laponite-NT hybrid particles were measured. Three different stages in the kinetics of adsorption of MB on the surface of NTs or hybrid laponite-NT particles were discovered to be a fast initial stage I (adsorption time $t = 0$ –10 min), a slower intermediate stage II (up to $t = 120$ min) and a long-lasting final stage III (up to $t = 24$ hr). The presence of these stages was explained accounting for different types of interactions between MB and adsorbent particles, as well as for the changes in the structure of aggregates of NT particles and the long-range processes of restructuring of laponite platelets on the surface of NTs. The analysis of experimental data on specific surface area versus the value of X_1 evidenced in favor of the model with linear contacts between rigid laponite platelets and NTs. It was also concluded that electrostatic interactions control the first stage of adsorption at low MB concentrations.

© 2015 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

Introduction

Recent studies have shown the good potential of carbon nanotubes (NTs) for adsorptive purification of water contaminated by toxic metals (Kabbashi et al., 2009; Adolph et al., 2012; Yu et al., 2013), organic matters (Bele, 2010; Lian et al., 2012) and synthetic dyes (Fugetsu et al., 2004; Gupta et al., 2013; Kerkez and Bayazit, 2014). Methylene Blue (MB) is frequently used as a model dye in investigations of adsorption

on carbon-based substances. The data on adsorption of MB by different types of carbons (Wang et al., 2005; Kavitha and Namasivayam, 2007; Qada et al., 2008) and NTs (Yan et al., 2005; Qu et al., 2008; Shahryari et al., 2010; Madrakiana et al., 2011; Norzilah et al., 2011; Ma et al., 2012; Li et al., 2013; Szlachta and Wójtowicz, 2013; Tabrizi and Yavari, 2015) were already reported.

The kinetic and equilibrium data for adsorption of MB on multi-walled NTs at different temperatures were analyzed

* Corresponding author. E-mail: lebovka@gmail.com (Nikolai Lebovka).

(Shahryari et al., 2010). Adsorption equilibrium was attained within ~2 hr. The estimated thermodynamic parameters suggested that the process of MB adsorption on NTs was spontaneous and endothermic. The same conclusions were done from adsorption investigation of MB on NT-based aerogel (Tabrizi and Yavari, 2015). Data on adsorption kinetics of MB on multi-walled NTs revealed that adsorption was rapid in the initial stage and then followed by a slower process to reach the plateau value (Szlachta and Wójtowicz, 2013). Study of the adsorption of MB on single-walled NTs testified that the nature of adsorption is mainly determined by charge-transfer and hydrophobic interactions (Yan et al., 2005). The presence of solubilization of NTs and formation of MB–NT adsorptive nanostructures in water has been demonstrated. Adsorption of MB on NTs at different pH was studied in details, and it was concluded that the adsorption mechanism may be due to π – π electron donor acceptor interactions and electrostatic attraction between positively charged dye ions and NTs (Li et al., 2013). The method of removal of MB from aqueous solution using multi-walled magnetic NTs was proposed (Qu et al., 2008; Madrakiana et al., 2011). The prepared magnetic NTs can be easily separated in magnetic field after they have been loaded with dye. The alkali-activated NTs demonstrated excellent adsorption capacity for MB (399 mg/g). The effects were attributed to the multiple adsorption interaction mechanisms (hydrogen bonding, π – π and electrostatic interactions, etc.) (Ma et al., 2012).

The adsorption capacity of NTs for MB is increased after heat treatment and it is decreased after acid modification (Norzilah et al., 2011). It was demonstrated that the adsorption of MB on modified NTs was mainly influenced by surface functional groups. Recently, a new type of hybrid adsorbent based on multi-walled NTs covered by platelets of laponite was described (Loginov et al., 2012). Stabilization of NTs in the presence of laponite was explained by the formation of the hydrophilic charged shells on the NTs surface. The presence of such shells was recently visualized using high resolution transmission electron microscopy (TEM) technique (Manilo et al., 2015). Hydride laponite-NT adsorbent can be effectively used for removal of MB from aqueous systems (Loginov et al., 2014). Moreover, the prepared hybrid adsorbent can be easily separated using filtration after being loaded with dye. However, the mechanism of adsorption of MB on the surface of hybrid laponite-NT adsorbent has not been fully understood yet.

The objective of this study is to investigate the mechanism of adsorption of MB onto hybrid laponite and NT particles in aqueous suspensions. The kinetics of adsorption and parameters of equilibrium adsorption at different values of laponite/NT ratio were measured. For elucidation of the nature of MB adsorption onto hybrid particles the studies of electrical conductivity and electrophoretic mobility were also performed.

1. Experimental

1.1. Materials

The multi-walled carbon nanotubes (NTs) were produced by catalytic chemical vapor deposition (CVD) method in the presence of Fe–Mo–Al catalyst (Specmash, Kyiv, Ukraine)

