UDK: 541.183.

DETERMINATION OF THE DIFFERENTIAL ISOSTERIC HEAT OF METHANOL VAPOR ADSORPTION ON ACTIVATED ANGREN KAOLIN

Khandamova D.K.

Tashkent Institute of Chemical Technology, PhP assistent, Uzbekistan, Tashkent,

ORCID:https://orcid.org/0000-0003-3370-1877

Abstract. In this study, white kaolin from the Angren deposit was activated with diluted sulfuric acid, and the adsorption properties of methanol vapor on the obtained adsorbent were investigated. Adsorption isotherms were recorded at temperatures of 293, 303, and 313 K. Based on these isotherms, the specific surface area, micro- and mesopore volumes, and saturation adsorption capacities of the adsorbent were determined. The differential isosteric heat of adsorption was calculated using the isosteric method. The results indicate that the activated kaolin exhibits high adsorption activity, and that physical adsorption as well as partial ion–molecular interactions occur between methanol molecules and the adsorbent surface.

Keywords: activated kaolin, adsorption isotherm, isosteric heat, methanol vapor, micro- and mesopores, specific surface area, BET equation.

Аннотация. В данной работе белый каолин Ангренского месторождения был активирован разбавленной серной кислотой, и исследованы адсорбционные свойства паров метанола на полученном адсорбенте. Изотермы адсорбции были получены при температурах 293, 303 и 313 К. На основе этих изотерм определены удельная поверхность, объемы микро- и мезопор, а также предельная адсорбционная емкость адсорбента. Дифференциальная изостерическая теплота адсорбции была рассчитана изостерическим методом. Полученные результаты показали, что активированный каолин обладает высокой адсорбционной активностью, и что на поверхности адсорбента имеют место как физическая адсорбция, так и частичные ионно-молекулярные взаимодействия между молекулами метанола и адсорбентом.

Ключевые слова: активированный каолин, изотерма адсорбции, изостерическая теплота, пары метанола, микро- и мезопоры, удельная поверхность, уравнение БЭТ.

Annotatsiya. Ushbu ishda Angren konining oq kaolin suyultirilgan sulfat kislota bilan faollashtirilgan va hosil bo'lgan adsorbentdagi metanol bug'larining adsorbsion xususiyatlari o'rganilgan.ulosa. Ushbu ishda Angren konining oq kaolin suyultirilgan sulfat kislota bilan faollashtirilgan va hosil bo'lgan adsorbentdagi

ISSN 3030-3907

metanol bug'larining adsorbsion xususiyatlari o'rganilgan. Adsorbsulosa. Ushbu ishda Angren konining oq kaolin suyultirilgan sulfat kislota bilan faollashtirilgan va hosil bo'lgan adsorbentdagi metanol bug'larining adsorbsion xususiyatlari o'rganilgan. Adsorbsion izotermlar 293, 303 va 313 k haroratlarda olingan.ushbu izotermlar asosida o'ziga xos sirt, mikro va mezopor hajmlari, shuningdek adsorbentning maksimal adsorbsion sig'imi aniqlangan. Adsorbsiyaning differentsial izosterik issiqligi izosterik usul bilan hisoblab chiqilgan. Natijalar shuni ko'rsatdiki, faollashtirilgan kaolin yuqori adsorbsion faollikka ega va adsorbent yuzasida metanol molekulalari va adsorbent o'rtasidagi fizik adsorbsiya va qisman ion-molekulyar o'zaro ta'sirlar sodir bo'ladi.

Kalit so'zlar. natijalar shuni ko'rsatdiki, faollashtirilgan kaolin yuqori adsorbsion faollikka ega va adsorbent yuzasida metanol molekulalari va adsorbent

INTRODUCTION.

At present, pollution of industrial and domestic wastewater with heavy metal ions, organic solvents, and volatile compounds represents one of the major global environmental problems. In addressing these issues, the development of effective, low-cost, and environmentally safe adsorbent materials is of great importance. In this context, activated sorbents based on natural clay minerals, particularly kaolin, are of significant scientific interest.

Kaolin clays are characterized by high chemical stability, good mechanical strength, and a developed porous structure. Their adsorption properties can be substantially enhanced through acid activation. During the acid activation process, exchangeable cations and certain impurities are removed from the kaolin structure, leading to the formation of micro- and mesopores and an increase in specific surface area.

