ISSN 2181-8622

Manufacturing technology problems

Scientific and Technical Journal Namangan Institute of Engineering and Technology

INDEX COPERNICUS INTERNATIONAL

Volume 9
Issue 4
2024

Google Scholar Crossref doi SLIB.UZ Scientific library of Uzbekistan

THERMODYNAMICS OF CONGO RED DYE ADSORPTION PROCESSES ON MINERAL AND CARBON ADSORBENTS

ERGASHEV OYBEK

Professor of Namangan Institute of Engineering and Technology, Namangan Uzbekistan
E-mail.: okergashev711@gmail.com

ABDIKAMALOVA AZIZA

Professor of Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan
Phone.: (0897) 501-7477, E-mail.: aziza.abdik@gmail.com
**Corresponding author*

BAKHRONOV KHAYOT

Professor of Tashkent university of information technologies named after Muhammad al-Khwarizmi, Tashkent, Uzbekistan
Phone.: (0897) 710-3758, E-mail.: baxronov@mail.ru

ASKAROVA DILZODA

PhD student of Namangan Institute of Engineering and Technology, Namangan, Uzbekistan
Phone.: (0899) 996-9026, E-mail.: dilzodaasqarova1@gmail.com

XUDOYBERDIYEV N

Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan

MEKHMONKHONOV MANSURXON

Researcher of Namangan Institute of Engineering and Technology, Namangan, Uzbekistan
Phone.: (0894) 274-8716, E-mail.: mexmonxonovm@gmail.com

XOLIKOV KAMOLIDDIN

Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan

Abstract: This paper investigates the thermodynamic aspects of the adsorption processes of Congo red dye on four different types of adsorbents: steam-activated brown coal, enriched bentonite from Navbahor deposit, carbon based on waste polyethylene terephthalate bottles and Fe-intercalated bentonite. The study focuses on the analysis of enthalpy and entropy changes, which allow to estimate the energy efficiency and spontaneity of the adsorption processes. The results show that the adsorption of the dye is endothermic and is accompanied by a decrease in entropy, which indicates a significant degree of ordering during adsorption. The role of temperature in the efficiency of adsorption processes is emphasized and recommendations for the use of these adsorbents for wastewater treatment are proposed.

Keywords: adsorption thermodynamics, Congo red dye, steam activated carbon, enriched bentonite, carbon from PET waste, Fe-intercalated bentonite, enthalpy change, entropy change, wastewater treatment, endothermic adsorption.

Introduction. Adsorption of synthetic dyes such as Congo red (CR) on different types of adsorbents is a key method for understanding the interactions between pollutants and their removal potential from aquatic systems. Congo red, known for its high chemical stability and color brilliance, poses significant challenges to traditional wastewater removal methods due to its resistance to degradation. Efficient removal of

such persistent organic compounds requires a thorough understanding of the thermodynamic basis of adsorption processes [1-5].

Comparative analysis of Congo red adsorption on carbon and bentonite adsorbents provides a unique opportunity to study the differences in the mechanisms of dye interaction with different types of adsorbents. The main focus of this work is on the assessment of thermodynamic parameters, such as the change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), which allow us to draw conclusions about the spontaneity and thermal effects of adsorption processes. These parameters not only help to assess the adsorption efficiency, but also provide an understanding of the physical and chemical nature of the interaction between the dye and adsorbents [6-9].

Mineral and carbon adsorbents differ in their porous structure and chemical composition, which affects the adsorption mechanisms on their surface and overall adsorption activity. Carbon adsorbents, such as activated carbon, typically have high porosity and a developed surface, which provides a large number of active sites for adsorption. These pores can be micro-, meso- and macroporous, which allows for the effective capture of molecules of various sizes. Unlike carbon, mineral adsorbents, such as bentonite, consist mainly of aluminosilicates and are characterized by a layered or lamellar structure, which affects their ion-exchange properties and the ability to interlayer adsorption. Adsorption mechanisms on bentonite can include both physical absorption and chemical adsorption due to the polarity and presence of functional groups on the mineral surface. These differences in structure and chemical composition determine the unique properties of each type of adsorbent in the processes of removing dyes from aqueous solutions [10-12].