(Melezhyk et al., 2005). NTs were purified by annealing to separate from the catalyst and mineral impurities, and treated by aqueous solutions of alkali (NaOH) and hydrochloric acid (HCl). Then samples were filtered to remove the excess acid and repeatedly washed by distilled water until the constant pH of ~7.5. The studied NTs were composed of concentric shells with inter-shell distance (d_{ss}) of 0.34 nm, their typical outer diameter (d_n) of 10–20 nm, their length (l_n) of 5–10 μ m, and the number of walls within the range of ~6–8 layers. The estimated density (ρ_n) of NTs decreases from 1.6 to ~1 g/cm³, while their outer diameter increased from 10 to 20 nm (Manilo et al., 2014). Typically, as-grown by CVD method the multi-walled carbon nanotubes have closed ends and the internal surface is unavailable to the absorption (Yao et al., 2008). It was supported by the adsorption data. The specific surface area of NTs (S_n), experimentally determined by nitrogen adsorption, was 254 ± 5 m²/g and was close to the theoretically estimated value of the outer specific area (Manilo et al., 2014) which was calculated as follows:

$$S_n^m = \pi d_n l_n \approx 260 \text{ m}^2/\text{g}.$$

The laponite RD (Rockwood Additives Ltd., Widnes, UK) is a typical synthetic swelling clay with the formula of $\text{Na}_{0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.4})\text{O}_{20}(\text{OH})_4]$. It is composed of charged disk-like platelets with thickness (h_l) about 1 nm and average diameter (d_l) about 25 nm (Zebrowski et al., 2003). The density of laponite (ρ_l) is equal to 2.53 g/cm³ (Zebrowski et al., 2003). Taking into account the shape, size and density of the laponite particles, their specific surface area (S_l^m) may be theoretically estimated as:

$$S_l^m = \frac{2}{h_l \rho_l} \approx 791 \text{ m}^2/\text{g}.$$

This value noticeably exceeded the experimental value (359–368 m²/g) determined by N₂ adsorption (Fripiat et al., 1982), or by H₂O adsorption (345.1 m²/g) (Fripiat et al., 1982). The laponite platelets are charged highly heterogeneously in aqueous suspensions. Their faces have large negative charge, while smaller surface charge of their edges (~10% of the total charge) is pH-dependent and positive in acidic medium. The negative surface charge of laponite RD, defined as its cation exchange capacity (CEC), was equal to 0.75 meq/g.

Cationic dye Methylene Blue (MB) with molecular formula $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$ (molecular weight (M_{MB}) of 319.85 g/mol) was chosen as adsorbate. The molecule of MB can be regarded approximately as a rectangular volume of dimensions 1.7 nm \times 0.76 nm \times 0.325 nm with effective areas of adsorption on face and edge surfaces equalling to 1.3 nm² and 0.55 nm², respectively (Johnson, 1957) (Fig. 1). The dye stock solution was prepared by dissolving the weighted solid crystal-hydrate $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S} \cdot 3\text{H}_2\text{O}$ (Merck, Darmstadt, Germany), with M_{MB} of 373.9 g/mol in distilled water to make a concentration of 100 mg/dm³. Then experimental solutions were prepared by diluting stock solution with distilled water to the designated concentration.

Hybrid laponite-NT systems were obtained by addition of the appropriate amounts of laponite and NTs to distilled water and subsequent sonication of mixtures using ultrasonic

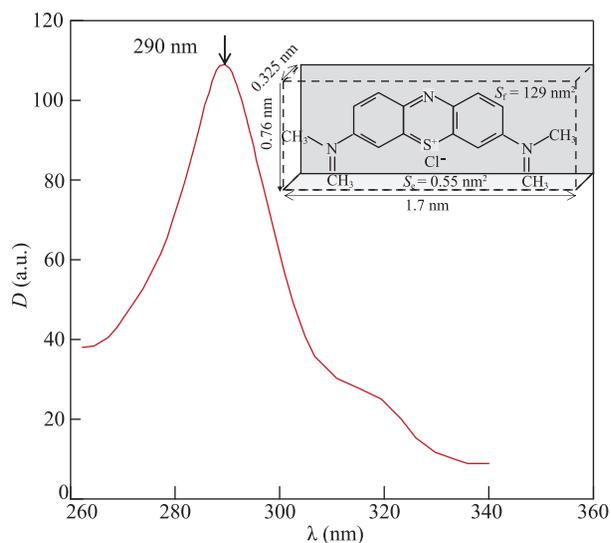


Fig. 1 – Structure and molecular dimensions of cationic dye Methylene Blue (MB) and its typical spectrum in water (the concentration of MB is 12 mmol/L) in the region 260–340 nm. D: optical density; λ : wavelength.

disperser (UZDN-20/40, UkrRosprylad, Sumy, Ukraine) at the frequency of 44 kHz and the output power of 150 W during 10 min. To prevent overheating, the suspensions were sonicated in a cold-water bath, and the temperature of suspension never exceeded 30°C. The laponite/NTs ratio ($X_1 = m_l/m_n$) (g/g), was changed in the range of 0–0.5. Preliminary microscopic observations have shown that an increase of X_1 resulted in efficient dispersion and disaggregation of NTs, and at $X_1 \approx 0.5$ formation of fully disaggregated suspensions was observed (Loginov et al., 2012).

1.2. Experimental techniques

Batch adsorption experiments were carried out using 0.01 wt.% suspension of laponite-NT hybrids and bulk MB solutions. 100 mL flask with suspension was shaken during the period up to 24 hr. Then the suspension was filtered using a 0.2 μm Millipore filter (Schleicher and Schuell BioScience GmbH, Dassel, Germany) and the filtrates were analyzed for MB concentration using ultraviolet–visible (UV–vis) spectrophotometer (Specord UV Vis, Analytik Jena AG, Jena, Germany) at 290 nm. MB showed two main absorption bands, one in the region of 500–650 nm and another in the region of 270–320 nm (Song et al., 2009). Aggregation of MB (with the formation of MB dimers, trimers and higher aggregates) and interactions with nanoparticle surfaces can gradually affect the structure of absorption spectrum in the region of 500–650 nm (Cenens and Schoonheydt, 1988; Schoonheydt and Heughebaert, 1992; Schoonheydt and Johnston, 2006), while the absorbance in the region of 260–340 nm (Fig. 1) usually displays only insignificant changes (Song et al., 2009). In the present work for determination of MB concentration the absorbance at 290 nm was analyzed. The content of MB was calculated using a standard curve based on the Lambert–Beer law.

