MODIFIED ATTAPULGITE APPLICATION IN REMOVAL OF SR^{2+}, CO^{2+} AND NI^{2+} IONS FROM MULTICOMPONENT SOLUTION

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ABSTRACT

Natural clays have been recommended as a green alternative sorbent, with low cost, good mechanical properties, and good tolerance to a harsh chemical environment. However, on a large scale, it is difficult to separate the clay particles from the solution; the centrifugation process involves a high speed, and the filtration procedure is prone to filter blockages. Therefore, a suitable method for the separation of clay particles is necessary to be found. To solve this problem, the clay should be modified. In this paper, attapulgite (ATP) as a natural clay was modified using double-layer hydroxide to produce LDH-ATP sorbent. Different sorption isotherm models of the modified attapulgite for the removal of Sr^{2+}, Co^{2+}, and Ni^{2+} ions from a multicomponent solution were evaluated, for instance, the extended Langmuir and Freundlich isotherm models. The results demonstrated that the extended Langmuir is more suitable than Freundlich isotherm (with R^2 values greater than 0.95). The maximum capacity was computed and found to be 2.6, 1.64, and 1.60 mmol/g for Ni^{2+}, Co^{2+}, and Sr^{2+}, respectively. Finally, the LDH-ATP can be recommended for the removal of Sr^{2+}, Co^{2+}, and Ni^2 ions from multicomponent media.

Keywords: *Attapulgite clay, Layered double hydroxide, Equilibrium isotherm, multicomponent solution.*

1. INTRODUCTION

Radioactive waste is an unavoidable legacy from the uses of radioactive materials in different fields including industrial, medical, research, and nuclear facility. Consequently, the management of this waste is a matter of relevance worldwide. To reduce the hazardous effects of the radioactive and toxic wastes released into the environment, improvement of treatment methods and technologies are involved.

There are different methods used for the treatment of waste streams such as adsorption [1, 2], ion exchange [3, 4], electrochemical cell [5], and chemisorption [6].

The usage of natural materials as sorbents has drawn considerable interest in the last decade, primarily due to the low cost, the intrinsically environmentally friendly properties, and the high selectivity of some metal ions,. Clays are suggested as a green alternative, with good mechanical

characteristics, low cost, and good resistance to a harsh chemical environment [7].

Attapulgite (ATP) as a clay mineral can be used as a sorbent. The micro-pores and channels give ATP a high surface area, further its adsorption capacity encourages its commercial application. Therefore, ATP has been recommended as a promising adsorbent for heavy metals removal [8], [9], [10] and [11] and adsorption of dyes [12] and [13]. However, on a large scale, it is difficult to separate ATP particles from solution, for example; the centrifugation process requires a very high speed, and the filtration procedure is prone to filter blockages. Hence, it is essential to find a suitable method for the separation of ATP particles simply and in a large scale. To solve this problem, modification of ATP is achieved using different materials [14], [15] [16] and [17].

In this work, Layered Double Hydroxide (LDH) material was applied to modify attapulgite. LDH is known as hydrotalcite-like compounds, anionic clays, and host-guest materials. LDH compounds demonstrate promising properties, for instance, surface areas, porous volumes, high adsorption capacity, good thermal stability, and regeneration efficiency [18] and [19] to sorb pollutants. These layers attract negatively-charged hydroxide ions to the surfaces of LDH crystals in aqueous solution to form metal hydroxides. Meanwhile, the charge compensating carbonate anion joined on the surface and edge could also bond with metal ions to form insoluble metal carbonates. Therefore, LDHs are used for ions removal. Hence, modification of attapulgite was achieved in this study by Mg–Al layered double hydroxides; the modified attapulgite was characterized and used for the removal of cobalt, nickel, and strontium ions in multicomponent solution.

