Accuracy of Dubinin-Astakhov and Dubinin-Radushkevich Adsorption Isotherm Models in Evaluating Micropore Volume of Bentonite

Navid Saeidi[1*], Mehdi Parvini[2]

Abstract

Accuracy of Dubinin-Astakhov (DA) and Dubinin-Radushkevich (DR) isotherm models were examined for evaluating micropore volume of several natural and pillared bentonite samples with type I and II isotherms. Afterwards, the obtained results were compared with the micropore volume calculated by Horvath–Kawazoe (HK) model. The results showed that the accuracy of DA and DR models for this purpose depends on isotherm types and range of relative pressure (P/P_0) in which the models are applied. It can be generally concluded that DA and DR can be used to calculate micropore volume of bentonite instead of HK which imposes more complicated calculations.

[1] Faculty of Chemical, Gas and Petroleum Engineering, Semnan University, Semnan 35195-363, Iran

[2] Faculty of Chemical, Gas and Petroleum Engineering, Semnan University, Semnan 35195-363, Iran

[*] Corresponding author, e-mail: n_saeidi@semnan.ac.ir

1 Introduction

Clay can be used in several applications due to its physical and chemical properties, such as large specific surface area, cation exchange capacity and adsorptive affinity for inorganic and organic ions from aqueous solution and water. Among the clays, bentonite is considered as a main candidate in the removal of pollutants such as lead and other heavy metal ions. Bentonite consists mostly of microcrystalline particles of montmorillonite which belongs to 2:1 clay minerals meaning that it has two tetrahedral sheets sandwiching a central octahedral sheet [1-4]. Since the existence of huge deposits of bentonite, there is a great potential for its utilization in removing various dilute pollutants and adsorption technology including the removal of heavy metal ions [5-8], phenols [9-11], organic molecules [12,13], polymers [14,15], pesticides [16], radio nuclides [17], dyes [18-20]. To apply bentonite in adsorption, the textural properties including surface area, pore size, micropore volume and mesopore volume must be determined. The textural properties of porous materils are very often determined by gas (N_2) adsorption isotherm data [8,21,22].

The empirical form of an adsorption isotherm was recognized as early as 1926 by Freundlich [23], and was later derived theoretically from the Langmuir equation [24] extended to heterogeneous surfaces considered to be a composite surface, composed of many homogeneous patches [25]. By adopting the Langmuir mechanism, but introducing a number of simplifying assumptions, the Brunauer–Emmet–Teller (BET) equation was subsequently derived for multilayer adsorption [26]. It is unquestionable that together with the concept of multilayer adsorption (leading to the BET equation) the theory of volume filling of micropores is one of the most stimulating concepts occupying the principal position in adsorption science [27]. Developed formerly, and based on the Weibull distribution of adsorption potential, the proposed equation by M. M. Dubinin [28] was considered to be a semi-empirical one. The fundamental relations are the Dubinin-Astakhov and Dubinin-Radushkevich equations [28,29]. The surface area, mesopore volume and micropore volume of such porous materials can be evaluated by means of BET, BJH [30] and both HK [31] and density functional theory (DFT)

[32] methods, respectively. According to literature, the HK and DFT methods are accurate ones; however they're somewhat complicated and time-consuming [33,34].

In this paper DA and DR isotherm models were applied to calculate the micropore volume of some bentonite samples and the results were compared with the results obtained by HK model. To calculate micropore volume by the methods, the data collected through N_2 adsorption-desorption isotherms was used. Several authors have applied the methods based on the HK model to determine the micropore size distributions and micropore volume of bentonite [21,22], [35-40]. Therefore, this model is considered as a valid one. However, as mentioned above, this model is complicated and time-consuming. In short, the aim of this paper is to study whether DA and DR isotherm models, which are simpler than HK, are accurate to assess micropore volume of bentonite or not.

2 Theoretical approach
2.1 Dubinin-Astakhov and Dubinin-Radushkevich equations

Dubinin-Astakhov and Dubinin-Radushkevich equations are given, respectively, in the following forms:

$$w = w_0 \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right] \qquad (1)$$

$$w = w_0 \exp\left[-B\left(\frac{T}{\beta}\right)^2 \log^2\left(\frac{P_0}{P}\right)\right] \qquad (2)$$

In Eqs. (1) and (2), w represents the volume of adsorbate filling the micropores, in the unit mass of adsorbent (cm^3/g), at temperature T and P/P_0, w_0 is the maximum volume of adsorbent per adsorbed mass, the micropore volume (cm^3/g), B is a parameter characterizing the microporous structure, β is the affinity coefficient of the characteristic curves, E_0 is the characteristic energy of adsorption, n is an equation parameter and A is the differential molar work of adsorption i.e., the differential Gibbs energy of adsorption, ΔG, defined by

$$A = -\Delta G = RT \ln\left(\frac{P_0}{P}\right) \qquad (3)$$

It must be noted that the DA equation is valid at the micropore filling mechanism, over a range of P/P_0 varying from 1E-7 to 0.02, and the DR equation is valid at both micropore filling and sub-monolayer formation mechanisms, over a range of P/P_0 varying from 1E-7 to 0.02 and 0.01 to 0.1, respectively.