The adsorption capacity (a) (g/g) was the ratio of the amount of dye adsorbed to the mass of NTs and was calculated using the following mass balance equation:

$$a = \frac{m_d^0}{m_n} \left(1 - \frac{m_d}{m_d^0} \right) \quad (1)$$

where, m_d^0 (g) and m_d (g) are the initial and final dye masses and m_n is the mass of NTs.

The electrical conductivity of suspensions was measured using the inductance, capacitance and resistance (LCR) meter 819 (Instek, Good Will Instrument Co., Ltd., New Taipei City, Taiwan) under the applied external voltage of 1.0 V at the frequency of 1 kHz. The measurements were carried out in a cell with two platinum plate electrodes with the distance of ~ 5 mm between them and effective cell volume of ~ 1 cm³. The electrical conductivity of distilled water (σ) was ~ 4 $\mu\text{S}/\text{cm}$. Electrical conductivity measurements were performed immediately after preparation of the samples.

Electrophoretic measurements of NTs, laponite and NT-laponite complex were performed by ZetaSizer NS device (Malvern Instruments Ltd, Malvern, Worcestershire, UK) at electric field gradients of several or several dozen of V/cm and at 25°C. The measurements are based on the combination of laser doppler velocimetry and phase analysis light scattering (PALS) in Malvern's M3-PALS technique. The instrument is suitable for determination of size distribution function ($F(R)$) in the range of 0.3–10 μm . Measurements of $F(R)$ are based on application of non-invasive back scatter technology. The electrophoretic mobility (μ) was converted into zeta potential (ζ) using the classical Smoluchowsky formula (Dukhin and Derjaguin, 1976).

The literature data evidence that laponite disks in aqueous suspensions are chemically unstable (Tiller, 1968a, 1968b; Thompson and Butterworth, 1992; Mourchid and Levitz, 1998; Savenko et al., 2013; Jatav and Joshi, 2014). Typically, dissolution is developed on a rather long time scale (several weeks) and it is minimal in basic media. In order to prevent the impact of the named chemical instability, freshly prepared suspensions were used and all experiments were performed at constant value of pH ~ 10.0 , adjusted using 0.05 mol/L borate buffers. This level of pH was used to prevent the fast degradation of laponite particles.

Experiments were carried out at a constant temperature of 298 K and were replicated 3–5 times. The mean values and the standard deviations were calculated. The error bars in all the figures correspond to the confidence level of 95%.

2. Results and discussion

Fig. 2 presents examples of time dependence of adsorption (a) at different values of X_1 . It is seen that three different stages of the kinetics could be distinguished. In all cases the adsorption of MB onto NTs and hybrid laponite-NT particles was rapid in the initial stage I (adsorption time $t = 0$ –10 min), followed by a slower process (stage II) up to $t = 120$ min. Note, that the presence of fast initial stage in the adsorption of MB on multi-walled NTs was also reported earlier (Szlachta and Wójtowicz, 2013).

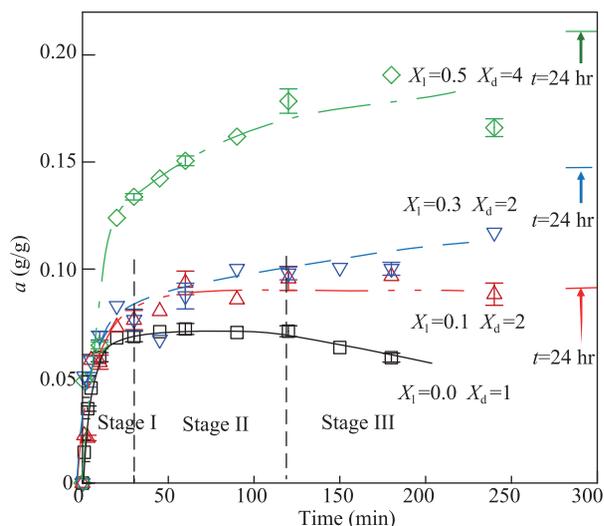


Fig. 2 – Typical time dependences of MB adsorption capacity (*a*) on laponite-NT hybrid particles at different values of the laponite/NTs ratio (X_1) and equilibrium relative concentration of dye (X_d). The chosen value of X_d approximately corresponds to that required for the monolayer adsorption at the given value of X_1 . MB: Methylene Blue; NT: nanotube.

It can be speculated that during stage I the adsorption of MB on the most active centers on the surface of particles may occur. During this stage the adsorption was governed by strong electrostatic interactions between positively charged cation of MB⁺ and negatively charged surfaces of laponite and NTs. The negative charge of the faces of laponite originates from the water-particle interactions as a result of hydrolysis while the negative charge of NTs is attributed to the dissociation of surface functional groups. According to FTIR spectra, the NT surface contained a small amount of hydroxyl and carboxylic groups (Manilo et al., 2014). Moreover, MB is an ideally planar molecule, and π - π stacking interactions between the hexagonal skeleton of NTs and aromatic backbone of MB (Chen et al., 2007) may also be rather important at this stage of adsorption.