For a deeper understanding of adsorption mechanisms, the heat of adsorption is an important thermodynamic parameter. In particular, the differential isosteric heat of adsorption provides information on the energetic heterogeneity of the adsorbent surface, the nature of active sites, and the strength of adsorbent–adsorbate interactions. Methanol vapor adsorption is widely used as a model system for evaluating the surface properties of adsorbents. Therefore, determining the adsorption behavior of methanol vapor on acid-activated Angren white kaolin and calculating its differential isosteric heat is of both scientific and practical relevance.

Activated kaolin-based sorbents are currently considered promising materials with high adsorption capacity for wastewater treatment, removal of heavy metal ions, and mitigation of technogenic environmental pollution [118; pp. 44–48, 119; pp. 116–119, 120; p. 36].

ISSN 3030-3907

LITERATURE REVIEW

In recent years, numerous studies have focused on the adsorption properties of adsorbents derived from kaolin and other natural clay minerals. These studies demonstrate that acid, alkaline, or thermal treatment can significantly modify the porous structure and surface energy of clay minerals. The literature reports that acid-activated kaolins exhibit high adsorption capacities toward heavy metal ions and organic compounds.

In particular, activation of kaolin with sulfuric or hydrochloric acid leads to an increase in specific surface area and a significant enlargement of micro- and mesopore volumes, thereby enhancing adsorption efficiency. For thermodynamic evaluation of adsorption processes, widely used models include the BET, Dubinin–Radushkevich, Langmuir, and Freundlich equations.

RESEARCH METHODOLOGY

The object of the study was Angren white kaolin (AKF-78 grade), which was activated by treatment with a 0.1 N sulfuric acid solution. The adsorption of methanol vapor on the activated kaolin and the determination of its differential isosteric heat were investigated.

RESULTS AND DISCUSSION

The preparation of adsorbents from local raw materials and the investigation of their colloidal-chemical and adsorption properties are of considerable theoretical and practical significance. In this study, an activated adsorbent was obtained by treating Angren white kaolin with a 0.1 N sulfuric acid solution.

The adsorption energy characteristics of the activated kaolin samples were studied using a high-vacuum McBain adsorption apparatus with methanol vapor as the adsorbate. Prior to the adsorption measurements, the system was evacuated to a residual pressure of 1.33×10^{-3} Pa and heated at 423 K for 4 hours to remove moisture and impurities. Adsorption isotherms of methanol vapor on activated kaolin were then obtained at three temperatures: 293, 303, and 313 K.