2.2 The Horvath–Kawazoe (HK) model

Everett and Powl [41] extended the work of Sams et al. [42] on the interaction energy of one adsorbate molecule with a single infinite-layer plane of adsorbent molecules. They indicated

that the potential energy of interaction, ε, between one adsorbate molecule and two parallel infinite layer planes whose nuclei are separated by a distance, x, can be expressed via the Lennard–Jones (12:6) potential. Later, Horvath and Kawazoe concluded that for a slit-like shaped pore filled with adsorbate molecules, ε, can be arranged as follows:

$$\varepsilon = \frac{N_a A_a + N_A A_A}{2\sigma^4}\left[-\left(\frac{\sigma}{z}\right)^4 + \left(\frac{\sigma}{z}\right)^{10} - \left(\frac{\sigma}{x-z}\right)^4 + \left(\frac{\sigma}{x-z}\right)^{10}\right] \qquad (4)$$

$$\sigma = \left(\frac{2}{5}\right)^{1/6} d_0 \qquad (5)$$

Where d_0 being the arithmetic mean diameter of the adsorbate molecule and the adsorbent atom. In Eq. (1), z is the internuclear distance between an adsorbate molecule and the plane of surface atoms of the adsorbent (one plate), N_a is the number of oxide ions per unit area of surface, and N_A is the number of adsorbate molecules per unit area of adsorbent surface. A_a and A_A are the dispersion constants, which are given by the Kirkwood–Muller equations [43] as follows:

$$A_a = \frac{6mc^2\alpha_a\alpha_A}{\alpha_A/\lambda_A + \alpha_a/\lambda_a} \qquad (6)$$

$$A_A = \frac{3}{2}\left(mc^2\alpha_A\lambda_A\right) \qquad (7)$$

Where m is the mass of an electron, c is the speed of light, α_a and λ_a are the polarizability and magnetic susceptibility of an adsorbent atom, respectively, and similarly α_A and λ_A are the polarizability and magnetic susceptibility of an adsorbate molecule. The sum $N_a A_a + N_A A_A$ is the so-called interaction parameter, which summarizes the physicochemical characteristics of the adsorbate-adsorbent system. Horvath and Kawazoe indicated the free energy change upon adsorption to the net potential energy of interaction between the layers. Thus, the following expression is derived for a slit-like pore geometry:

$$RTLn\frac{P}{p_0} = N_{Av}\frac{N_a A_a + N_A A_A}{\sigma^4(x-2d_0)}$$
$$\left[\frac{\sigma^4}{3(x-d_0)^3} - \frac{\sigma^{10}}{9(x-d_0)^9} - \frac{\sigma^4}{3d_0^3} + \frac{\sigma^{10}}{9d_0^9}\right] \qquad (8)$$

Where P_0 is the saturation vapour pressure, R is the universal gas constant, and N_{Av} is Avogadro number.

Everett and Powl indicated that the potential energy of interaction, ε, between one adsorbate molecule and the inside wall of a cylindrical pore of radius x can be expressed via the Lennard–Jones potential. Thus, for a cylindrical pore composed of a single layer of oxide ions and filled with adsorbate molecules, ε, can be arranged as follows:

$$\varepsilon = \frac{5}{2}\pi \left[\frac{3}{10} \frac{N_a A_a + N_A A_a}{d_0^{\,4}} \right]$$

$$\left[\frac{21}{32} \left(\frac{d_0}{x} \right)^{10} \sum_{k=0}^{\infty} \alpha_k \left(\frac{r}{x} \right)^{2k} - \left(\frac{d_0}{x} \right)^4 \sum_{k=0}^{\infty} \beta_k \left(\frac{r}{x} \right)^{2k} \right] \quad (9)$$