In the previous work [20], preliminary studies on the modified attapulgite were carried out from which the kinetic behavior of the sorption process for Sr^{2+}, Ni^{2+}, and Co^{2+} ions was estimated, as well as the preparation and characterization of the sorbent were carried out in the previous work. While in this work, the application to remove Sr^{2+}, Ni^{2+}, and Co^{2+} ions from multicomponent solution was studied.

2. METHODS AND MATERIALS
2.1. Materials
Raw ATP was purchased from Alfa Chemika Company (India). Strontium Chloride, Nickel Chloride, and Cobalt Chloride were purchased from Aldrich Company. Aluminum Nitrate and Magnesium Nitrate were purchased from Alpha Chemika Company. The pH was adjusted by the addition of NH_4OH and/or HNO_3 which obtained from Fluka.

2.2. Preparation of LDH-ATP
ATP was modified using LDH to produce LDH-ATP according to the procedure described in the previous work [20]; ten g of ATP clay was dispersed in 100 mL of 1.0 mol/L HCl for 1.0 h at 70°C with the aid of magnetic stirrer to produce a homogeneous dispersion. Then a certain amount of magnesium and aluminum nitrates was dissolved in deionized water and transferred into the above dispersion under vigorous magnetic stirring for 1.0 h after adjusting of pH at 9.5–10.0 using 1.0 mol/L NH_4OH solution. The resulting slurry was aged, followed by filtration and washing with deionized water repeatedly.

The collected product (LDH-ATP) was dried at 70°C.

2.3. Equilibrium investigations

Batch sorption experiments were conducted by introducing 20 mL of the multicomponent solution with a known total initial concentration of the metal ions into glass bottles containing accurately weighed amounts, 0.05 g, of the sorbent. The total concentration of the sorptive solution was ranged from 10^{-4} to 10^{-2} mol/L. The glass bottles were shaken using a shaker water bath at a constant temperature until sorption equilibrium was established. The pH of the mixtures (pH = 5.0) was maintained with 0.1 mol/L NaOH and/or 0.1 mol/L HCl solutions. All the experiments were performed at four different temperatures, 298, 303, 313, and 323 K. After equilibrium time (30 min), then centrifugation was used to remove the sorbent from the liquid phase. Atomic absorption spectrophotometry (Buck Scientific model 210 VGP, USA) has been used to determine the equilibrium concentrations of Co^{2+}, Ni^{2+}, and Sr^{2+} ions. The amount of metal ions sorbed (q_e, mmol/g) was computed using the following equation.

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

where C_0 and C_e are the initial and equilibrium concentrations of the metal ions (mol/L), V is the volume of sample in litter and m is the mass of LDH-ATP in gram.

3. RESULTS AND DISCUSSION
3.1. Sorption isotherms

Generally, the sorption isotherm clarifies how sorbents interact with sorbates, so it is significant in optimizing the utilization of sorbents. The amount sorbed (mmol/g) of Co^{2+}, Ni^{2+}, and Sr^{2+} ions onto LDH-ATP at temperatures of 298, 303, 313, and 323 K was computed by changing the

initial total molarity of metal ions from 10^{-4} to 10^{-2} mol/L in a multicomponent solution. All other parameters were kept constant. The study of the sorption behavior of a material when the solution contains more than one component is extremely valuable. The isotherm models for the sorption of a single component are not suitable due to the presence of altered metal ions in the solution. More complex mathematical isotherm models are required for the multicomponent systems. Some popular isotherm models for a multicomponent system, for example, extended Langmuir and Freundlich isotherm models were utilized. Both isotherms were fitted employing the nonlinear fitting method as shown in Figs. 1 and 2. From the experimental data, increasing the initial total molarity of Co^{2+}, Sr^{2+}, and Ni^{2+} increased the amount sorbed. This increase could be explained with the high driving force for mass transfer.

