ISSN NO. 2320-5407

Journal Homepage: - www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI: 10.21474/IJAR01/9972
DOI URL: http://dx.doi.org/10.21474/IJAR01/9972

RESEARCH ARTICLE

ADSORPTION OF COPPER FROM AQUEOUS SOLUTION BY MOROCCAN ATTAPULGITE: KINETIC AND THERMODYNAMIC STUDIES.

N. El Bardiji, K. Ziat and M. Saidi.
Laboratory of Physico-Chemistry of Materials, Natural Substances and Environment, Department of Chemistry,
Faculty of Sciences and Techniques, Abdelmalek Essaâdi University, Tangier (Morocco).

……

Manuscript Info

Manuscript History
Received: 05 September 2019
Final Accepted: 07 October 2019
Published: November 2019

Key words:-
Treated Attapulgite; Copper adsorption; Kinetic molding; Thermodynamic study.

Abstract

In this paper, Moroccan treated attapulgite (MTATP) was used as a mineral adsorbent for removal of copper ions from aqueous solution. Fourier transform infrared spectroscopy (FTIR) was used to study the functional groups of attapulgite. Kinetic analysis of the experimental results was carried out by using the pseudo-first-order, pseudo-second-order and the intraparticle diffusion models. The modeling results showed that the pseudo-second-order model is able to describe the adsorption behavior of copper onto attapulgite more accurately. Thermodynamic parameters such as Gibbs free energy (ΔG°), the enthalpy (ΔH°) and the entropy change (ΔS°) of sorption were calculated. Outcomes reveals that the sorption process is spontaneous and exothermic.

……

Introduction:-

Water quality problem is one of the most serious challenge that humanity is facing in our age. The industrial wastewater contaminated by heavy metals is a major responsible of the water pollution. Copper is one of the most toxic heavy metals. Hence, the removal of copper from aqueous solutions is extremely important.

Several methods can be applied to remove heavy metals from aqueous solutions, such as ion exchange, membrane separation, and electro-chemical process. Among these techniques, adsorption has been considered as an effective and economical method with high potential for the removal, recovery and recycling of metals from wastewater [1].

Many kinds of clay minerals have been used for adsorption of copper ions from aqueous solutions, such as kaolinite, montmorillonite and sepiolite [2-4]. Attapulgite, one of common clay minerals, is a crystalline hydrated magnesium aluminum silicate mineral with large amount of reactive OH^- groups and exchangeable cation ions. Hence, attapulgite (ATP) is a suitable material for the removal of heavy metal ions from aqueous solutions [5].

Acid activation is a usual method applied for improving the surface properties of clay minerals. Hence, acid treatment of attapulgite can eliminate impurities, change its composition and increase its area and pore volume as well as the number of adsorption sites by disaggregation of attapulgite particles [6-7].

In order to understand the nature of sorbate-sorbent interactions, the kinetic study of a liquid-solid adsorption process requires adequate mathematical expressions. Among several kinetics models proposed in the literature,

Corresponding Author:-N. El Bardij.
Address:**-** Laboratory of Physico-Chemistry of Materials, Natural Substances and Environment, Department of Chemistry, Faculty of Sciences and Techniques, Abdelmalek Essaâdi University, Tangier (Morocco).

pseudo-first order (PFO) and pseudo-second order (PSO) and intraparticl diffusion models are the most used to describe the mechanism of adsorption process.

In this paper, Moroccan treated attapulgite is applied to remove copper ions from aqueous solution. Fourier transform infrared spectroscopy (FTIR) was used to study the surface and functional group of this adsorbent. The adsorption kinetic of copper onto MTATP was examined by applying the pseudo-first order, pseudo-second order models and the intraparticle diffusion models. The thermodynamic parameters related with the process were also evaluated.

Materials and methods:-

Materials

The attapulgite was obtained from National Office of Hydrocarbons and Mines (ONHYM) of Morroco. The ATP samples were ground by mortar and treated with hydrochloric acid (analytical reagent grade, Sigma-Aldrich) 37% at concentration of 3 mol L^{-1} for 12 hours. The treated sample was thoroughly washed with bi-distilled water to remove all acid and then filtered. The treated attapulgite was dried in the oven at 373 K for 12 h, and then sieved to obtain particles smaller than 63 µm.