Where r is the distance of the nucleus of a gas molecule from the central axis of the cylinder, and the expansion coefficients, α_k and β_k, are given by

$$\alpha_k = \left(\frac{-4.5 - k}{k} \right)^2 \alpha_k - 1 \quad (10)$$

And

$$\beta_k = \left(\frac{-1.5 - k}{k} \right)^2 \beta_k - 1 \quad (11)$$

Where $\alpha_0 = \beta_0 = 1$. Using the mentioned results, Saito and Foley [44] obtained the following equation for cylindrical pores by means of a method similar to that of Horvath and Kawazoe:

$$RTLn\frac{p}{p_0} = \frac{3}{4} \pi N_{Av} \frac{A_a N_a + A_A N_A}{d_0^{\,4}}$$

$$\sum_{k=0}^{\infty} \left\{ \frac{1}{k+1} \left(1 - \frac{d_0}{x} \right)^{2k} \times \left[\frac{21}{32} \alpha_k \left(\frac{d_0}{x} \right)^{10} - \beta_k \left(\frac{d_0}{x} \right)^4 \right] \right\} \quad (12)$$

On deriving this equation, the authors deemed that adsorption only takes place on the inside wall of the cylinder for micropores, and approximated interactions upon adsorption by the interactions between the gas molecules and the oxide ions of the adsorbent. Taking into account the experimental results that can be attained from adsorption of probe molecules, adsorbed volume and P/P_0 at equilibrium conditions, the pore size distribution of a given material can be derived from Eqs. (8) or (12). In both cases, the microporous volume is calculated as the adsorbed volume corresponding to pores with size up to 20 Å [45]. It must be mentioned that the HK method is valid at the micropore filling mechanism.

3 Result and discussion

In this work, the nitrogen adsorption-desorption isotherm experimental data [22, 23] was used to calculate micropore volume. The data is concerning a natural bentonite, S_1, some intercalated and pillared bentonite samples, S_2, S_3, S_4 and S_5, and some pillared bentonite samples, S_6, S_7, S_8, S_9, S_{10}, S_{11} and S_{13}. Figure 1 illustrates the nitrogen adsorption-desorption isotherm data of the mentioned samples.

As can be seen in Fig. 1A, the adsorption isotherm of the natural clay, S1, is of type II in the Brunauer, Deming and Teller (BDDT) classification [43]. The adsorption isotherms at low P/P_0 of the intercalated and pillared samples, S_2, S_3, S_4 and S_5, are of type I in the same classification with an important uptake at low P/P_0, characteristic of highly microporous materials. The
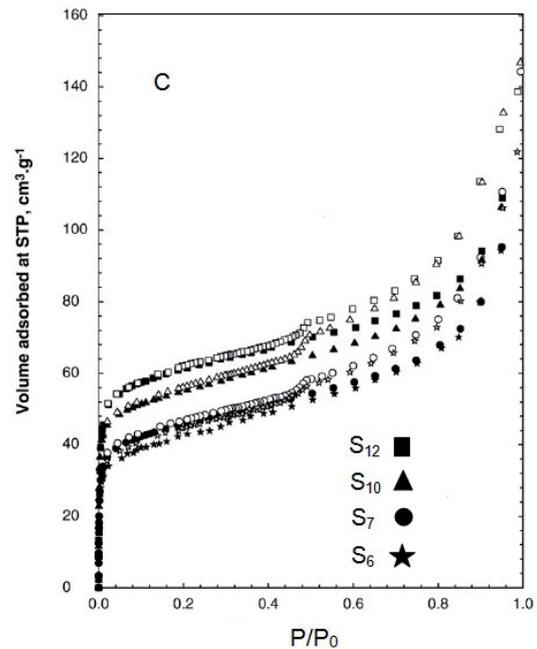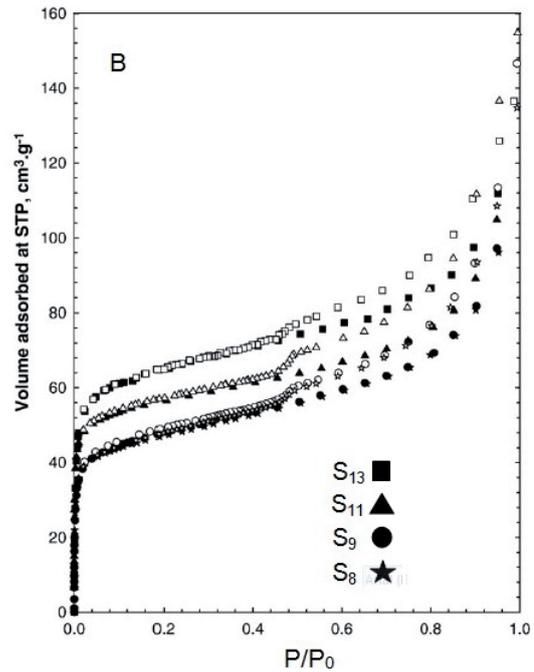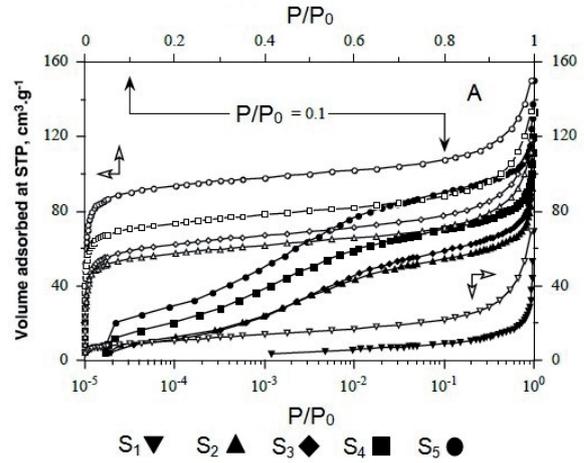
Fig. 1 Nitrogen adsorption-desorption isotherms of the samples under study [22, 23]