Stage II corresponded to the slower rate of adsorption, and could be explained by the presence of other types of surface adsorption sites. Note that the presence of initial rapid stage I and later on slower process (stage II) was previously observed in adsorption kinetics of MB on multi-walled NTs (Szlachta and Wójtowicz, 2013).

At longer time of adsorption (stage III) different behaviors of the system were observed as a function of the X_1 value. During stage III the value of a decreased continuously with time for pure NTs ($X_1 = 0$). This behavior can reflect the partial desorption of MB from the surface of NTs at the late stage of adsorption owing to the development of aggregation of NT particles in aqueous medium. At small values of X_1 ($X_1 = 0.1$) the adsorbed amount (a) rapidly reached a plateau. At larger values of X_1 a continuous increase in a was observed for longer time and the plateau regime was reached at $t = \sim 24$ hr. The time required for attaining the adsorption equilibrium was dependent upon the value of X_1 , and it turned to be ~ 3 hr for

$X_1 = 0.1$ and ~ 24 hr for $X_1 = 0.3$ and 0.5 . The long period of time necessary to reach the adsorption equilibrium for $X_1 = 0.3$ and 0.5 can reflect the long-lasting processes of equilibration of MB molecules that were initially not uniformly distributed between different adsorbent particles. The presence of the similar long-lasting processes of equilibration of the cationic surfactant cetyltrimethylammonium bromide (CTAB) molecules on the surface of laponite was previously reported (Savenko et al., 2013).

Fig. 3 shows the adsorbed amount of MB (a) versus equilibrium relative concentration of dye (X_d , equalling to m_d/m_n) at different values of X_1 . Analysis has shown that all isotherms can be successfully fitted by a Langmuir-type equation:

$$\frac{a}{a_m} = \frac{KX_d}{1 + KX_d} \quad (2)$$

where, the value of a_m corresponds to a monolayer adsorption of MB and K is the equilibrium constant related to the free energy of adsorption.

It is interesting that at small values of X_d , the linear relationships of $a = Ka_m X_d$ for different values of X_1 were observed with the same value of $Ka_m = 0.0968 \pm 0.0004$ (with a coefficient of determination $r^2 = 0.999$) (see inset in Fig. 3).

Fig. 4 demonstrates the values of monolayer adsorption (a_m) and specific surface area (S , m²/g) versus the value of X_d . The specific surface area of the hybrid laponite-NT particles was calculated as (Itodo et al., 2010):

$$S = a_m s N_A / M \approx 2061 a_m \quad (3)$$

where, s (1.3 nm²) is the face surface of one molecule of MB, N_A (6.022×10^{23} mol⁻¹) is the Avogadro number and M (373.9 g/mol) is the molecular mass of the MB + 3H₂O unit.

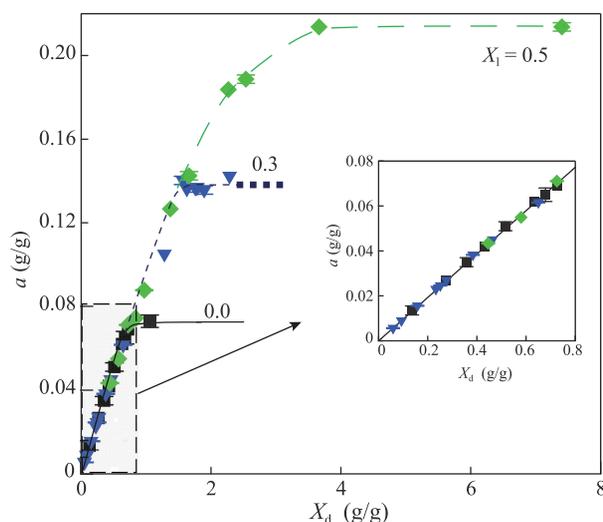


Fig. 3 – Adsorption capacity (*a*) versus equilibrium relative concentration of dye (X_d) at different values of the laponite/NTs ratio (X_1). Inset plot shows the initial section of isotherms at small X_d and different values of X_1 . NT: nanotube.

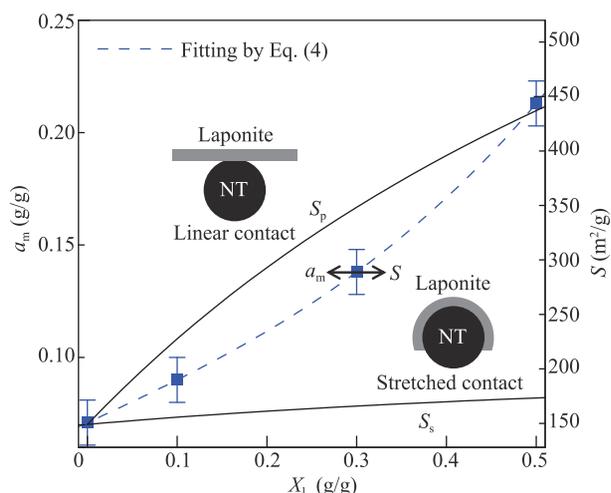


Fig. 4 – Dependence of monolayer adsorption (a_m) and specific surface area (S) of the hybrid laponite-NT particles on the value of the laponite/NTs ratio (X_1) estimated using stretched (S_s) and linear (S_p) contact models. Dashed line corresponds to the experimental data fitting by parabolic equation (Eq. (4)). NT: nanotube.