ISSN 3030-3907

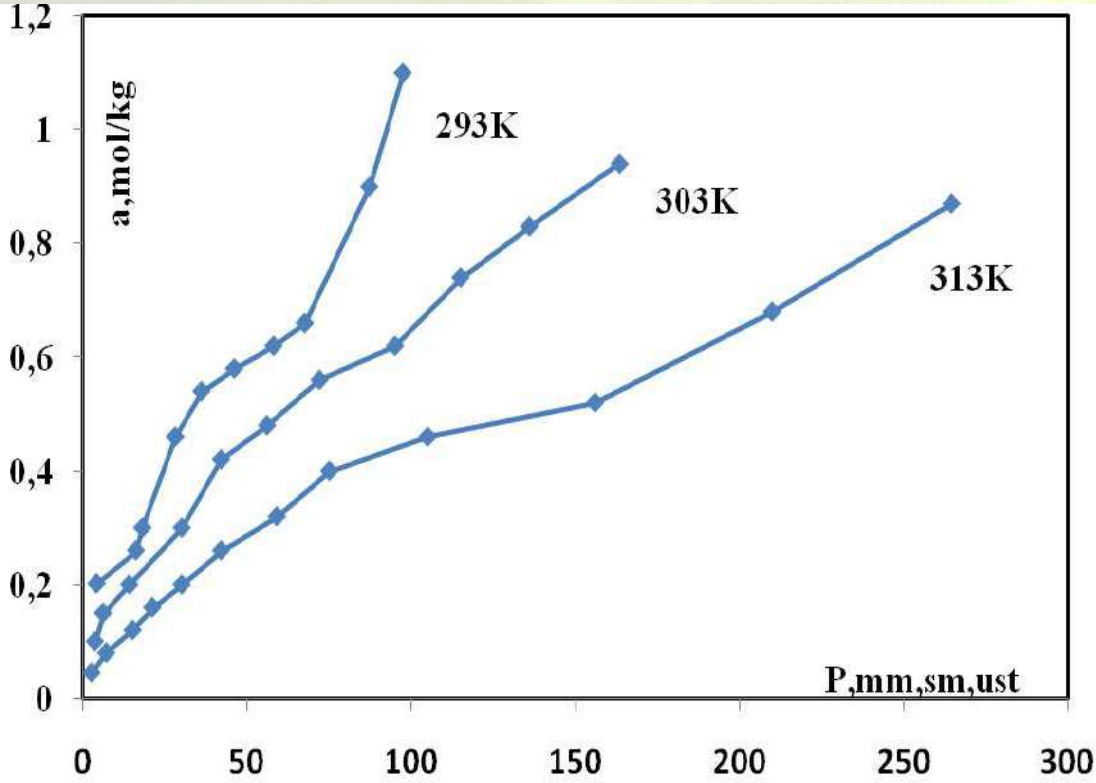


Figure 1. Adsorption of methanol vapors on activated Angren kaolin at various temperatures. 293K; 303K; 313K.

Based on the obtained adsorption isotherms, the specific surface area (S), micro (Wo) and mesoporous (Wme) volumes, and saturation volumes (Vs) of activated kaolin were determined. The calculation results are presented in Table

1-Table

Structural-sorption indicators of activated kaolin by methanol vapor adsorption

Adsorbent	Ҳарорат и, К	S •10^3, $м^2/кг$	$W_{ме}$•10^3, $м^3/кг$	W_0•10^3, $м^3/кг$	V_s•10^3, $м^3/кг$
Activated Kaolin	293	94,6	6,6	19,8	26,4

Based on the adsorption isotherms obtained, it can be observed that the saturation adsorption capacity (a_s) of the adsorbent decreases with increasing temperature. In particular, at a temperature of 293 K and a saturated methanol vapor pressure of 97.4 mm Hg, the saturation adsorption capacity is a_s = 1.10 mol/kg. When the temperature increases to 303 K and the saturated vapor pressure of methanol reaches 163.5 mm Hg, the saturation adsorption capacity decreases to a_s = 0.94 mol/kg. At 313 K and a saturated vapor pressure of 265.5 mm Hg, the saturation adsorption capacity further decreases to a_s = 0.87 mol/kg.

ISSN 3030-3907

The shapes of the adsorption isotherms at 293, 303, and 313 K are similar, which indicates that the adsorption process occurring at these temperatures is predominantly physical in nature. During the adsorption of methanol vapor on activated Angren kaolin, an increase in temperature (1 – 293 K; 2 – 303 K; 3 – 313 K) leads to a decrease in the degree of adsorption. Such isotherm behavior is characteristic of micro- and mesoporous adsorbents.

According to the literature, kaolin clays predominantly exhibit mesoporous properties. Treatment of kaolin with weakly concentrated sulfuric acid leads to changes in pore structure due to the leaching of exchangeable ions and soluble salts, resulting in the formation of micro- and mesopores.

The specific surface area of the activated Angren kaolin, calculated using the BET equation, was found to be $S = 94.6 \times 10^3$ m²/kg. Using the Dubinin–Radushkevich equation, the micropore volume of the adsorbent was determined to be $W_0 = 19.8 \times 10^{-3}$ m³/kg, while the mesopore volume was $W_me = 6.6 \times 10^{-3}$ m³/kg. The total saturation adsorption volume was $V = 26.4 \times 10^{-3}$ m³/kg.

The sorption parameters of the activated Angren kaolin were calculated based on the adsorption isotherms obtained at 293 K.

Based on the experimental results, it can be noted that the microporosity of the adsorbent obtained from activated Angren kaolin составляет about 60% of the total porosity. This indicates the opening of interlayer spaces in kaolin as a result of methanol vapor adsorption, which leads to the formation of micropores.

Typically, the heat of adsorption is determined using a sensitive calorimeter or specialized equipment for the direct measurement of high-vacuum adsorption isosteres. However, due to the complexity and practical difficulties associated with operating such equipment, the differential heat of adsorption in this study was calculated using adsorption isotherms obtained with a McBain apparatus.

Based on the adsorption isotherms measured at different temperatures, adsorption isosteres can be constructed. For this purpose, a constant adsorption amount (a, mol/kg) is selected, and the corresponding equilibrium pressures of the adsorbate are determined from the isotherms obtained at different temperatures (293, 303, and 313 K). Using these data, adsorption isosteres are constructed.

The dependence of the amount of adsorbed methanol on vapor pressure (P, mm Hg) and temperature (T, K) is presented in Fig.