adsorption isotherm of the other samples is of type II in the mentioned classification (Figs. 1B and C) with a lower uptake at low P/P_0 than type I classification. The observed narrow hysteresis behaviour showed that these samples had mesopores with parallel layers. According to the types of isotherms and the above mentioned remarks it can be concluded that S_2, S_3, S_4 and S_5 samples contain more micropores volume than other samples. Table 1 summarizes the textural properties of the samples.

As can be seen in Table 1, the fractions of mesopore volume, V_{meso}/V_{total}, in S_2, S_3, S_4 and S_5 samples are lower than 0.4. However, these fractions in other samples are above 0.6. Thus, in good agreement with the above mentioned remarks about type I and II isotherms, it can be said that S_2, S_3, S_4 and S_5 samples contain more micropore volumes than other samples. As mentioned earlier, the DA equation is valid over a range of P/P_0 varying from 1E-7 to 0.02, and the DR equation is valid over ranges of P/P_0, from 1E-7 to 0.02 and 0.01 to 0.1 individually. Thus, the adsorption isotherms were fitted to the DA and DR equations over these ranges. Table 2 presents the obtained results, the micropore volume, w_0, by fitting the adsorption isotherm data of the samples to both the DA and DR equations. According to the correlation coefficients, R^2, it can be deduced that the adsorption isotherms have properly correlated to the both isotherm models.

In this work, the obtained results through fitting Nitrogen adsorption isotherm data to DA and DR isotherm models were compared with the calculated micropore volume by HK method. Tables 3 and 4 show the results.

Table 3 shows the results concerning the samples with the isotherms of type I. As can be seen in Table 3, the error differences, Δ, relevant to the obtained results by fitting isotherms to DA model are very low and, also, less than the error difference calculated in other cases.

Table 4 indicates the results regarding the samples with the isotherms of type II. As can be seen in Table 4, the error differences, Δ, relevant to the obtained results by fitting isotherms to DR_1 model are very low and, also, less than the error difference calculated in other cases. According to the both tables, as can be predicted, it was concluded that DR_2, fitting isotherm data to DR model at sub-monolayer formation mechanism, isn't proper to evaluate micropore volumes of the both types of samples, the samples with isotherms of type I and type II. It is likely due to that in set out of this mechanism and after the knee, in the curve isotherms, micropores cease to contribute to the adsorption process.

In DA equation, Eq. (1), n is an exponent usually varying between 1 and 3. Exponent n depends on the width of the distribution curve of adsorption energy (of pores with different sizes). As be said about activated carbon [46], values of n equal or above 3 represent molecular sieve carbons with narrow pores, while values less than 2 belong to less microporous carbons with wider pore size distribution. The value of 2 (original DR equation) shows an intermediate condition among different cases. Therefore, based on the above mentioned remarks and Tables 3 and 4, it can be said when a sample contains high micropore volume then its n, in DA equation, is higher than 2. Thus, DR

Table 1 Textural properties of the samples under study.