Dependencies of monolayer adsorption on X_1 can be well fitted (with a coefficient of determination $r^2 = 0.9996$) by the following parabolic equation:

$$a_m = (0.072 \pm 0.002) + (0.137 \pm 0.021)X_1 + (0.289 \pm 0.040)X_1^2. \quad (4)$$

At $X_1 = 0$ (i.e., for pure NTs) the specific surface area of NTs in water was $S_n^0 \approx 149 \text{ m}^2/\text{g}$ and it was noticeably smaller than the maximally possible value (theoretically estimated), $S_n^m \approx 260 \text{ m}^2/\text{g}$ (Manilo et al., 2014). This can be explained by high aggregation of hydrophobic NT particles in water that results in screening of some portion of the surface of NT particles. Moreover, some places on the NTs surface may not be suitable for effective adsorption of MB dye. Adsorption of MB on the surface of NTs is governed by different driving forces, i.e., van der Waals attractive interaction, π - π stacking interactions between aromatic rings of NTs and MB, and electrostatic interactions between the cationic dye and the negatively charged surface of NTs (Fugetsu et al., 2004).

Additional information on the contribution of different forces into mechanism of MB adsorption onto laponite-NTs complex particles can be extracted from electrokinetic and electrical conductivity measurements of the system. According to our electrokinetic data, at pH ~ 10.0 the laponite clay disks and NTs have negative charge and their zeta potential values (ζ) turned to be -47 and -43 mV, respectively. The observed hetero-coagulation and formation of laponite-NTs hybrid particles evidently reflect the presence of attractive interactions between similarly charged species. A number of theoretical and experimental works have demonstrated that unusual attractive interactions can exist for similarly and highly charged colloidal particles (Lebovka, 2014). The observed hetero-coagulation between similarly charged NTs and

laponite clay disks can be related to highly heterogeneous distribution of the negatively charged functional groups on the surface of NTs. Also, the highly charged laponite disk can be effectively immobilized on the neutral fraction of the NT surface due to strong attraction between it and the equivalent image charge, produced in the conductive surface of NT (Leite et al., 2012).

An increase of X_1 from 0 to 1 caused a monotonic decrease of the negative ζ of laponite-NT hybrid particles (value of ζ changed from -40 to -32 mV), and the value of zeta potential reached saturation at the level of -31 mV at $X_1 \geq 0.4$. The observed behavior of the zeta potential reflects the immobilization of laponite platelets on the surface of NTs and formation of hybrid laponite-NT particles. Summarizing the electrokinetic data, one can say that adsorption/heteroadagulation of laponite disks onto NT stabilizes the nanotubes suspension as a result of hydrophilization of their surface, and gives some (by about 20%) decrease of the negative electrokinetic potential of nanotubes; at the same time their zeta potential values remain high enough to facilitate the adsorption of cationic dye due to Coulomb interactions.

The size distribution functions $F(R)$ for the studied systems revealed the presence of species with different sizes depending on the value of X_1 (Fig. 5). At small value of X_1 , three distinctive species were observed, i.e., large aggregates of non-stabilized NTs ($R \approx 2\text{--}3 \mu\text{m}$), intermediate aggregates of partially stabilized NTs ($R \approx 0.3\text{--}1 \mu\text{m}$) and smaller species (100–200 nm) that can be attributed to the stabilized NT-laponite hybrid particles. At higher concentration of laponite ($X_1 = 0.3\text{--}0.5$), single species with the size of 200–300 nm were observed. However, at larger ratio ($X_1 = 0.7$), two different species that can be attributed to the stabilized NT-laponite hybrid particles (200–700 nm) and free laponite clay disks not coupled with NTs (40–100 nm) were observed. The adsorption data in the present work were obtained for the range of $X_1 \leq 0.5$, where the fraction of the free laponite disks was insignificant.

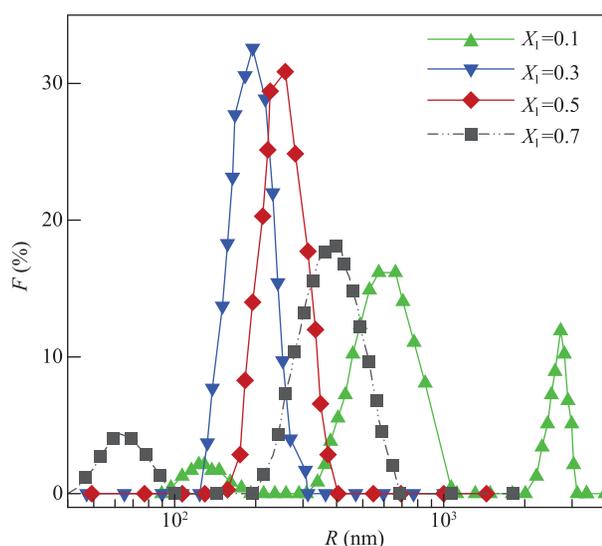


Fig. 5 – Size distribution function ($F(R)$) of hybrid systems in water at different values of the laponite/NT ratio (X_1). R: particle sizes; NT: nanotube.

The surface area of the hybrid laponite-NT particles can depend on the model of association between laponite and NT particles. The total mass of hybrid particles was equal to $m_n + m_t$. The surface of hybrid particles was approximately equal to the surface of pure NTs for the stretched contact between laponite and NT (the flexible platelet wraps the tube), i.e., it was equal to the sum of the surface of NTs and laponite particles for the linear contact between particles (the rigid platelet contacts with tube) (Fig. 4).