The copper salt ($CuSO_4.5H_2O$) (analytical reagent grade, Riedel-de Haën) was used to prepare the copper solutions by dissolving the appropriate amount in bi-distilled water.

Characterization

Surface functional groups of the ATP and MTATP are characterized using the Fourier transforms infrared spectrophotometer (Vertex 70). Infrared absorbance data were recorded at room temperature in the wavenumber region 400–4000 cm^{-1}.

Adsorption experiments

The adsorption kinetics experiments were carried out by adding 0.2 g of the MTATP to 25 mL of 150, 200, 250, 300, 350 and 400 mg L^{-1} of copper solution at room temperature. The mixtures were agitated with a shaker (WTW OxiTop IS 6) placed in an incubator (Refrigerated Incubators FTD I.S. Co.), at appropriate time intervals from 5 to 300 min. The solid was separated by centrifugation and the filtrate was analyzed by means of atomic absorption spectrophotometry using a spectrophotometer (Jobin Yvon 2) to determine the residual copper concentration. In order to obtain the thermodynamic nature of the adsorption process, the experiments were conducted at different temperatures 283, 293, 303 and 313 K.

The adsorption capacity of the adsorbent was determined as follows [8]:

$$\mathrm{q_t} = \frac{(\mathrm{C_0} - \mathrm{C_t})\, V}{\mathrm{m}} \qquad (1)$$

where q_t is the adsorbed amount at time t (mg g^{-1}), C_0 and C_t are the copper concentrations in the bulk solution initially and at the time t, respectively (mg L^{-1}), V is the volume of the solution (L) and m is the mass of the adsorbent (g).

Adsorption kinetics models

In order to investigate the adsorption mechanism, the kinetic data obtained were analyzed using the pseudo-first-order, pseudo-second-order and the intraparticle diffusion models.

The linear method was applied for analyzing kinetic data to obtain the rate constants for the PFO and PSO models. The linear equations of these models for adsorption in a liquid-solid system are represented as follows [9-10]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (2)$$

$$\frac{\mathrm{t}}{q_t} = \frac{1}{\mathrm{k_2 q_e^2}} + \frac{1}{\mathrm{q_e}}\mathrm{t} \qquad (3)$$

where k_1 is the adsorption rate constants for the PFO model (min^{-1}), k_2 is the adsorption rate constants for the PSO model ($g.mg^{-1}.min^{-1}$) and q_e is the amount adsorbed at equilibrium ($mg.g^{-1}$).

The parameters of PFO model, k_1 and q_e, can be determined experimentally by plotting log (q_e-q_t) versus t. On the other hand, the slope and intercept of the straight line obtained by plotting t/q versus t allows to calculate the values of k_2 and q_e of PSO model.

The adsorption process can be influenced by one or more steps, such as external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step [11]. The possibility of intraparticle diffusion can be verified by applying the intraparticle diffusion model proposed by Weber and Morris [12]:

$$q_t = k_d t^{1/2} + C_d \qquad (4)$$

where k_d is the diffusion rate constant in the pores (mg g^{-1} $min^{1/2}$) and C_d is the intercept (mg g^{-1}). If the Weber–Morris plot of q_t versus t gives a straight line, then the sorption process is controlled by intraparticle diffusion only. However, if this plot exhibit a multi-linearity, then no less than two steps influence the adsorption process.

Thermodynamic parameters

In order to determine the effect of temperature on the adsorption process, the standard enthalpy (ΔH°) and the standard entropy (ΔS°) can be calculated from the slope and intercept of the line plotted by ln (K_d) versus 1/T, respectively, using the following equations [13]:

$$K_d = \frac{V}{m}\frac{C_0 - C_e}{C_e} \qquad (5)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (6)$$

where R is the gas constant (J mol^{-1} K^{-1}), C_e is the copper concentration in the bulk solution at equilibrium, T is the temperature (K) and K_d is the distribution constant (mL g^{-1}).