ISSN 3030-3907

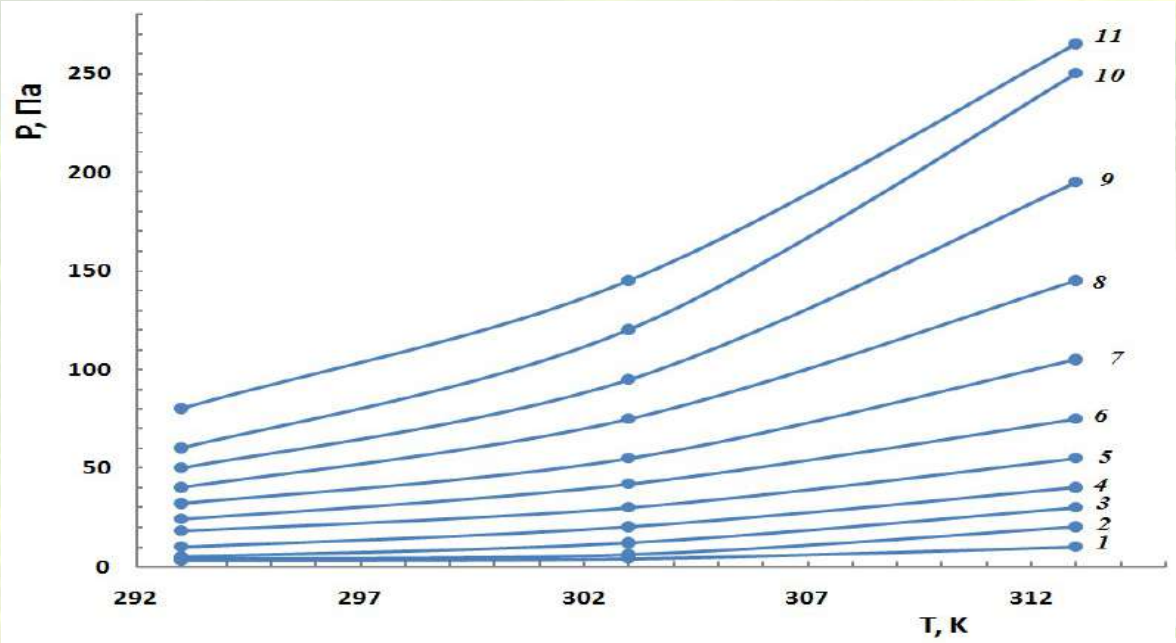


Figure 2. Isosteres of the dependence of methanol vapor adsorption on activated kaolin on P = f (T,K)

It is known that the differential heat of adsorption can be determined from the dependence of the adsorption isoster ln P on 1000/T. The differential heat of adsorption (Q_a) is calculated by determining the tangent of the slope of the straight line on the coordinate axes according to the expression

$Q_a=R\cdot tg\alpha$, where α is the angle between the adsorption isoster and the abscissa axis. Based on the obtained results, when the equilibrium pressure of adsorbed methanol vapor (P, mm Hg) is expressed in logarithmic form (ln P) and the temperature (T, K) is converted to 1000/T, linear adsorption isosteres with different slopes are obtained. For a constant amount of adsorption, these straight lines have different angular slopes, and the tangent of the angle (tg α) can be readily determined.

Thus, the dependence ln P = f(1000/T) yields straight lines with different slopes on the coordinate axes, as shown in Fig. 4.7.

In order to evaluate the energy released as a result of the interaction between methanol vapor molecules and the active centers of the adsorbent, the differential isosteric heat of adsorption was determined using the adsorption isotherms obtained at different temperatures.