As a rough approximation we can assume that at $X_1 \leq X_1^m = 0.5X_1$, the NT specific surface area linearly grows with X_1 as:

$$S_n = S_n^0 + (S_n^m - S_n^0)X_1/X_1^m \quad (5)$$

where, S_n^0 (~149 m²/g) and S_n^m (~260 m²/g) (Manilo et al., 2014) are the surface areas at $X_1 = 0$ and $X_1 = X_1^m$, respectively.

The specific surface area of the hybrid laponite + NT particles for the stretched (S_s) and the linear contact models (S_p) can be estimated as

$$S_s = S_n/(1 + X_1) \quad (6)$$

$$S_p = (S_n + S_1^m X_1)/(1 + X_1) \quad (7)$$

respectively. Here, S_1^m of 791 m²/g is the theoretically estimated surface area for laponite.

The dependences of S_s and S_p on X_1 are presented in Fig. 4. The linear contact model gave overestimated values and was more appropriated for description of the experimental data than the stretched contact model.

It is interesting to estimate the contribution of laponite surface charges to adsorption of MB on hybrid laponite-NT particles. Accounting for the cation exchange capacity (CEC) of faces of laponite (0.75 meq/g), the degree of coverage of faces by MB⁺ ions (f_{MB^+}) can be estimated as:

$$f_{MB^+} = 1000/(0.75M_{MB}) = 3.57C_d/C_1 = 3.57X_d/X_1. \quad (8)$$

This means that the total covering of faces ($f_{MB^+} = 1$) requires $X_d \approx 0.084$ for $X_1 = 0.3$ and $X_d \approx 0.14$ for $X_1 = 0.5$. The estimated values were noticeably smaller as compared to those required for formation of monolayer of MB. The experimental adsorption data evidenced that $X_d \approx 1.5$ for $X_1 = 0.3$ and $X_d \approx 3.4$ for $X_1 = 0.5$ (Fig. 3). It can be assumed that mechanism of charge governed adsorption of MB on the laponite-NT hybrid particles is not essential for the studied systems.

To check this assumption the electrical conductivity (σ) of MB and of 0.1 wt.% laponite suspension versus the concentration of MB (C_d) in the absence (sample A) and presence (sample B, $X_1 = 0.5$) of NTs was done (Fig. 6). At small concentration of MB (below inflection point (C_d^c), i.e., $C_d \leq C_d^c \approx 0.03$ wt.%), the electrical conductivity of samples A and B exceeded the electrical conductivity of MB and was weakly dependent upon the value of C_d . However, above C_d^c the strong dependence of σ on C_d for both samples A and B were observed. At $C_1 = 0.1$ wt.%, Eq. (8) gives $C_d \approx 0.028$ wt.% that is close to the inflection points of curves $\sigma(C_d)$ at $C_d \approx C_d^c = 0.03$ wt.%. Thus, such behavior can be explained by strong adsorption of mobile MB⁺ ions on the negatively charged faces of laponite particles.

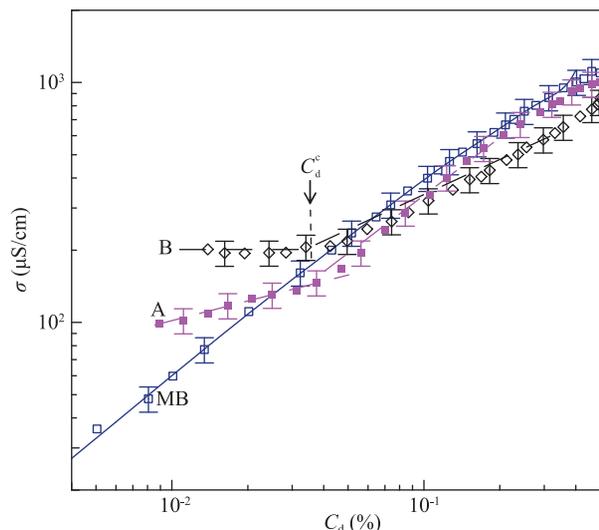


Fig. 6 – Electrical conductivity (σ) of MB and 0.1 wt.% laponite suspension versus the concentration of MB (C_d) in the absence (sample A) and presence (sample B, $X_1 = 0.5$) of NTs. C_d^c : inflection point. Methylene Blue: MB.

At high concentrations of MB, i.e., $C_d > 0.5$ wt.%, electrical conductivity of the sample B (0.1 wt.% of laponite and 0.2 wt.% of NTs) was noticeably smaller than that for MB solution or the sample A (0.1 wt.% of laponite). This evidently reflects the stronger binding of the cations of MB on the surface of hybrid laponite-NT particles.

3. Conclusions

Three different stages in the kinetics of adsorption of MB on the surface of NTs or hybrid laponite-NT particles were discovered, i.e., the fast initial stage I ($t = 0-10$ min), slower intermediate stage II (up to $t = 120$ min) and the long-duration final stage III (up to $t = 24$ hr). The presence of these stages may be explained by different types of interactions between MB and adsorbent particles, as well as by the charges in structure of aggregates of NT particles and the long-lasting processes of equilibration of CB molecules that were initially nonuniformly distributed between different adsorbent particles. The laponite platelets cover the surface of NTs and facilitates their dispersing in water (Loginov et al., 2012). Moreover, the hybrid laponite-NT particles have the higher values of monolayer adsorption capacity than that for the original NTs (Loginov et al., 2014). The analysis of specific surface area (S) versus the laponite/NT ratio (X_1) evidenced in favor of the model with linear contacts between rigid laponite platelets and NTs. The model of stretched contact, when the flexible laponite particle wraps around the surface of NT, failed to give appropriate estimation of S . The electrical conductivity data evidenced that electrostatic interactions controlled the adsorption at small concentrations of MB, and the stronger binding of the MB cations of on the surface of hybrid laponite-NT particles was observed.