The standard Gibbs free energy (ΔG°) can be calculated by the equation:

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \qquad (7)$$

Model performance indicators

The comparison of the performance of the models was carried out based on statistical parameter called the determination coefficient (R^2) expressed as follows [14]

$$R^2 = \frac{\sum_{i=1}^{N}\left(q_{exp} - \overline{q_{cal}}\right)^2}{\sum_{i=1}^{N}\left(q_{exp} - \overline{q_{cal}}\right)^2 + \sum_{i=1}^{N}\left(q_{exp} - q_{cal}\right)^2} \qquad (8)$$

where N is the number of experimental data, q_{exp} and q_{cal} are the experimental and calculated adsorbed amount (mg g^{-1}), whereas $\overline{q_{cal}}$ (mg g^{-1}) is the average of the calculated adsorbed amount.

Result and discussion:-

FTIR Analysis

The FTIR spectra of ATP and MTATP are shown in Fig. 3. The bands at 3627 and 3592 cm^{-1} are attributed to O–H stretching vibrations of the octahedral cations Me–Me–OH (Me = Fe, Al, …) at the edges of the channels [6]. The bands at 3439 and 1652 cm^{-1} correspond to the stretching mode and bending vibration of O–H bond of free and adsorbed water, respectively [15]. The strongest band observed at 1427 cm^{-1} in the infrared spectrum of ATP is associated with the stretching vibration of carbonate groups (CO_3^{2-}). The corresponding deformation vibration is observed at 874 and 712 cm^{-1} [16]. The bands appearing at 2515 and 1797 cm^{-1} are also an indication of the presence of carbonate groups [17,18]. These bands disappear in the infrared spectrum of MTATP due to the action of the acid. Similar observations were reported by Boudrihe et al. [19]. The narrow and broad peaks located at 1162 and 1036 cm^{-1} are assigned to the stretching mode of Si–O bond [20,21]. The peak at 915 cm^{-1} corresponds to Al–Al–OH deformation, and it is a consequence of the dominantly dioctahedral character of attapulgite [22]. The bands located at 797, 779 and 695 cm^{-1} are attributed to the Si–O of quartz and Me–O stretching vibration [23]. The bands at 524 and 474 cm^{-1} are assigned to the bending mode of O–Si–O, Si–O–Si and Si–O–Al [24,18].