Sample	S_{BET}(m²/g)	V_{meso}(cm³/g)	V_{total}(cm³/g)	V_{meso}/V_{total}	V_{HK}(cm³/g)	Reference
S_1	37	0.068	0.107	0.63	0.017	[22]
S_2	236	0.068	0.173	0.39	0.089	[22]
S_3	256	0.072	0.183	0.39	0.096	[22]
S_4	304	0.074	0.207	0.36	0.114	[22]
S_5	391	0.071	0.232	0.31	0.145	[22]
S_6	152	0.133	0.187	0.71	0.079	[23]
S_7	165	0.165	0.213	0.77	0.082	[23]
S_8	171	0.147	0.207	0.71	0.084	[23]
S_9	174	0.164	0.216	0.76	0.085	[23]
S_{10}	201	0.154	0.219	0.70	0.098	[23]
S_{11}	209	0.163	0.222	0.73	0.097	[23]
S_{12}	226	0.131	0.213	0.61	0.106	[23]
S_{13}	236	0.121	0.210	0.58	0.113	[23]

Abbreviations: S_{BET}, BET specific surface area; V_{meso}, mesopore volume assessed by BJH method; V_{total}, total pore volume at $P/P_0 = 0.99$; V_{HK}, micropore volume derived from Korvath–Kawazoe (HK) model.

Table 2 Micropoe volume calculated by DA and DR.

Sample	w_o^{DA} (cm³/g)	w_o^{DR1} (cm³/g)	w_o^{DR2} (cm³/g)	R^2_{DA}	R^2_{DR1}	R^2_{DR2}
S_1	0.016	0.017	0.012	-	0.95	0.95
S_2	0.088	0.311	0.162	-	0.96	0.98
S_3	0.096	0.334	0.164	-	0.96	0.98
S_4	0.109	0.391	0.166	-	0.94	0.99
S_5	0.141	0.441	0.192	-	0.95	0.97
S_6	0.038	0.071	0.041	0.97	-	0.98
S_7	0.043	0.08	0.046	0.98	-	0.99
S_8	0.045	0.083	0.047	0.98	-	0.97
S_9	0.05	0.086	0.048	0.99	-	0.99
S_{10}	0.056	0.099	0.055	0.99	-	0.99
S_{11}	0.059	0.103	0.057	0.96	-	0.99
S_{12}	0.062	0.092	0.061	0.98	-	0.99
S_{13}	0.066	0.104	0.065	0.99	-	0.99

Abbreviations: w_o^{DA}, the micropore volume calculated using DA equation in the range $0.0001 < P/P_0 < 0.01$; w_o^{DR1}, the micropore volume calculated using DR equation in the range $0.0001 < P/P_0 < 0.01$; w_o^{DR2}, the micropore volume calculated using DR equation in the range $0.01 < P/P_0 < 0.1$; R^2_{DA}, correlation coefficient in fitting the isotherm data to DA equation; R^2_{DR1}, correlation coefficient in fitting the isotherm data to DR equation in the range $0.0001 < P/P_0 < 0.01$; R^2_{DR2}, correlation coefficient in fitting the isotherm data to DR equation in the range $0.01 < P/P_0 < 0.1$.

Table 3 Comparison of the micropore volume obtained by DA and DR isotherm models by HK method for the samples having type I isotherms.

Sample	V_{HK} (cm³/g)	w_o^{DA} (cm³/g)	w_o^{DR1} (cm³/g)	w_o^{DR2} (cm³/g)	$^a\Delta^{DA}_{HK}$	$^a\Delta^{DR1}_{HK}$	$^a\Delta^{DR2}_{HK}$
S_1	0.017	0.016	0.017	0.012	1	0	29
S_6	0.079	0.038	0.071	0.041	52	10	48
S_7	0.082	0.043	0.08	0.046	47	2	44
S_8	0.084	0.045	0.083	0.047	46	1	44
S_9	0.085	0.05	0.086	0.048	42	1	43
S_{10}	0.098	0.056	0.099	0.055	43	1	44
S_{11}	0.097	0.059	0.103	0.057	39	6	41
S_{12}	0.106	0.062	0.092	0.061	41	13	42
S_{13}	0.113	0.066	0.104	0.065	41	1	42

^{a} Δ^y_x is the error difference: $\Delta^y_x \% = \dfrac{V_x - w_o^y}{V_x} \times 100$.

Table 4 Comparison of the micropore volume obtained by DA and DR isotherm models by HK method for the samples having type II isotherms.

Sample	V_{HK} (cm³/g)	w_o^{DA} (cm³/g)	w_o^{DR1} (cm³/g)	w_o^{DR2} (cm³/g)	$^a\Delta^{DA}_{HK}$	$^a\Delta^{DR1}_{HK}$	$^a\Delta^{DR2}_{HK}$
S_2	0.089	0.088	0.311	0.162	1	84	45
S_3	0.096	0.096	0.334	0.164	0	71	41
S_4	0.114	0.109	0.391	0.166	4	70	30
S_5	0.145	0.141	0.441	0.192	3	67	24

^{a} Δ^y_x is the error difference: $\Delta^y_x \% = \dfrac{V_x - w_o^y}{V_x} \times 100$.

equation with n equal 2 can't properly evaluate micropore volume of the sample. However, in intermediate condition, about our samples with fraction of micropore volume around 0.4 and less, the DR equation can properly assessed the micropore volume of sample over the range of micropore filling mechanism.

