ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 9, Issue 11 , November 2022

Adsorption Characteristics of Intercalated Aluminosilicates with Respect to Dyes

Sharipova A.Sh., Seitnazarova O.M., Ibodullaeva S.M., Abdikamalova A.B.

Associate professor, Karakalpak State University, Nukus, Karakalpakstan
Associate professor, Karakalpak State University, Nukus, Karakalpakstan
Doctoral student, Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan
Leading researcher, Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan

ABSTRACT: The results of studying the adsorption activity of Fe and Fe+Cu of intercalated bentonite, kaolin and vermiculite with respect to methylene blue and Congo red are highlighted. Based on the higher value of the correlation coefficient of 0,964-0,999, the kinetic dependences of methylene blue adsorption can be attributed to pseudo II order equations, therefore, the adsorption rate is determined not only by the rate of diffusion processes, but also by the rate of chemical interaction between the adsorbate and adsorbent particles. It was found that intercalation led to an increase in the adsorption activity of layered systems with respect to the anionic dye several times.

KEYWORDS: intercalation, bentonite, kaolin, vermiculite, methylene blue, congo red, adsorption.

I.INTRODUCTION

All over the world, intercalated smectites, having active ions between the layers, have shown themselves to be an effective adsorbent, an active photocatalyst in various processes of transformation of organic substances. The microporosity and catalytic properties of smectite clays modified by intercalation and acid treatment have made them the subject of intense research in recent years [1, 2]. Supported inorganic reagents are rapidly becoming new and environmentally acceptable materials to improve process efficiency or to replace environmentally unacceptable reagents and catalysts [3]. In recent years, considerable attention has been paid to the study of the structures and crystal-chemical properties of clay minerals. Clay minerals, especially montmorillonites, are widely used as adsorbents and acid catalysts [4, 5]. Recently, significant efforts have been made to study the role of acid-treated clays as supports for many catalysts in various organic reactions [6–8]. Recent developments in the design and application of supported catalysts open up significant potential for pure synthesis [9]. Suitable polynuclear metal hydroxy cations after intercalation with smectite clays produce so-called columnar clays with a larger pore size compared to zeolite, which can act as effective adsorbents and catalysts for FCC (liquid catalytic cracking), as well as for other organic synthesis [10, eleven]. This article presents the results of a study of the adsorption activity of the dye + intercalated adsorbent system.

II. SIGNIFICANCE OF THE SYSTEM

The results of studying the adsorption activity of Fe and Fe+Cu of intercalated bentonite, kaolin and vermiculite with respect to methylene blue and Congo red are highlighted. The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

III. METHODOLOGY

Intercalated systems based on mineral systems and Fe^{3+} and Cu^{2+} polyoxocations were synthesized, the physicochemical characteristics of which were covered in the earlier works of the authors [12-16].

Studies of the adsorption characteristics of intercalated aluminosilicates were carried out: Fe-KR (Fe intercalated Krantau bentonite), Fe-NSCHB (Fe intercalated Navbakhor bentonite), Fe-OK (Fe intercalated enriched kaolin), Fe-B (Fe intercalated vermiculite) in relation to various dyes. In this study, dyes were chosen as adsorbates: methylene blue (MG) and Congo red (KK).

To determine the kinetic parameters of the dye adsorption process, the process was carried out in a static mode at different adsorbent contact times. To explain the kinetic parameters of these processes in the dissertation work, the pseudo I (1) and pseudo II order (4.2) models were used, which are characterized by the following equations:

$$ln(A_s - A_t) = ln(A_s) - k_1 t. \tag{1}$$

$$\frac{t}{A_t} = \frac{1}{k_2 A_s^2} + \frac{t}{A_s}, \tag{2}$$

Where

k_1 - rate constant of the pseudo-I-order equation, g/mg*min; A_s and A_t are the amount of adsorption at equilibrium and at time t, respectively, k_2 - rate constant of the pseudo II-order equation, g/mg*min.