3.2. Extended Langmuir isotherm model

The extended Langmuir model can be applied to characterize the multicomponent sorption data. Equation 2 represents the extended Langmuir formula for the competitive sorption in a multicomponent system [21]

$$q_{e,i} = \frac{Q_i^o b_i C_{e,i}}{1 + \sum_{j=1}^{N} b_j C_{e,j}}$$

where, $q_{e,i}$ (mmol/g) is the equilibrium amount sorbed of metal ion for the component i in the multicomponent solution, Q_i^o (mmol/g) is the maximum monolayer sorption capacity for the component i. $C_{e,i}$ and $C_{e,j}$ are the equilibrium concentrations of the components i and j (mmol/L) respectively; b_i and b_j are the affinity of sorbent towards the sorbates i and j, respectively, j =1, 2, 3,…, N, and N is the

number of components in the experimental isotherm. For the sorption of Sr^{2+}, Co^{2+}, and

$$q_{e,Sr} = \frac{Q_{Sr}^0 b_{Sr} C_{e,Sr}}{1 + b_{Sr} C_{e,Sr} + b_{Co} C_{e,Co} + b_{Ni} C_{e,Ni}}$$

Ni^{2+} in a multicomponent solution, extended Langmuir formula becomes;

$$q_{e,Co} = \frac{Q_{Co}^0 b_{Co} C_{e,Co}}{1 + b_{Co} C_{e,Co} + b_{Sr} C_{e,Sr} + b_{Ni} C_{e,Ni}}$$

$$q_{e,Ni} = \frac{Q_{Ni}^0 b_{Ni} C_{e,Ni}}{1 + b_{Ni} C_{e,Ni} + b_{Sr} C_{e,Sr} + b_{Co} C_{e,Co}}$$

Fig. 1 demonstrates the extended Langmuir plots; the maximum monolayer sorption capacity values were computed and reported in Table 1. The results revealed that the extended Langmuir equation fits the data accurately well with the R^2 values of 0.97, 95 and 0.96, for nickel, cobalt, and strontium ions, respectively. For monolayer sorption onto a surface with a finite number of identical sites, the Langmuir equation is highly suitable. The Q_o and b values of Langmuir constants for the sorption of all ions increased with temperature showing that the sorption capacity and intensity of sorption are large at high temperature.

3.3. Freundlich isotherm model

Freundlich model offers the earliest identified empirical sorption isotherm through assuming an exponentially decaying sorption site energy distribution [22]. This phenomenon can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption The Freundlich isotherm model was applied in this work to clarify the sorption of the mentioned metal ions in a tertiary solution according to Eq. (6). This empirical formula assumes that the stronger binding sites can be occupied first and that the binding strength decreases with the increasing degree of site occupation [23] and [24]. Fig. 2 reveals the sorption isotherm according to the Freundlich model, the values of the isotherm parameters are listed in Tables 2. From this Table, it can be seen that the Langmuir model has higher values of R^2 than the Freundlich model, therefore, the Langmuir model yields a better fit than the Freundlich model in tertiary systems. This demonstrated the applicability of monolayer coverage of Ni^{2+}, Co^{2+}, and Sr^{2+} ions onto the surface of the prepared materials and also to a homogeneous distribution of active sites on the prepared materials' surface; since Langmuir equation assumes that the sorbent surface is energetically homogeneous [25].

$$q_{e,i} = K_{F,i} \sum_{i=1}^{N} C_{e,i}^{1/n_i}$$

where $K_{F,i}$ is Freundlich constant for the component i indicating sorbent capacity, $mmol/g/(mmol/L)^{1/n}$, n is Freundlich constant that represents the surface heterogeneity of the sorbent, known as sorbent intensity. For the sorption of Cs^+, Co^{2+} and Pb^{2+} in a multicomponent system, Freundlich equation becomes;