4 Conclusions

In this paper, micropore volume of several bentonite samples with various textural properties was calculated by DA and DR isotherm models and compared with the micropore volume obtained by HK method. The results showed that DA model is accurate for the sample with high micropore volume and with type I isotherms. In contrast, DR model is valid for the sample having mediocre micropore volume and with type II isotherms. Finally, DR model is not precise for evaluating micropore volume of the all samples over the range of sub-monolayer mechanism ($0.01 < P/P_0 < 0.1$).

References

[1] Salem, A., Karimi, L. "Physico-chemical variation in bentonite by sulfuric acid activation." *Korean Journal of Chemical Engineering*. 26(4), pp. 980-984. 2009. DOI: 10.1007/s11814-009-0162-2

[2] Saeidi, N., Lotfollahi, M. N. "A Procedure for Preparation of Semi-activated Carbon Fiber without any Treatment under High Temperature." *International Journal of Engineering TRANSACTIONS A: Basics*. 27(10), pp. 1519-1526. 2014. DOI: 10.5829/idosi.ije.2014.27.10a.05

[3] Orolinova, Z., Mockovciakova, A. "Structural study of bentonite/iron oxide composites." *Materials Chemistry and Physics*. 114(2-3), pp. 956-961. 2009. DOI: 10.1016/j.matchemphys.2008.11.014

[4] Caglar, B., Afsin, B., Tabak, A., Eren, E. "Characterization of the cation-exchanged bentonites by XRPD, ATR, DTA/TG analyses and BET measurement." *Chemical Engineering Journal*. 149(1-3), pp. 242-248. 2009. DOI: 10.1016/j.cej.2008.10.028

[5] Wang, S., Dong, Y., He, M., Chen, L., Yu, M. "Characterization of GMZ bentonite and its application in the adsorption of Pb (II) from aqueous solutions." *Applied Clay Science*. 43(2), pp. 164-171. 2009. DOI: 10.1016/j.clay.2008.07.028

[6] Tahir, S. S., Naseem, R. "Removal of Cr(III) from tannery wastewater by adsorption onto bentonite clay." *Separation and Purification Technology*, 53(3). pp. 312-321. 2007. DOI: 10.1016/j.seppur.2006.08.008

[7] Eren, E., Afsin, B. "An investigation of Cu (II) adsorption by raw and acid-activated bentonite: A combined potentiometric, thermodynamic, XRD, IR, DTA study." *Journal of Hazardous Material*. 151(2-3), pp. 682-691. 2008. DOI: 10.1016/j.jhazmat.2007.06.040

[8] Xu, D., Tan, X. L., Chen, C. L., Wang, X. K. "Adsorption of Pb(II) from aqueous solution to MX-80 bentonite: Effect of pH, ionic strength, foreign ions and temperature." *Applied Clay Science*. 41(1-2), pp. 37-46. 2008. DOI: 10.1016/j.clay.2007.09.004

[9] Randelovic, M., Purenovic, M., Zarubica, A., Purenovic, J., Matovic, B., Momcilovic, M. "Synthesis of composite by application of mixed Fe, Mg (hydr) oxides coatings onto Bentonite -A use for the removal of Pb (II) from water." *Journal of Hazardous Material*. 199-200, pp. 367-374. 2012. DOI: 10.1016/j.jhazmat.2011.11.025

[10] Rawajfih, Z., Nsour, N. "Characteristics of phenol and chlorinated phenols sorption onto surfactant-modified bentonite." *Journal of Colloid and Interfacial Science*. 298(1), pp. 39-49. 2006. DOI: 10.1016/j.jcis.2005.11.063

[11] Andini, S., Cioffi, R., Montagnaro, F., Pisciotta, F., Santoro, L. "Simultaneous adsorption of chlorophenol and heavy metal ions on organophilic bentonite." *Applied Clay Science*. 31(1-2), pp. 126-133. 2006. DOI: 10.1016/j.clay.2005.09.004

[12] Akcay, M., Akcay, G. "The removal of phenolic compounds from aqueous solutions by organophilic bentonite." *Journal of Hazardous Material*. 113(1-3), pp. 189-193. 2004. DOI: 10.1016/j.jhazmat.2004.06.026

[13] Ayari, F., Srasra, E., Trabelsi-Ayadi, M. "Retention of organic molecule "quinalizarin" by bentonitic clay saturated with different cations." *Desalination*. 206(1-3), pp. 499-506. 2007. DOI: 10.1016/j.desal.2006.03.578