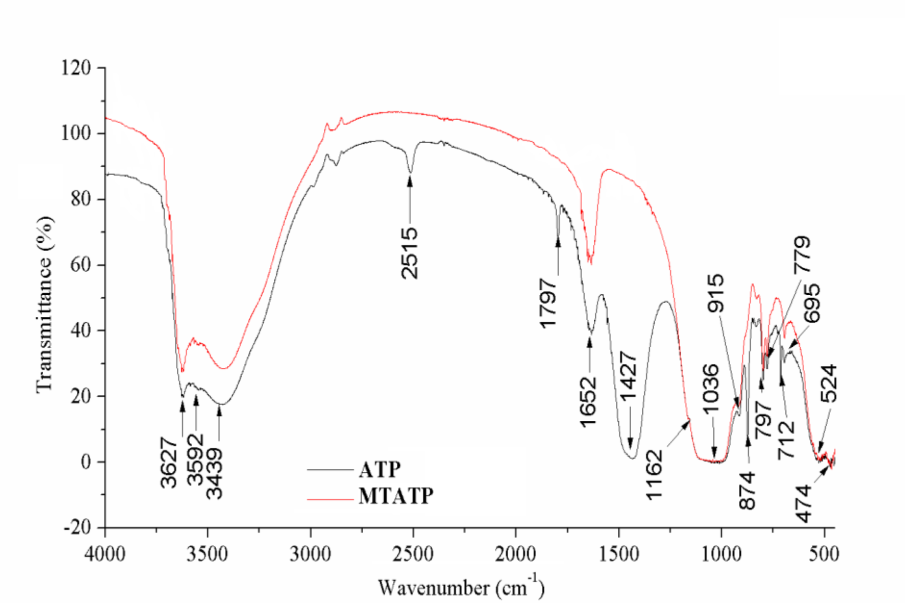

Figure 1: Infrared spectra of ATP and MTATP

Kinetic study

The PFO and PSO models were applied to analyze the adsorption kinetics of copper onto MTATP. Figures 2 and 3 show the obtained linear plots of the PFO and PSO models. The parameters of both kinetic models are listed in Table 1. Outcomes show that the correlation coefficients obtained by the PSO equation are higher than those determined from the PFO equation. In addition, the experimental sorption capacity values are very different from those calculated by the PFO model, while they are very close to those determined by the PSO model. All these findings confirm that the copper sorption kinetic by MTATP is pseudo-second order.

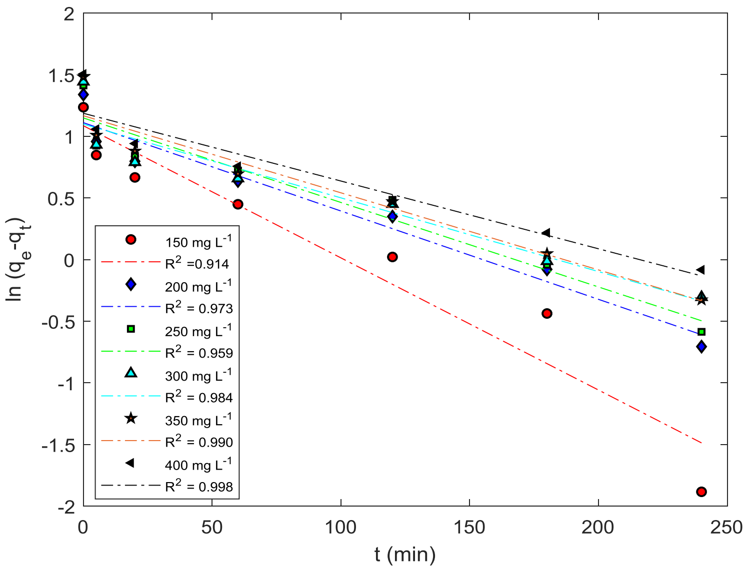

Figure 2:-The pseudo-first-order kinetic model for copper adsorption onto MTATP.

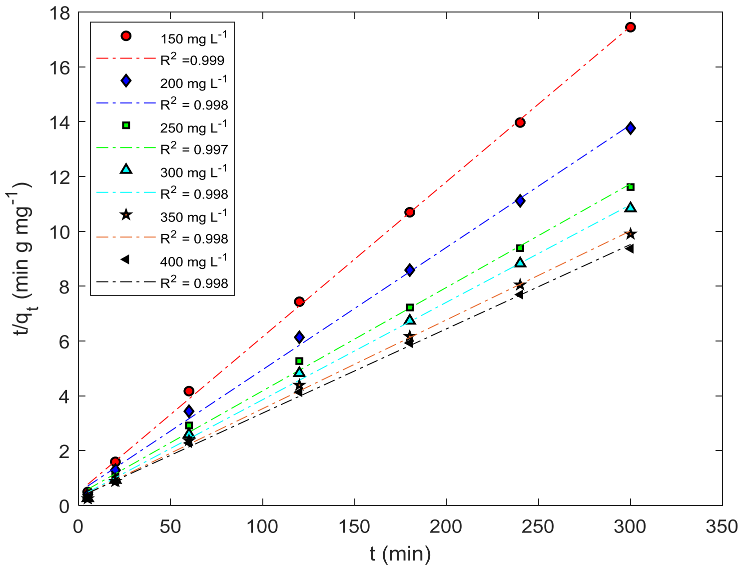

Figure 3:-The pseudo-second-order kinetic model for copper adsorption onto MTATP.

Table 1:- Kinetic parameters of PFO and PSO models.