ISSN 3030-3907

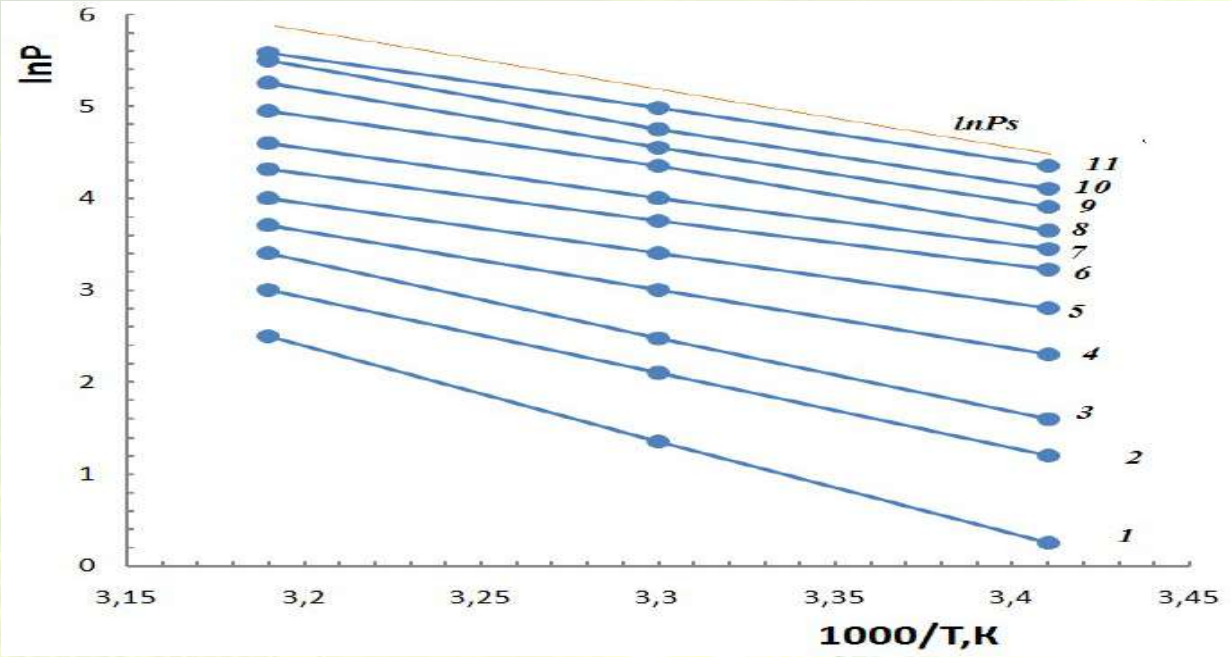


Figure 3. A series of isosteres of methanol vapor adsorption on activated kaolin. lnPs= methanol saturated vapor pressure

The differential isosteric heat of adsorption is directly proportional to the slopes of the isosters. As a result of the conducted research, it was established that the amount of high adsorption heat of kaolin is equal to Q = 68 kJ/mol (see Fig. 4).

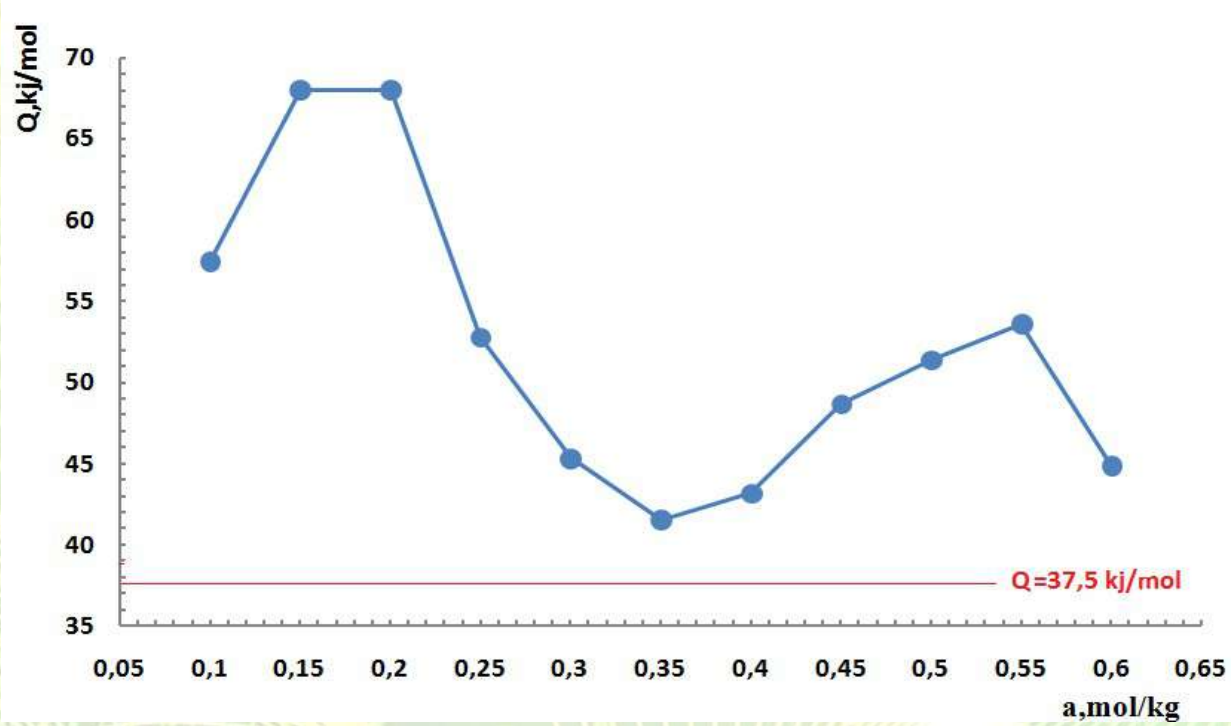


Figure 4. Isosteric differential heat of adsorption of methanol vapor on activated kaolin