[14] Demirbas, A., Sari, A., Isildak, O. "Adsorption thermodynamics of stearic acid onto bentonite." *Journal of Hazardous Material*. 135(1-3), pp. 226-231. 2006. DOI: 10.1016/j.jhazmat.2005.11.056

[15] Bacquet, M., Martel, B., Morcellet, M., Benabadji, K. I., Medjahed, K., Mansri, A., Meniai, A. H., Bencheikh B. L. "Adsorption of poly (4-vinylpyridine) onto bentonites." *Material Letters*, 58(3-4), pp. 455-459. 2004. DOI: 10.1016/S0167-577X(03)00524-X

[16] Asselman, T., Garnier, G. "Adsorption of model wood polymers and colloids on bentonites." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 168(2), pp. 175-182. 2000. DOI: 10.1016/S0927-7757(00)00430-1

[17] Bojemueller, E., Nennemann, A., Lagaly, G. "Enhanced pesticide adsorption by thermally modified bentonites." *Applied Clay Science*. 18(5-6), pp. 277-284. 2000. DOI: 10.1016/S0169-1317(01)00027-8

[18] Bors, J., Dultz, S., Riebe, B. "Organophilic bentonites as adsorbents for radionuclides: I. Adsorption of ionic fission products." *Applied Clay Science*. 16(1-2), pp. 1-13. 2000. DOI: 10.1016/S0169-1317(99)00041-1

[19] Yue, Q. Y., Li, Q., Gao, B. Y., Wang, Y. "Kinetics of adsorption of disperse dyes by polyepicholorohydrin-dimethylamine cationic polymer/bentonite." *Separation and Purification Technology*. 54(3), pp. 279-290. 2007. DOI: 10.1016/j.seppur.2006.10.024

[20] Eren, E., Afsin, B. "Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated bentonite surfaces." *Dyes and Pigments*. 76(1), pp. 220-225. 2008. DOI: 10.1016/j.dyepig.2006.08.019

[21] Safa Ozca, A., Erdem, B., Ozcan, A. "Adsorption of Acid Blue 193 from aqueous solutions onto BTMA-bentonite." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 266(1-3), pp. 73-81. 2005. DOI: 10.1016/j.colsurfa.2005.06.001

[22] Gil, A., Gandia, L. M. "Microstructure and quantitative estimation of the micropore- size distribution of an alumina-pillared clay from nitrogen adsorption at 77K and carbon dioxide adsorption at 273K." *Chemical Engineering Science*. 58(14), pp. 3059-3075. 2003. DOI: 10.1016/S0009-2509(03)00182-9

[23] Basoglu, F. T., Balci, S. "Micro-mesopore analysis of Cu^{2+} and Ag^+ containing Al-pillared bentonite." *Applied Clay Science*. 50(1), pp. 73-80. 2010. DOI: 10.1016/j.clay.2010.07.004

[24] Freundlich, H. "*Colloid and Capillary Chemistry*." London: Methuen. 1926.

[25] Langmuir, I. "The Adsorption of Gases on Plane Surfaces of Glass, Mica, and Platinum." *Journal of American Chemical Society*. 40(9), pp. 1361-1403. 1918. DOI: 10.1021/ja02242a004

[26] Saeidi, N., Parvini, M., Sarsabili, M. R. "Studying Performance of Dubinin-astakhov and Dubinin-raduchkevic Equations to Evaluate Nanopore Volume and Pore Size of MCM-41 Particles." *International Journal of Engineering (IJE), TRANSACTIONS A: Basics*. 27(10), pp. 1511-1518. 2014. DOI: 10.5829/idosi.ije.2014.27.10a.04

[27] Brunauer, S., Emmett, P. H., Teller, E. "Adsorption of gases in multimolecular layers." *Journal of American Chemical Society*. 60(2), pp. 309-319. 1938. DOI: 10.1021/ja01269a023

[28] Terzyk, A. P., Gauden, P. A., Kowalczyk, P. "What kind of pore size distribution is assumed in the Dubinin–Astakhov adsorption isotherm equation?." *Carbon*. 40(15), pp. 2879-2886. 2002. DOI: 10.1016/S0008-6223(02)00219-1

[29] Dubinin, M. M. "*Characterisation of Porous Solids*." London: The Society of Chemical Industry. 1979.