C_0	$q_{e,exp}$	PFO				PSO			
		$q_{e,cal}$	k_1	Δq_e	R^2	$q_{e,cal}$	k_2	Δq_e	R^2
150	17.192	6.779	0.2391	10.413	0.914	17.669	0.0066	0.476	0.999
200	21.792	11.759	0.0152	10.033	0.973	22.371	0.0041	0.579	0.998
250	25.826	15.825	0.0143	10.001	0.959	26.455	0.0035	0.629	0.997
300	27.683	18.598	0.0120	9.085	0.984	28.089	0.0042	0.407	0.998
350	30.289	20.816	0.0840	9.473	0.990	30.864	0.0036	0.575	0.998
400	32.019	22.867	0.0108	9.152	0.998	32.467	0.0032	0.448	0.998

The modeling of the experimental data with the model of Weber and Morris is shown in figure 4. The data exhibit three linear plots, indicating that three steps were involved in the copper adsorption onto MTATP. The initial stage, fast adsorption stage, can be attributed to the diffusion of adsorbates through the solution to the external surface of MTATP and through the boundary layer to the surface of MTATP. The second stage described the gradual adsorption of adsorbates. The last stage was attributed to the final equilibrium for which the intraparticle diffusion started to slow down due to extremely low concentration of adsorbates in solution [25].

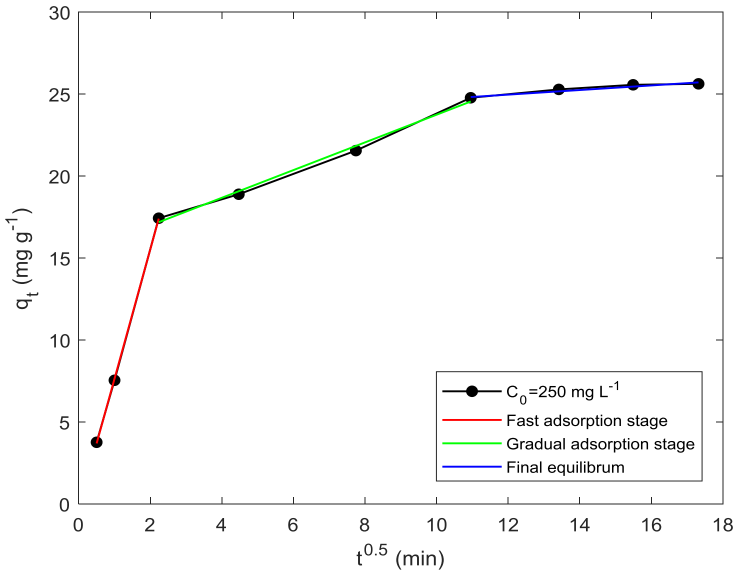

Figure 4:-The intraparticle diffusion model for copper adsorption onto MTATP.

Thermodynamic study

Figure 5 presents the dependence of logarithm of K_d on 1/T in order to estimate the values of ΔG◦, ΔH◦ and ΔS◦ for the adsorption process. The results are listed in Table 3.

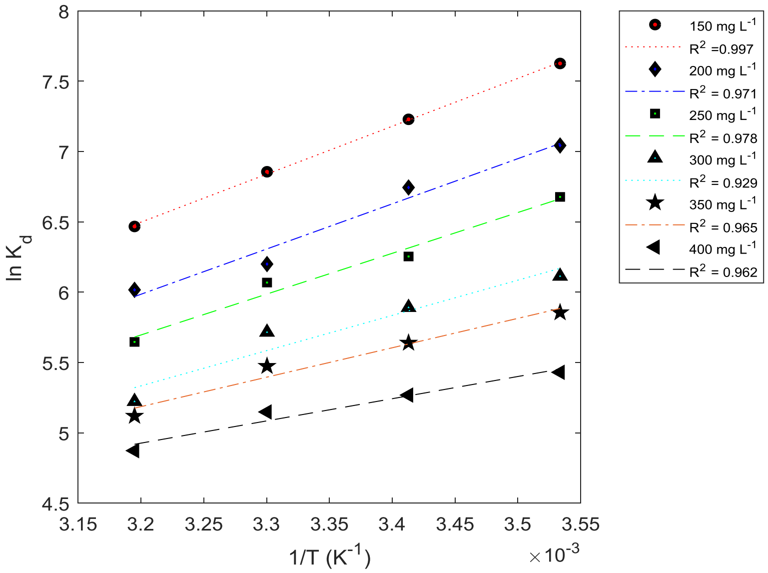

Figure 5:-K_d versus 1/T plot for copper adsorption onto MTATP (pH = 4.5, C_0 = 250 mg L^{-1} and m= 0.2 g).