IV. EXPERIMENTAL RESULTS

The adsorption of selected dyes by nature differs significantly from the sorption of previously studied inorganic cations and anions [16]. It was found that Cu^{2+} cations are mainly adsorbed due to the formation of complex compounds and less due to ion exchange [16, 17]. Due to the inability of the cationic dye MG to form chelate compounds with cations in the structure of intercalated aluminosilicates, in addition to the inability of intercalated systems to ion exchange, one can expect a decrease in the adsorption of MG on intercalated adsorbents. On the contrary, one can assume an increase in the amount of adsorption of anionic dyes, which proceed exclusively due to ion-exchange reactions, as well as due to the presence of available pores in size.

The kinetic dependences of the sorption of MG and CC dyes on intercalated aluminosilicates were analyzed using the above kinetic models, the results of which are presented in Table 1. one.

Table 1
Kinetic parameters of models for the process of MB adsorption on intercalated materials

Model		Adsorbents			
		Fe-CR	Fe-NSChB	Fe-OК	Fe-B
I- order	k_1	0,218	0,289	0,152	0,208
	A_s	0,325	0,341	0,112	0,145
	A_t	0,231	0,253	0,098	0,132
	R^2	0,886	0,861	0,912	0,934
II- order	K_2	0,096	0,101	0,081	0,084
	A_s	0,212	0,198	0,092	0,126
	A_t	0,185	0,184	0,081	0,121
	R^2	0,986	0,995	0,964	0,999

Based on a higher value of the correlation coefficient of 0,964-0,999, these kinetic dependences can be attributed to pseudo II order equations, therefore, the rate of MB adsorption is determined not only by the rate of diffusion processes, but also by the rate of chemical interaction between the adsorbate and adsorbent particles.

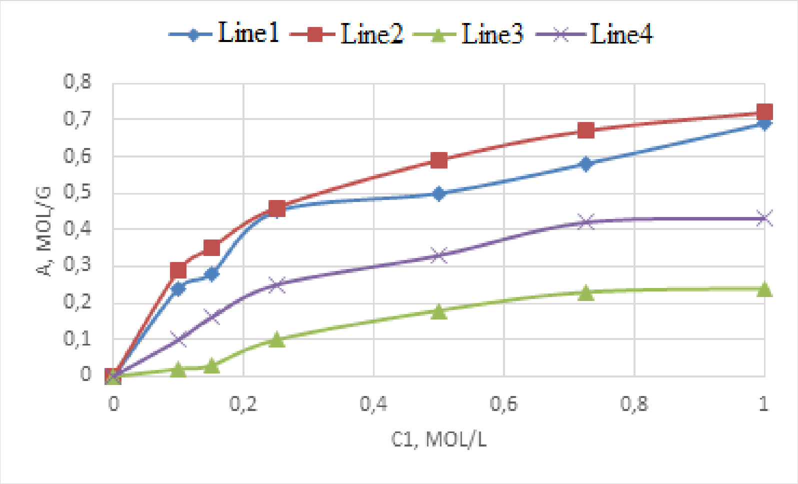

Fig. 1. Isotherms of MG adsorption on adsorbents at 20˚C and pH=7, adsorbent dose 1g/l, initial concentration of MG solution 0.01-2 mmol/l: 1) Fe-CR; 2) Fe-NSCHB; 3) Fe-OK; 4) Fe-B.

From the experimental results it has been established that the time to reach the maximum sorption capacity for intercalated bentonites and kaolin is 1.5-2 hours for MG, and more than 3 hours for CC. As in the case of inorganic ions, more time is spent to achieve adsorption equilibrium in the "dye-intercalated vermiculite" system (at least 10 hours). All subsequent experiments on the adsorption of dyes were carried out after the expiration of certain times. As expected, intercalation did not lead to a decrease in the sorption characteristics of all samples compared to the initial materials, which indicates that adsorption proceeds due to the formation of chemical bonds between the negatively charged surface of aluminosilicates and large MB cations. The calcination of these adsorbents significantly reduces the adsorption of MG on them; naturally, in this process, the number of negatively charged active centers of intercalated materials and the total volume of available pores decrease. However, there is still more adsorption amount on the calcined starting materials.