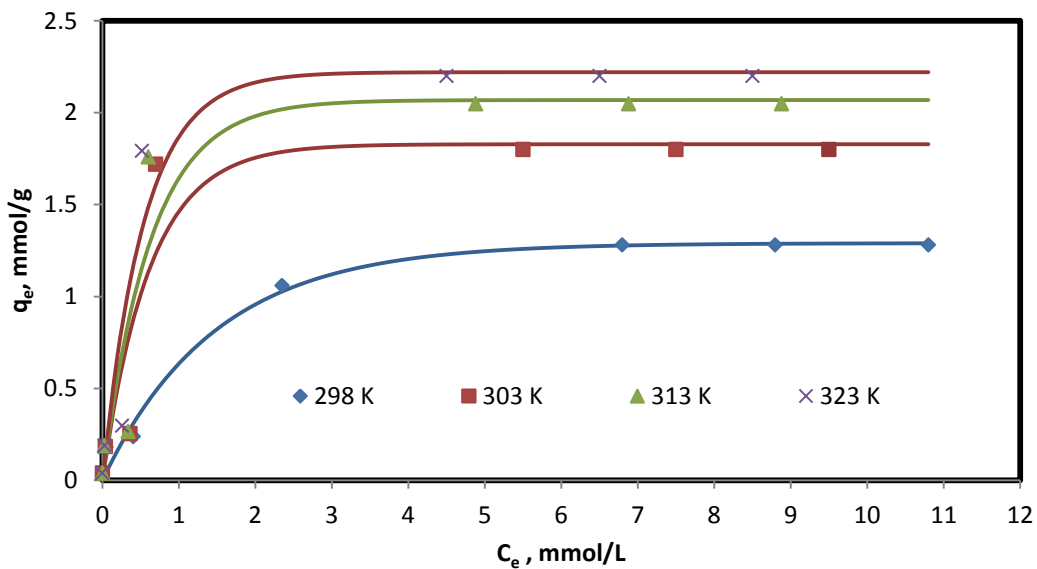$$q_{e,Sr} = K_{F,Sr} \left(C_{e,Sr}^{1/n_{Sr}} + C_{e,Co}^{1/n_{Co}} + C_{e,Ni}^{1/n_{Ni}} \right)$$

$$q_{e,Co} = K_{F,Co} \left(C_{e,Co}^{1/n_{Co}} + C_{e,Sr}^{1/n_{Sr}} + C_{e,Ni}^{1/n_{Ni}} \right)$$