Acknowledgments

The research has been performed in the frame of cooperation agreement between the National Academy of Sciences of Ukraine and Hungarian Academy of Sciences. This work was also supported by National Academy Science of Ukraine (No. 43/15H).

REFERENCES

- Adolph, M.A., Xavier, Y.M., Kriveshini, P., Rui, K., 2012. Phosphine functionalised multiwalled carbon nanotubes: a new adsorbent for the removal of nickel from aqueous solution. *J. Environ. Sci.* 24 (6), 1133–1141.
- Bele, C., 2010. Carbon nanotubes as a new solid phase extraction sorbent for analysis of environmental pollutants. In: Marulanda, J.M. (Ed.), *Carbon Nanotubes*. InTech, Rijeka, Croatia, pp. 523–541.
- Cenens, J., Schoonheydt, R.A., 1988. Visible spectroscopy of methylene blue on hectorite, laponite B, and barasym in aqueous suspension. *Clay Clay Miner.* 36 (3), 214–224.
- Chen, W., Duan, L., Zhu, D.Q., 2007. Adsorption of polar and nonpolar organic chemicals to carbon nanotubes. *Environ. Sci. Technol.* 41 (24), 8295–8300.
- Dukhin, S.S., Derjaguin, B.V., 1976. *Electrophoresis*. Nauka, Moscow, USSR.
- Fripiat, J.J., Letellier, M., Cases, J.M., Francois, M., Delon, J.F., Rouquerol, J., 1982. Comportement microdynamique et thermodynamique de l'eau dans les suspensions argileuses. *Stud. Surf. Sci. Catal.* 10, 449–477.
- Fugetsu, B., Satoh, S., Shiba, T., Mizutani, T., Lin, Y.B., Terui, N., et al., 2004. Caged multiwalled carbon nanotubes as the adsorbents for affinity-based elimination of ionic dyes. *Environ. Sci. Technol.* 38 (24), 6890–6896.
- Gupta, V.K., Kumar, R., Nayak, A., Saleh, T.A., Barakat, M.A., 2013. Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. *Adv. Colloid Interf. Sci.* 193–194, 24–34.
- Itodo, A.U., Itodo, H.U., Gafar, M.K., 2010. Estimation of specific surface area using Langmuir Isotherm Method. *J. Appl. Sci. Environ. Manag.* 14 (4), 141–145.
- Jatav, S., Joshi, Y.M., 2014. Chemical stability of laponite in aqueous media. *Appl. Clay Sci.* 97–98, 72–77.
- Johnson Jr., C.E., 1957. Methylene blue adsorption and surface area measurements. Proceedings of the 131st National Meeting of the American Chemical Society (Apr 7–12).
- Kabbashi, N.A., Atieh, M.A., Al-Mamun, A., Mirghami, M.E.S., Alam, M.D.Z., Yahya, N., 2009. Kinetic adsorption of application of carbon nanotubes for Pb(II) removal from aqueous solution. *J. Environ. Sci.* 21 (4), 539–544.
- Kavitha, D., Namasivayam, C., 2007. Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. *Bioresour. Technol.* 98 (1), 14–21.
- Kerkez, Ö., Bayazit, S.S., 2014. Magnetite decorated multi-walled carbon nanotubes for removal of toxic dyes from aqueous solutions. *J. Nanoparticle Res.* 16, 2431.
- Lebovka, N.I., 2014. Aggregation of charged colloidal particles. In: Müller, M. (Ed.), *Polyelectrolyte Complexes in the Dispersed and Solid State I: Principles and Applications*. Springer, New York/Heidelberg, pp. 57–96.
- Leite, F.L., Bueno, C.C., Da Roiz, A.L., Ziemath, E.C., Oliveira Jr., O.N., 2012. Theoretical models for surface forces and adhesion and their measurement using atomic force microscopy. *Int. J. Mol. Sci.* 13 (10), 12773–12856.
- Li, Y.H., Du, Q.J., Liu, T.H., Peng, X.J., Wang, J.J., Sun, J.K., et al., 2013. Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes. *Chem. Eng. Res. Des.* 91 (2), 361–368.
- Lian, F., Chang, C., Du, Y., Zhu, L.Y., Xing, B.S., Liu, C., 2012. Adsorptive removal of hydrophobic organic compounds by carbonaceous adsorbents: a comparative study of waste-polymer-based, coal-based activated carbon, and carbon nanotubes. *J. Environ. Sci.* 24 (9), 1549–1558.
- Loginov, M., Lebovka, N., Vorobiev, E., 2012. Laponite assisted dispersion of carbon nanotubes in water. *J. Colloid Interface Sci.* 365 (1), 127–136.
- Loginov, M., Lebovka, N., Vorobiev, E., 2014. Hybrid multiwalled carbon nanotube — laponite sorbent for removal of methylene blue from aqueous solutions. *J. Colloid Interface Sci.* 431, 241–249.
- Ma, J., Yu, F., Zhou, L., Jin, L., Yang, M.X., Luan, J.S., et al., 2012. Enhanced adsorptive removal of methyl orange and methylene blue from aqueous solution by alkali-activated multiwalled carbon nanotubes. *ACS Appl. Mater. Interfaces* 4 (11), 5749–5760.
- Madrakiana, T., Afkhami, A., Ahmadi, M., Bagheri, H., 2011. Removal of some cationic dyes from aqueous solutions using magnetic-modified multi-walled carbon nanotubes. *J. Hazard. Mater.* 196, 109–114.
- Manilo, M., Lebovka, N., Barany, S., 2014. Characterization of the electric double layers of multi-walled carbon nanotubes, laponite and nanotube + laponite hybrids in aqueous suspensions. *Colloids Surf. A Physicochem. Eng. Asp.* 462, 211–216.
- Manilo, M.V., Lebovka, N.I., Barany, S., 2015. Stability of multi-walled carbon nanotube + laponite hybrid particles in aqueous suspensions. *Colloids Surf. A Physicochem. Eng. Asp.* 481, 199–206.
- Melezyk, A.V., Sementsov, Y.I., Yanchenko, V.V., 2005. Synthesis of porous carbon nanofibers on catalysts fabricated by the mechanochemical method. *Russ. J. Appl. Chem.* 78 (6), 924–930.
- Mourchid, A., Levitz, P., 1998. Long-term gelation of laponite aqueous dispersions. *Phys. Rev. E* 57 (5), R4887–R4890.
- Norzilah, A.H., Fakhru'l-Razi, A., Choong, T.S.Y., Chuah, A.L., 2011. Surface modification effects on CNTs adsorption of methylene blue and phenol. *J. Nanomater.* 1–18, 495676.
- Qada, E.N.E., Allen, S.J., Walker, G.M., 2008. Adsorption of basic dyes from aqueous solution onto activated carbons. *Chem. Eng. J.* 135 (3), 174–184.
- Qu, S., Huang, F., Yu, S.N., Chen, G., Kong, J.L., 2008. Magnetic removal of dyes from aqueous solution using multi-walled carbon nanotubes filled with Fe₂O₃ particles. *J. Hazard. Mater.* 160 (2–3), 634–647.
- Savenko, V., Bulavin, L., Rawiso, M., Loginov, M., Vorobiev, E., Lebovka, N.I., 2013. Sedimentation stability and aging of aqueous dispersions of laponite in the presence of cetyltrimethylammonium bromide. *Phys. Rev. E* 88 (5), 1–8, 052301.
- Schoonheydt, R.A., Johnston, C.T., 2006. Surface and interface chemistry of clay minerals. In: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), *Handbook of Clay Science*. Elsevier Ltd., Amsterdam, pp. 87–113.
- Schoonheydt, R.A., Heughebaert, L., 1992. Clay adsorbed dyes: methylene blue on laponite. *Clay Miner.* 27 (1), 91–100.
- Shahryari, Z., Goharrizi, A.S., Azadi, M., 2010. Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes. *Int. J. Water Resour. Environ. Eng.* 2 (2), 16–28.
- Song, S.M., Hou, X.L., Wu, Y.B., Shuang, S.M., Yang, C., Inoue, Y., et al., 2009. Study on the interaction between methyl blue and human serum albumin by fluorescence spectrometry. *J. Lumin.* 129 (3), 169–175.