Table 2:-Thermodynamic parameters of copper adsorption of onto MTATP.

C_0	T (K°)	ΔG° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	ΔH° (kJ mol^{-1})	R^2
150	313	-15.714	-40.330	-28.337	0.997
	303	-16.117			
	293	-16.521			
	283	-16.924			
200	313	-15.511	-35.816	-26.721	0.971
	303	-15.869			
	293	-16.227			
	283	-16.585			

250	313	-14.784	-24.134	-29.872	0.978
	303	-15.083			
	293	-15.381			
	283	-15.680			
300	313	-13.852	-22.296	-20.831	0.929
	303	-14.075			
	293	-14.298			
	283	-14.521			
350	313	-13.469	-12.541	-17.394	0.965
	303	-13.595			
	293	-13.720			
	283	-13.845			
400	313	-12.628	-1.057	-13.131	0.962
	303	-12.690			
	293	-12.721			
	283	-12.832			

The negative values of ΔG◦ indicated that the adsorption of copper onto MTATP is spontaneous and feasible. However, the negative values of ΔG◦ decreased with increasing temperature, indicating that the adsorption process is more favorable at low temperatures. The negative values of the standard enthalpy ΔH° confirm that the adsorption process is exothermic. The negative value of entropy change ΔS° shows a decreased disorder at the solid/liquid interface during copper adsorption. As the temperature increases, the mobility of copper ions increases causing the ions to escape from the solid phase to the liquid phase. Therefore, the amount of copper that can be adsorbed will decrease [26].

Conclusions:-

The present paper reveals that the Moroccan treated attapulgite is a low-cost alternative adsorbent for efficient removal of copper ions from aqueous solutions. The results of kinetic studies show that the PSO model gives a better fit of the experimental results. In addition, the copper diffusion in the pores is not the only mechanism limiting the sorption kinetics. Outcomes of the thermodynamic study indicate that the decrease of the temperature favours the copper sorption onto MTATP. The negative ΔG° and ΔH° values indicate that the adsorption of copper ions is a spontaneous and exothermic process.

References:-

1. Y. S. Ho, C. T. Huang, H. W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, Process Biochem. 37 (2002) 1421–1430.
2. G. Suraj, C. S. P. Iyer, M. Lalithambika, Adsorption of cadmium and copper by modified kaolinites, Appl. Clay Sci. 13 (1998) 293–306.
3. K.G Bhattacharyya., S.S. Gupta, Kaolinite, montmorillonite, and their modified derivatives as adsorbents for removal of Cu (II) from aqueous solution, Sep. Purif. Technol. 50 (2006) 388-397
4. L.I. Vico, Acid–base behaviour and Cu2+ and Zn2+ complexation properties of the sepiolite/water interface, Chem. Geol. 198 (2003) 213–222.
5. Q. Fan, D. D. Shao, J. Hu, W. Wu, X. K. Wang, Comparison of Ni2+ sorption to bare and ACT-graft attapulgites: Effect of pH, temperature and foreign ions, Surf. Sci. 602 (2008) 778-785
6. N. Frini-Srasra, E. Srasra, Acid treatment of south Tunisian palygorskite: Removal of Cd(II) from aqueous and phosphoric acid solutions, Desalination 250 (2010) 26–34.
7. P. Pushpaletha, M. Lalithambika, Modified attapulgite: An efficient solid acid catalyst for acetylation of alcohols using acetic acid, Appl. Clay Sci. 51 (2011) 424–430.
8. X. Xie, R. Deng, Y. Pang, Y. Bai, W. Zheng and Y. Zhou, Adsorption of copper(II) by sulfur microparticles, Chem. Eng. J. 314 (2017) 434–442.
9. S. Lagergren, About the theory of so-called adsorption of soluble substances, Kungl. Sven. Vetenskapsakademiens Handl. 24 (1898) 1–39.
10. G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolites, Water Res. 18 (1984) 1501-1507.