$$q_{e,Ni} = K_{F,Ni} \left(C_{e,Ni}^{1/n_{Ni}} + C_{e,Co}^{1/n_{Co}} + C_{e,Sr}^{1/n_{Sr}} \right)$$
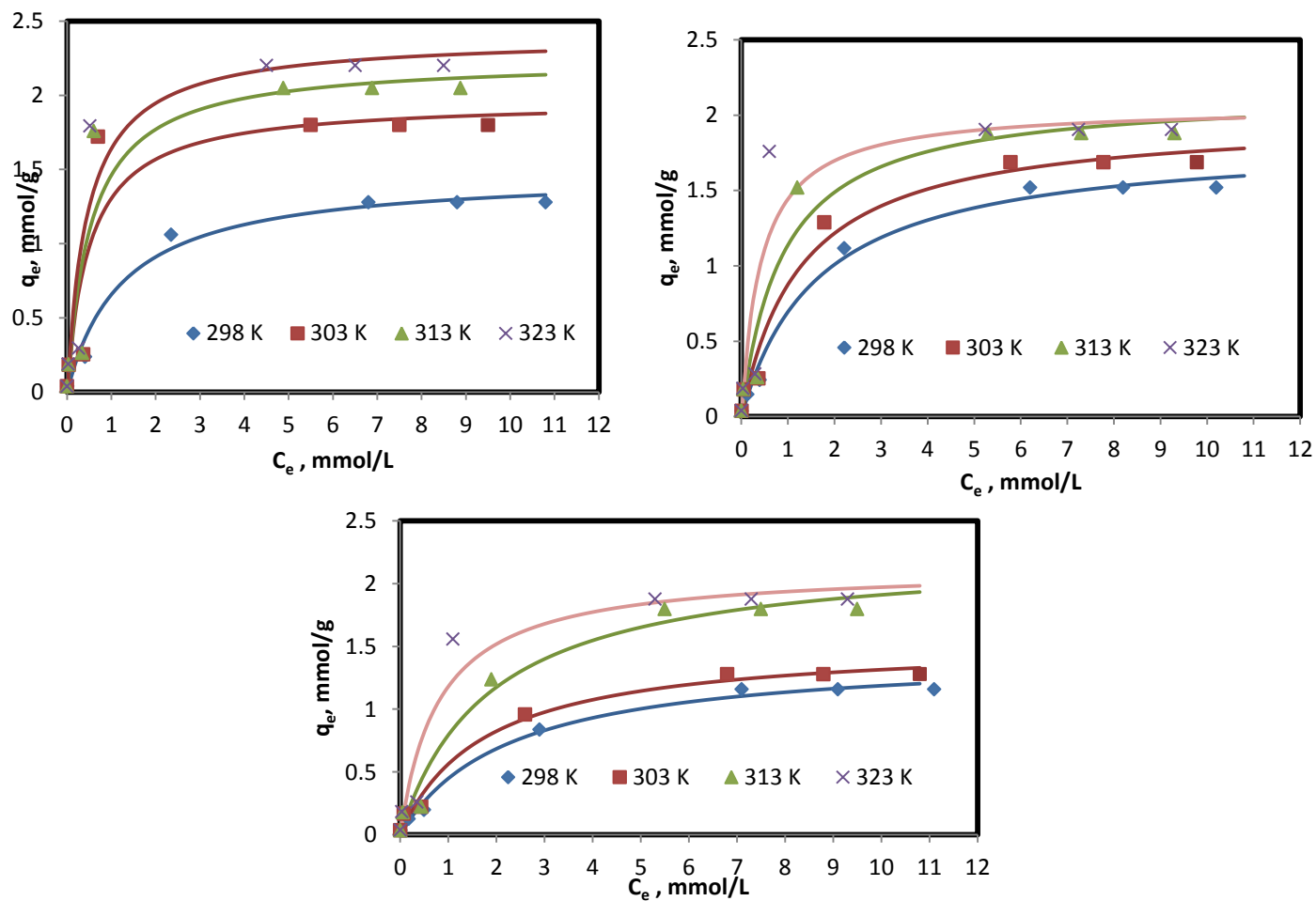
Fig.1. Experimental isotherms and nonlinear Langmuir fittings for sorption of (a) Ni^{2+}, (b) Co^{2+} and (c) Sr^{2+} onto LDH-ATP at different temperatures
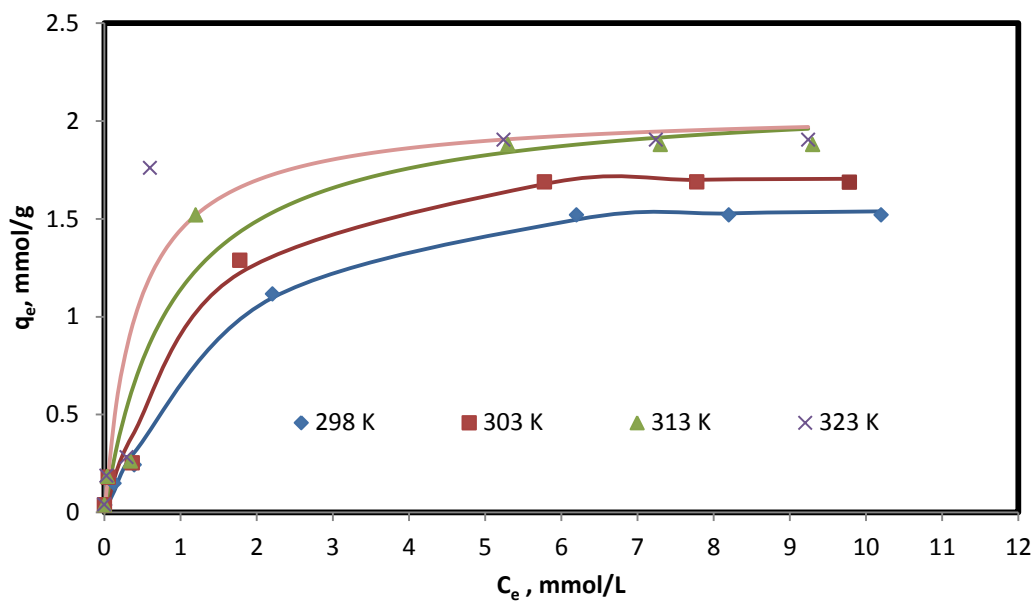
Table 1. The calculated parameters of Langmuir isotherm model for Ni^{2+}, Co^{2+}, and Sr^{2+} ions sorbed onto LDH-ATP at different temperatures.