- Szlachta, M., Wójtowicz, P., 2013. Adsorption of methylene blue and Congo red from aqueous solution by activated carbon and carbon nanotubes. *Water Sci. Technol.* 68 (10), 2240–2248.
- Tabrizi, N.S., Yavari, M., 2015. Methylene blue removal by carbon nanotube-based aerogels. *Chem. Eng. Res. Des.* 94, 516–523.
- Thompson, D.W., Butterworth, J.T., 1992. The nature of laponite and its aqueous dispersions. *J. Colloid Interface Sci.* 151 (1), 236–243.
- Tiller, K.G., 1968a. Stability of hectorite in weakly acidic solutions I. A chemical study of the dissolution of hectorite with special reference to the release of silica. *Clay Miner.* 7 (3), 245–259.
- Tiller, K.G., 1968b. Stability of hectorite in weakly acidic solutions II. Studies of the chemical equilibrium and the calculation of free energy. *Clay Miner.* 7 (3), 261–270.
- Wang, S.B., Zhu, Z.H., Coomes, A., Haghseresht, F., Lu, G.Q., 2005. The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. *J. Colloid Interface Sci.* 284 (2), 440–446.
- Yan, Y.M., Zhang, M.N., Gong, K.P., Su, L., Guo, Z.X., Mao, L.Q., 2005. Adsorption of methylene blue dye onto carbon nanotubes: a route to an electrochemically functional nanostructure and its layer-by-layer assembled nanocomposite. *Chem. Mater.* 17 (13), 3457–3463.
- Yao, Y.J., Zhang, S.P., Yan, Y.J., 2008. CVD synthesis and hydrogen storage properties of multi-walled carbon nanotubes. *Proceedings of the 2nd IEEE International Nanoelectronics Conference*, 2008. INEC 2008. Shanghai, China, pp. 140–143 (Mar 24–27).
- Yu, F., Wu, Y.Q., Ma, J., Zhang, C., 2013. Adsorption of lead on multi-walled carbon nanotubes with different outer diameters and oxygen contents: kinetics, isotherms and thermodynamics. *J. Environ. Sci.* 25 (1), 195–203.
- Zebrowski, J., Prasad, V., Zhang, W., Walker, L.M., Weitz, D.A., 2003. Shake-gels: shear-induced gelation of laponite-PEO mixtures. *Colloids Surf. A Physicochem. Eng. Asp.* 213 (2–3), 189–197.