11. V. Fierro, V. Torné-Fernández, D. Montané, A. Celzard, Adsorption of phenol onto activated carbons having different textural and surface properties, Microporous Mesoporous Mater. 111 (2008) 276–284
12. W. J. Weber, Physicochemical processes for water quality control, Wiley Interscience, 1972.
13. G. Rytwo, E. Ruiz-Hitzky, Enthalpies of adsorption of methylene blue and crystal violet to montmorillonite. J. Therm. Anal. Calorim. 71 (2003) 751-759.
14. Y. El Boundati, K. Ziat, A. Naji, M. Saidi, Generalized fractal-like adsorption kinetic models: Application to adsorption of copper on Argan nut shell, J. Mol. Liq. 276 (2019) 15–26.
15. M. Zhang, L. Shi, S. Yuan, Y. Zhao, J. Fang, Synthesis and photocatalytic properties of highly stable and neutral TiO_2/SiO_2 hydrosol, J. Colloid Interf. Sci. 330 (2009) 113–118.
16. K. Nakamoto, Infrared spectra of inorganic and coordination compounds, John Wiley and Sons (1963).
17. S. Gunasekaran, G. Anbalagan, S. Pandi, Raman and infrared spectra of carbonates of calcite structure, J. Raman Spectrosc. 37 (2006) 892–899.
18. Y.S. Al-Degs, M.I. El-Barghouthi, A.A. Issa, M.A. Khraisheh, G.M. Walker, Sorption of Zn(II), Pb(II), and Co(II) natural sorbents: Equilibrium and kinetic studies, Water Res. 40 (2006) 2645– 2658.
19. L. Boudriche, R. Clavet, B. Hamidi, H. Balard, Effect of acid treatment on surface properties evolution of attapulgite clay: An application of inverse gas chromatography, Colloids Surf. A: Physicochem. Eng. Asp. 392 (2011) 45–54.
20. R.L. Frost, O.B. Locos, J. Ruan, J.T. Kloprogge, Near infrared and mid-infrared spectroscopic study of sepiolites and palygorskites, Vib. Spectrosc. 27 (2001) 1–3.
21. R.L. Frost, Y. Xi, H. He, Synthesis, characterization of palygorskite supported zero-valent iron and its application for methylene blue adsorption, J. Colloid Interf. Sci. 341 (2010) 153–161.
22. M. Suárez, E. García-Romero, FTIR spectroscopic study of palygorskite: Influence of the composition of the octahedral sheet, Appl. Clay Sci. 31 (2006) 154 – 163.
23. K.C. Nebagha, K. Ziat, L. Rghioui, M. Khayet, M. Saidi, K. Aboumaria, A. El Hourch, S. Sebti, Adsorptive removal of copper(II) from aqueous solutions using low cost Moroccan adsorbent. Part I: Parameters influencing Cu(II) adsorption, J. Mater. Environ. Sci. 6 (2015) 3022–3033.
24. E.M.A. Khalil, F.H. ElBatal, Y.M. Hamdy, H.M. Zidan, M.S. Aziz, A.M. Abdelghany, Infrared absorption spectra of transition metals-doped soda lime silica glasses, Physica B 405 (2010) 1294–1300.
25. X. Zou, J. Pan, H. Ou, X. Wang, W. Guan, C. Li, Y. Yan, Adsorptive removal of Cr (III) and Fe (III) from aqueous solution by chitosan/attapulgite composites: Equilibrium, thermodynamics and kinetics, Chem. Eng. J. 167 (2011) 112–121
26. W.S. Wan Ngah, M.A.K.M. Hanafiah, Adsorption of copper on rubber (Hevea brasiliensis) leaf powder: Kinetic, equilibrium and thermodynamic studies, Biochem. Eng. J. 39 (2008) 521–530