Temp, K	Ni^{2+}			Co^{2+}			Sr^{2+}		
	Q_o mmol/g	b l/mol	R^2	Q_o mmol/g	b l/mol	R^2	Q_o mmol/g	b l/mol	R^2
298	2.60	0.66	0.96	1.64	0.47	0.99	1.6	0.34	0.99
303	2.87	0.54	0.97	2.20	0.60	0.96	1.7	0.45	0.96
313	2.90	0.54	0.97	2.69	0.66	0.96	2.4	0.38	0.97
323	2.98	1.07	0.98	2.71	0.89	0.95	2.6	0.82	0.96

Table 2. The calculated parameters of Freundlich isotherm model for Ni^{2+}, Co^{2+}, and Sr^{2+} ions sorbed onto the prepared material at different temperatures.

Temp, K	Ni^{2+}			Co^{2+}			Sr^{2+}		
	K_F, mmol/g /(mmol/L)$^{1/n}$	1/n	R^2	K_F, mmol/g /(mmol/L)$^{1/n}$	1/n	R^2	K_F, mmol/g /(mmol/L)$^{1/n}$	1/n	R^2
298 k	0.59	0.42	0.92	0.60	0.52	0.95	0.40	0.55	0.97
303 k	0.78	0.50	0.94	0.70	0.47	0.91	0.51	0.49	0.96
313k	0.94	0.52	0.92	0.89	0.47	0.91	0.70	0.55	0.94
323k	1.35	0.36	0.70	1.09	0.43	0.86	1.07	0.46	0.86

4. CONCLUSION

Attapulgite modification was successfully carried out using LDH and used as a novel material for the sorption of Sr^{2+}, Co^{2+}, and Ni^{2+} from a multicomponent solution. Isotherm studies showed that the extended Langmuir isotherm model fits well the sorption data of the three ions. The maximum monolayer sorption capacity was computed and found to be 2.6, 1.64, and 1.60 mmol/g for Ni^{2+}, Co^{2+}, and Sr^{2+}, respectively. From the results, one can conclude that LDH-ATP can be employed as a candidate sorbent for the removal of Sr^{2+}, Co^{2+}, and Ni^2 ions from multicomponent media.

REFERENCES

[1] Borai E.H., Hamed M.G., El-Kamash A.M., et al. Template polymerization synthesis of hydrogel and silica composite for sorption of some rare earth elements. Journal of Colloid and Interface Science. 456, 228–245, 2015.

[2] Hamed M.M., Hassan R.S., Metwally S.S. Retardation behavior of alum industrial waste for cationic and anionic radionuclides. Process Safety and Environmental Protection 124, 31–38, 2019.

[3] Metwally S.S., Hassan R.S., El-Masry, et al. Gamma-induced radiation polymerization of kaolin composite for sorption of lanthanum, europium and uranium ions from lowgrade monazite leachate. Journal of Radioanalytical and Nuclear Chemistry. 315, 39–49, 2018.