In activated Angren kaolin, the heat of adsorption of methanol vapors changes gradually, and the dependence curves of the function $Q_a = f(a)$are characterized by a wave-like shape. The heat of adsorption gradually decreases

ISSN 3030-3907

from $Q_a = 68.0$ kJ/molto $Q_a = 41.57$ kJ/mol. At the maximum value of the heat of adsorption ($Q_{\max} = 68.0$ kJ/mol), a stoichiometric interaction of protons with the methanol molecules on the adsorbent surface occurs; that is, under these conditions, an ion–molecular complex is formed.

Conclusions and Recommendations

Based on the conducted experiments, it was established that at an adsorption saturation of a = 0.1 mol/kg, the initial heat of adsorption is Qa = 57.44 kJ/mol. At a = 0.15 mol/kg, the heat of adsorption reaches its maximum value of Qa = 68.0 kJ/mol and remains unchanged up to a =0.35 mol/kg. Beyond this point, the heat of adsorption decreases, and at a =0.35 mol/kg it drops to Qa = 41.57 kJ/mol.

Furthermore, the functional dependence Qa = f(a) exhibits a second maximum, reaching Qa = 53.6 kJ/mol at an adsorption saturation of a =0.55 mol/kg. At this stage, an intensive interaction between the adsorbent and the adsorbate occurs. With further increases in adsorption saturation, the heat of adsorption continues to decrease, and at a = 0.6 mol/kg, the heat of sorption equals Qa = 44.9 kJ/mol. At higher saturation levels, the heat of sorption approaches the heat of condensation of methanol, Q=37.5 kJ/mol. [120; 41-45).

LIST OF REFERENCES

1. Gouider, M., Feki, M., & Majdoub, H. (2018). Iron contamination in drinking water and its treatment methods. Environmental Technology, 40(13), 1645–1657.
2. Drosos, M., et al. (2021). "Phosphate and Ammonium Removal from Wastewaters Using Natural-Based Innovative Bentonites." Molecules, 26(21), 6684.
3. Kurniawan, T. A., et al. (2020). "Bentonite-Based Composites for Wastewater Treatment." Journal of Environmental Management, 261, 110234.
4. Mazumdar, A., & Mazumdar, P. (2021). "Determination of Total Iron Content in Water Using UV-Vis Spectroscopy." Journal of Environmental Chemical Analysis, 43(2), 112-118.
5. Nidheesh, P. V., & Gandhimathi, R. (2012). Electrocoagulation process for the treatment of textile wastewater containing Fe2+. Separation and Purification Technology, 98, 57-64.
6. Li, Y., & Du, Q. (2007). *Adsorption of heavy metal ions from aqueous solutions by modified bentonite.* JournalofHazardousMaterials, 143(1-2), 29-35.
7. Sari, A., Tuzen, M., &Uluozlu, O. D. (2007). *Biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (Lentinussajor-caju) biomass: Equilibrium, kinetic and thermodynamic studies.* Bioresource Technology, 99(6), 1554-1560.
8. Jaroniec, M., & Madey, R. (1989). "The use of the Dubinin-Radushkevich model in the analysis of adsorption data." Surface Science Reports, 10(3), 1-36.

ISSN 3030-3907

9. Dim P. E., Mustapha L. S., Termtanun M., Okafor J. O. Adsorbtion of chromium() and iron () ions onto acid-modified kaolinite: Izotherm, kinetics and thermodynamics studiyes. Arabian journal of Chemistry (2021) 14,103064/2021. 158-165.
10. Vreebug J., "Discolouration in Drinking WaterSystems: a Particular Approach," The Netherlands:Delft Cluster, 2007.
11. Zhu H., JiaY., WuX., & Wang, H. (2009). Removal of ferrous iron from groundwater by oxidation and coagulation. Journal of Hazardous Materials, 162(2–3), 1109–1115.

ISSN 3030-3907