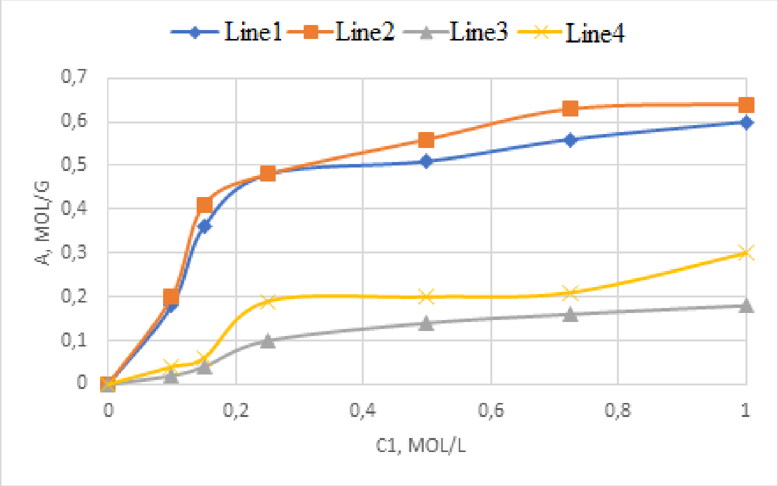

Fig. 2. Adsorption isotherms of MG on calcined (500°C) adsorbents at 20˚C and pH=7, adsorbent dose 1g/l, initial concentration of MG solution 0.01-2 mmol/l: 1) Fe-CR; 2) Fe-NSCHB; 3) Fe-OK; 4) Fe-B.

The adsorption of MB on natural aluminosilicates calcined at 500°C (Fig. 2) occurs on the outer basal surface and, of course, in mesopores—voids between contacting particles. According to the results of studies of textural characteristics, it is known that natural montmorillonite-containing clays (KR and NSCHB) have an insignificant volume of micropores, while they are completely absent in natural vermiculite and the OK sample. From the data in Fig.

1 and 2, it can be seen that the adsorption capacity for MG is in excellent agreement with the CFU value. The experimental results showed that the sorption capacity of intercalated aluminosilicates for an anionic dye is much higher than previously obtained data based on their natural precursors (Fig. 3). Probably, the anionic activity of materials is primarily related to the charge of the surface of the material.