[4] El-Kamash A.M., El-Gammal B., El-Sayed A.A. Preparation and evaluation of cerium(IV) tungstate powder as inorganic exchanger in sorption of cobalt and europium ions from aqueous solutions. Journal of Hazardous Materials. 141(3) 719–728, 2007.

[5] Rasha A.H., Mohamed H. M., Ali M. B., et al. Process control on removal of iron from industrial wastewater using electrochemical technique.

Journal of Advanced Engineering Trends. 40(1) (1–6) 2021.

[6] Naser A.A., Sharaf El-deen G.E., Ahmed A. Bhran, et al. Elaboration of Impregnated Composite for Sorption of Europium and Neodymium Ions from Aqueous Solutions. Journal of Industrial and Engineering Chemistry. 32, 264–272, 2015.

[7] Metwally S.S., Ayoub R.R., Modification of natural bentonite using a chelating agent for sorption of ^{60}Co radionuclide from aqueous solution. Applied Clay Science. 126, 33–40, 2016.

[8] Miaoying H., Yi Z., Yang Y., Boping H., Yuanming Z., Adsorption of cobalt(II) ions from aqueous solutions by palygorskite. Applied Clay Science. (54) 292–296, 2011.

[9] Yuke Z., Tianhu C., Haibo L., Bin X., Jingjing X., Kinetics and thermodynamics of Eu(III) and U(VI) adsorption onto palygorskite. Journal of Molecular Liquid. 219, 272–278, 2016.

[10] Hao W., Xuejiang W., Jinxing M., Peng X., Jianfu Z. Removal of cadmium (II) from aqueous solution: A comparative study of raw Palygorskite clay and a reusable waste–struvite/Palygorskite obtained from nutrient-rich wastewater. Journal of Hazardous Material. 329, 66–76, 2017.

[11] Kilincarslan K., Eral A.M., Akyil Erenturk S. Removal of cesium and strontium using natural Palygorskite: evaluation of adsorption isotherm and thermodynamic data. Radioanalytical and Nuclear Chemistry. 311, 1459–1464, 2017.

[12] Ran Y., Dawei L., Aimin L., Hu Y. Adsorption properties and mechanisms of palygorskite for removal of various ionic dyes from water. Applied Clay Science. 151, 20–28, 2018.

[13] Laifu Z., Aidong T., Peng Y., Jianjun W., Qingjie W., Xin W., Yan C. Palygorskite-template amorphous carbon nanotubes as a superior adsorbent for removal of dyes from aqueous

solutions. Journal of Colloid and Interface Science. 537, 450–457, 2019.

[14] Sherman L.Z. Jiokenga, Liliane M. Dongmoa, Ervice Y., Manuel N., Ignas K. Tonlé Sensitive stripping voltammetry detection of Pb(II) at a glassy carbon electrode modified with an amino-functionalized Palygorskite Sens. Actuator B 242, 1027–1034, 2017.

[15] Jindong C., Wenjun L., Aifeng G., Tiantian L., Chao L., Haifeng L., Luru J. Preparation of a novel carboxylate-rich palygorskite as an adsorbent for Ce^{3+} from aqueous solution. Journal of Colloid and Interface Science. 512, 657–664, 2018.

[16] Xujian L., Xing Z., Heng Y., Qi Z. Atomic-layered Mn clusters deposited on palygorskite as powerful adsorbent for recovering valuable REEs from wastewater with superior regeneration stability. Journal of Colloid and Interface Science 509, 395–405, 2018.

[17] Wenkai D., Yushen L., Wenbo W., Li Z., Yongfeng Z., Yuru K., Aiqin W. A new route to fabricate high-efficient porous silicate adsorbents by simultaneous inorganic-organic functionalization of low-grade palygorskite clay for removal of Congo red. Microporous and Mesoporous Materials 277, 267–276, 2019.

[18] Khan I.A., O'Hare D. Intercalation chemistry of layered double hydroxides: recent developments and applications. Journal of Material Chemistry. 12, 3191–3198, 2002.