[30] Saeidi, N., Lotfallahi, M. N. "A procedure to form powder activated carbon into activated carbon monolith." *The International Journal of Advanced Manufacturing Technology*. 81(5), pp. 1281-1288. 2015. DOI: 10.1007/s00170-015-7311-z

[31] Carvalho, A. P., Mestre, A. S., Pires, J., Pinto, M. L., Rosa, M. E. "Granular activated carbons from powdered samples using clays as binders for the adsorption of organic vapours." *Microporous and Mesoporous Materials*. 93(1-3), pp. 226-231, 2006. DOI: 10.1016/j.micromeso.2006.03.001

[32] Gaspard, S., Altenor, S., Dawson, E. A., Barnes, P. A., Ouensanga, A. "Activated carbon from vetiver roots: Gas and liquid adsorption studies." *Journal of Hazardous Material*. 144(1-2), pp. 73-81. 2007. DOI: 10.1016/j.jhazmat.2006.09.089

[33] Olivares-Marín, M., Fernández-González, C., Macías-García, A., Gomez-Serrano, V. „Preparation of activated carbon from cherry stones by chemical activation with $ZnCl_2$." *Applied Surface Science*. 252(17), pp. 5967-5971. 2006. DOI: 10.1016/j.apsusc.2005.11.008

[34] Ding, Z., Kloprogge, J. T., Frost, R. L. "Porous clays and pillared clays-based catalysts. Part 2: a review of the catalytic and molecular sieve applications." *Journal of Porous Materials.* 8(4), pp. 273-293. 2001. DOI: 10.1023/A:1013113030912

[35] Horvath, G., Kawazoe, K. "Method for the calculation of effective pore size distribution in molecular sieve carbon." *Journal of Chemical Engineering of Japan*. 16(6), pp. 470-475. 1983. DOI: 10.1252/jcej.16.470

[36] Brandt, K. B., Kydd, R. A. "Characterization of synthetic microporous pillared beidellites of high thermal stability." *Chemistry of Materials*. 9(2), pp. 567-572. 1997. DOI: 10.1021/cm960403r

[37] Canizares, P., Valverde, J. L., Sun Kou, M. R., Molina, C. B. "Synthesis and characterization of PILCs with single and mixed oxide pillars prepared from two different bentonites, a comparative study." *Microporous and Mesoporous Materials*. 29(3), pp. 267-281. 1999. DOI: 10.1016/S1387-1811(98)00295-9

[38] Ge, Z., Li, D., Pinnavaia, T. J. "Preparation of alumina-pillared montmorillonites with high thermal stability, regular microporosity and Lewis/BrZonsted acidity." *Microporous Materials*. 3(1-2), pp. 165-175. 1994. DOI: 10.1016/0927-6513(94)00020-4

[39] Hutson, N. D., Hoekstra, M. J., Yang, R. T. "Control of microporosity of Al_2O_3-pillared clays: effect of pH, calcinations temperature and clay cation exchange capacity." *Microporous and Mesoporous Materials*. 28(3), pp. 447-459. 1999. DOI: 10.1016/S1387-1811(98)00334-5

[40] Storaro, L., Lenarda, M., Ganzerla, R., Rinaldi, A. "Preparation of hydroxy Al and Al/Fe pillared bentonites from concentrated clay suspensions." *Microporous Materials*. 6(2), pp. 55-63. 1996. DOI: 10.1016/0927-6513(95)00081-X

[41] Everett, D. H., Powl, J. C. "Adsorption in slit-like and cylindrical micropores in the Henry's law region." *Journal of the Chemical Society, Faraday Transactions 1*. 72, pp. 619-636. 1976. DOI: 10.1039/F19767200619

[42] Sams, J. R., Constabaris, G., Halsey, G. D. "Second virial coefficients of neon, argon, krypton and xenon with a graphitized carbon black." *Journal of Physical Chemistry*. 64(11), pp. 1689-1690. 1960. DOI: 10.1021/j100840a020

[43] Gregg, S. J., Sing, K. S. W. "*Adsorption, surface area and porosity*." London: Academic Press. 1991.

[44] Saito, A., Foley, H. C. "Curvature and parametric sensitivity in models for adsorption in micropores." *AIChE Journal*. 37(3), pp. 429-436. 1991. DOI: 10.1002/aic.690370312

[45] Gil, A., Grange, P. "Comparison of the microporous properties of an alumina pillared montmorillonite and an activated carbon from nitrogen adsorption at 77 K." *Langmuir*. 13(16), pp. 4483-4486. 1997. DOI: 10.1021/la9620566

[46] Dastgheib, S. A., Karanfil, T. "The effect of the physical and chemical characteristics of activated carbons on the adsorption energy and affinity coefficient of Dubinin equation." *Journal of Colloid Interfacial Science*. 292(2), pp. 312-321. 2005. DOI: 10.1016/j.jcis.2005.06.017