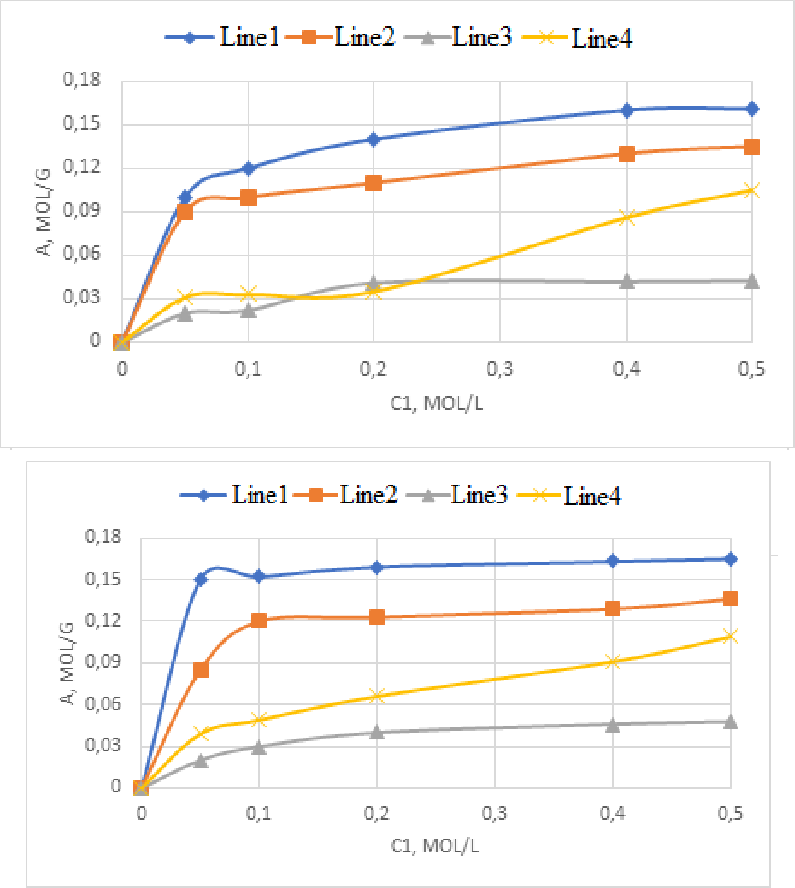

Fig. 3. Adsorption isotherms of CA on calcined (500°C) adsorbents at 20˚C and pH=7, adsorbent dose 1 g/l, initial concentration of CA solution 0.01-1 mmol/l, A): 1) Fe-CR; 2) Fe-NSCHB; 3) Fe-OK; 4) Fe-B. B) 1) Fe/Cu-CR; 2) Fe/Cu-NSCB; 3) Fe/Cu-OK; 4) Fe/Cu-B.

The value of CC adsorption on calcined Fe-CR; Fe-NSCHB and Fe-OK in 2; 2.04 and 1.45, and the adsorption capacity of Fe-B is 4 times higher than that of natural forms. The adsorption capacity for CC decreases in the following order: Fe-CR>Fe-NSCHB> Fe-B>Fe-OK, which corresponds rather to the number of anion exchange centers, rather than to a change in the total specific surface area of these pillar adsorbents. However, the adsorption capacity for Ca anions decreases upon calcination starting from 250°C for these sorbents, since calcination leads to a decrease in the available pore surface, while the adsorption of inorganic anions (PO_4^{3+}, CN^-) has the same high values [17]. Despite the almost identical values, when adsorption equilibrium occurs, the curves in Figures A and B (Fig. 3) differ in shape, which is the result of the inequality in the pore sizes of these adsorbents. It is well known that the KK dye has relatively large molecular sizes, due to which they are not able to be adsorbed on micropores. It is likely that the sharp increase in the Fe/Cu adsorption isotherms of intercalated montmorillonites is primarily associated not only with the presence of available pores, but also with a large amount of surface anion-exchange ions.

V. CONCLUSION AND FUTURE WORK

Thus, on the basis of kinetic models, it has been established that the rate of adsorption of dyes is determined not only by the rate of diffusion processes, but also by the rate of chemical interaction between the particles of the adsorbate and the adsorbent. At the same time, an increase in the adsorption capacity for anionic CA by several times was established as a result of the intercalation of aluminosilicates. However, calcination at high temperatures somewhat reduces the adsorption capacity for large anions, while for inorganic anions this indicator remains high as before.

REFERENCES

[1]. Ding Z., Kloprogge J.T., Frost R.L., Lu G.Q., Zhu H.Y. Porous clays and pillared clays-based catalysts. Part 2: A review of the catalytic and molecular sieve applications // Journal of Porous Materials. 2001. No. 4(8). DOI:10.1023/A:1013113030912.

[2]. Theng B.K.G. Clay Mineral Catalysis of Organic Reactions. Boca Raton: CRC Press, Taylor & Francis Group, 2018.: CRC Press, 2018. . ISBN:9780429465789.

[3]. Phukan, A.L., Ganguli, J.N., & Dutta, D.K. (2003). ZnCl2-Zn^{2+-}Montmorillonite composite: efficient solid acid catalyst for benzylation of benzene. Journal of Molecular Catalysis A-chemical, 202, 279-287.