[19] Bujdosó T., Patzkó Á., Galbács Z., Dékány I. Structural characterization of arsenate ion exchanged MgAl-layered double hydroxide. Applied Clay Science 44, 75–82, 2009.

[20] Amira A. Mohammed, Ola A. Abdel Moamen, Sayed S. Metwally, Ahmed M. El-Kamash, Ibrahim Ashour, Mohammed S. Al-Geundi, Utilization of Modified Attapulgite for the Removal of Sr(II), Co(II), and Ni(II) Ions from Multicomponent System, Part I: Kinetic Studies, Environmental Science and Pollution Research 2019. https://doi.org/10.1007/s11356-019-07292-3

[21] Ghaly M., El-Sherief E.A., Metwally S.S., Saad E.A., Utilization of nano-cryptomelane for the removal of cobalt, cesium and lead ions from multicomponent system: Kinetic and equilibrium studies, Journal of Hazardous Materials 352, 1–16, 2018.

[22] Freundlich, H.M.F., "Über die Adsorption in Lösungen", Z. Phys. ChemLeipzig", 57A, 385–470, 1906.

[23] Serykh, A.I. Nature of Cadmium Cationic Sites in Cadmium-Modified ZSM-5 Zeolite According to the Drift Studies of Molecular Hydrogen Adsorption, Microporous and Mesoporous Materials 80 (2005) 321–326.

[24] Ratkowsky, D.A. "Handbook of Nonlinear Regression Models", New York: Marcel Dekker, 1990.

[25] Ho, Y.S., Isotherms for the sorption of lead onto peat: Comparison of linear and non-linear methods Pollution Journal and Environmental Studies 15, 81-86, 2006.

الملخص

الطمي الطبيعي يتم استخدامه كمادة مازة وذلك لأنه يتميز ببعض الخصائص مثل رخص الثمن وله خصائص ميكانيكية جيدة وصديق للبيئة. ورغم تلك المميزات فإنه يصعب فصل جزيئات الطمي عن المحلول ، وهذا يتضح عند استخدام عملية الطرد المركزي حيث أن عملية الفصل تتطلب سرعة عالية للغاية ، وبالنسبة لاستخدام ورق الترشيح فهو عرضة للانسداد. لذلك من الضروري إيجاد طريقة بديلة لفصل جزيئات الطمي ببساطة وعلى نطاق واسع. للتغلب على هذه المشكلة يمكن تحسين خواص الطمي. لذلك اهتمت هذه الدراسة بتحسين خواص الإمتزاز للأتابيولجيت (ATP) – كأحد أنواع الطمي الطبيعي – وذلك باستخدام مادة كيميائية تسمى هيدروكسيد مزدوج الطبقات لينتج LDH–ATP. ثم تم دراسة الأيزوثيرم للمادة المحسنة لإزالة أيونات كل من الأسترانشيوم والكوبلت والنيكل من محلول متعدد المكونات وذلك عن طريق دراسة بعض النماذج مثل نماذج لانجمير وفريندليش غير الخطية. وقد أظهرت النتائج أن نموذج لانجمير هو الأفضل تطبيقاً لهذا النظام حيث أن قيمة معامل التصحيح كانت أكبر من ٠.٩٥ (R^2>0.95). وتم حساب قيمة سعة التحميل ووجد أنها تساوي ٢.٦ ، ١.٦٤ و ١.٦٠ مللى مول/جرام وذلك لأيونات النيكل و الكوبلت و الأسترانشيوم على التوالي. ومن مجمل النتائج يمكن استنتاج أن مادة LDH–ATP هى مادة مرشحة لإزالة أيونات كل من الأسترانشيوم و الكوبت والنيكل من المحاليل متعددة المكونات.

الكلمات الدالة:

طمي الأتابيولجايت ، هيدروكسيد مزدوج الطبقات ، الإتزان الأيزوثيرمي ، محلول متعدد المكونات.