[4]. Zatta L., Ramos L.P., Wypych F. Acid Activated Montmorillonite as Catalysts in Methyl Esterification Reactions of Lauric Acid // Journal of Oleo Science. 2012. No. 9(61). pp. 497–504. DOI:10.5650/jos.61.497.

[5]. Zhu R., Chen Q., Zhou Q., Xi Y., Zhu J., He H. Adsorbents based on montmorillonite for contaminant removal from water: A review // Applied Clay Science. 2016. (123). pp. 239–258. DOI:10.1016/j.clay.2015.12.024.

[6]. Temuujin J., Jadambaa T., Burmaa G., Erdenechimeg S., Amarsanaa J., MacKenzie K.J.D. Characterization of acid activated montmorillonite clay from Tuulant (Mongolia) // Ceramics International. 2004. No. 2(30). pp. 251–255. DOI:10.1016/S0272-8842(03)00096-8.

[7]. Rahman A., Moersilah, Alanas E., Paristiowati M., Wismar V. Synthesis of organoclay chitosan-acid-activated montmorillonite from Indonesian bentonite 2021. C. 040042. DOI:10.1063/5.0042075.

[8]. Shinde S.G., Shrivastava V.S. Ni and Zn modified acid activated montmorillonite clay for effective removal of carbol fuchsin dye from aqueous solution // SN Applied Sciences. 2020. No. 4(2). P. 519. DOI:10.1007/s42452-020-2295-1.

[9]. Luna F., Cecilia J., Saboya R., Barrera D., Sapag K., Rodríguez-Castellón E., Cavalcante C. Natural and Modified Montmorillonite Clays as Catalysts for Synthesis of Biolubricants // Materials. 2018. No. 9(11). S. 1764. DOI: 10.3390/ma11091764.

[10]. Grenall A. Montmorillonite Cracking Catalyst. Demonstration of Presence of Hydrogen Ion in Heated Filtrol Clay Catalysts // Industrial & Engineering Chemistry. 1949. No. 7(41). S. 1485–1489. DOI:10.1021/ie50475a046.

[11]. Fatimah I., Wijaya K., Setyawan K.H. Synthesis ZrO2-Montmorillonite and Application as Catalyst in Catalytic Cracking of Heavy Fraction of Crude Oil // Bulletin of chemical reaction engineering and catalysis. 2010. No. 1–3(3). DOI:10.9767/bcrec.3.1-3.17.9-13.

[12]. Abdikamalova A.B., Kalbaev A.M., Mamataliev N.N., Sharipova A.I., Eshmetov I.D. Colloidal-chemical aspects of creating intercalated systems based on aluminosilicates. Monograph. - T .: "NAVRUZ", 2021. - 319 p.

[13]. Abdikamalova A.B., Kalbaev A.M., Mamataliev N., Utashev Y.I., Eshmetov I.D. Study of the surface properties of modified clays. Ilmiy ahborotnoma Samarkand davlat university. 2021 yil, 1-dream (125). 46-50 b.

[14]. Abdikamalova A.B, Mamataliev N.N., Utashev Yo.I, Xaydarov.D.M., Eshmetov.I.D, Kalbaev A.M. Columnar clays intercalated with iron compounds. International journal of advanced research in science, engineering and technology vol. 8, issue 3, march 2021 pp 16903-16910.

[15]. Utashev. E.I., Mamataliev N.N., Kalbaev A.M., Abdikamalova A.B., Sobirova R.Kh. Investigation of the processes of intercalation of vermiculite with polyoxocations Fe^{3+} and Cu^{2+}. Universum: technical sciences: electron. scientific magazine - 2021. 6(87) pp. 35-39.

[16]. Abdikamalova A.B., Mamataliev N.N., Kalbaev A.M., Eshmetov I.D., Reymov A.M. Sorption characteristics of aluminosilicates in relation to inorganic substances. Science and Education in Karakalpakstan. No. 1 (16) 2021 No. 1 ISSN 2181-9203. pp: 82-87.