The objective of this study is to investigate in detail the thermodynamic aspects of Congo red adsorption, identifying key differences and similarities in the behavior of this dye on carbon and mineral (bentonite) adsorbents. The results of such a comparative analysis will be of fundamental importance for the development of new and optimization of existing wastewater treatment methods, which contributes to improving the environmental safety and sustainability of industrial processes.

Experimental part

The following samples were taken as the object of the study: 1) brown coal (UC) steam-activated at 850ºC; 2) enriched bentonite from the Navbahor deposit (ENB); 3) carbon based on polyethylene terephthalic bottle waste (APET), obtained by activating a mixture of PET waste, a pore-forming agent (1%) and thermally expanded graphite (10%) at 700ºC; 4) Fe-intercalated ENB (FeENB), obtained at a ratio of Fe3+/ENB=10 mmol/g.

Congo red is an azo dye, an acid-base indicator of red-brown color and poorly soluble crystals in cold water. Chemical formula $C_{32}H_{22}N_6Na_2O_6S_2$.

Adsorption isotherms of KK from aqueous solutions on samples were obtained at different temperatures in the concentration range of 1-60 mg/g. Quantitative determination of dyes was carried out by scanning spectrophotometry in the range of 190-700 nm using a UV/V-5100 spectrophotometer (Shanghai Metash Instruments Co.). The effect of temperature was studied in the range of 25-60°C, pH from 3 to 9. Adsorption

capacity with respect to KK was measured by determining the optical density at a characteristic wavelength of 505 nm, which was determined experimentally.

The experiments to determine the adsorption capacity were carried out in the following order: first, solutions of dyes in water with a concentration of 1 to 60 mg/l were prepared and the optical densities of these solutions were determined. A standard calibration graph was constructed based on the data obtained. 0.05 g of aluminosilicate samples in powder form were added to 50 ml solutions with 7 different concentrations. The flasks were slightly shaken and then left to stand at rest until equilibrium was established. The time to establish adsorption equilibrium was determined from the adsorption kinetics curve. The kinetics of the adsorption process was studied only for one concentration for each aluminosilicate sample. After adsorption equilibrium was established, the optical densities of the solutions were measured and their concentrations were calculated using the calibration graph data. The amount of adsorbed dye was determined by the formula:

$$A = \frac{(C_0 - C_1) * V}{m}, \quad (1)$$

where A is the amount of adsorbed adsorbate, mg/g; C_0 and C_1 are the initial and equilibrium concentration of the adsorbate in the solution, mg/l; V is the volume of the solution, l; m is the mass of the adsorbent.

The conclusion about the spontaneous flow of the adsorption process or its forced nature can be made by considering the process from a thermodynamic point of view. As is known from the course of colloid chemistry, the change in the free surface Gibbs energy (ΔG°) is a fundamental criterion for the spontaneity of each process, including adsorption. The absorption of the adsorbate on the surface of the adsorbent occurs at negative values of ΔG° at a given temperature. The value of free energy for adsorption was calculated using the equation:

$$G^0 = -RTlnK, \quad (2)$$

where K is the distribution coefficient ($K = \frac{C_s}{C_1}$), R - is the universal gas constant, 8.314 *J/mol*K.*

The distribution coefficient is the ratio of the concentration values of the adsorbate in the adsorbed phase and the volume of the solution. Free surface energy and enthalpy are related to each other through entropy by means of the equation:

$$G^0 = \Delta H^0 - T\Delta S^0, \quad (3)$$

where, ΔS^0- entropy of the system.

Using equation (3), the values of the surface Gibbs free energy were found at different temperatures of the CC adsorption process; graphs of the dependence of the surface energy on the process temperature were constructed based on the obtained data. From this graph, the values of ΔH^0 were found by the slope of the straight line and ΔH^0 by the intersection with the ordinate of the coordinate.

Results and discussion

The adsorption isotherms of KK on the selected objects are shown in Fig. 1.

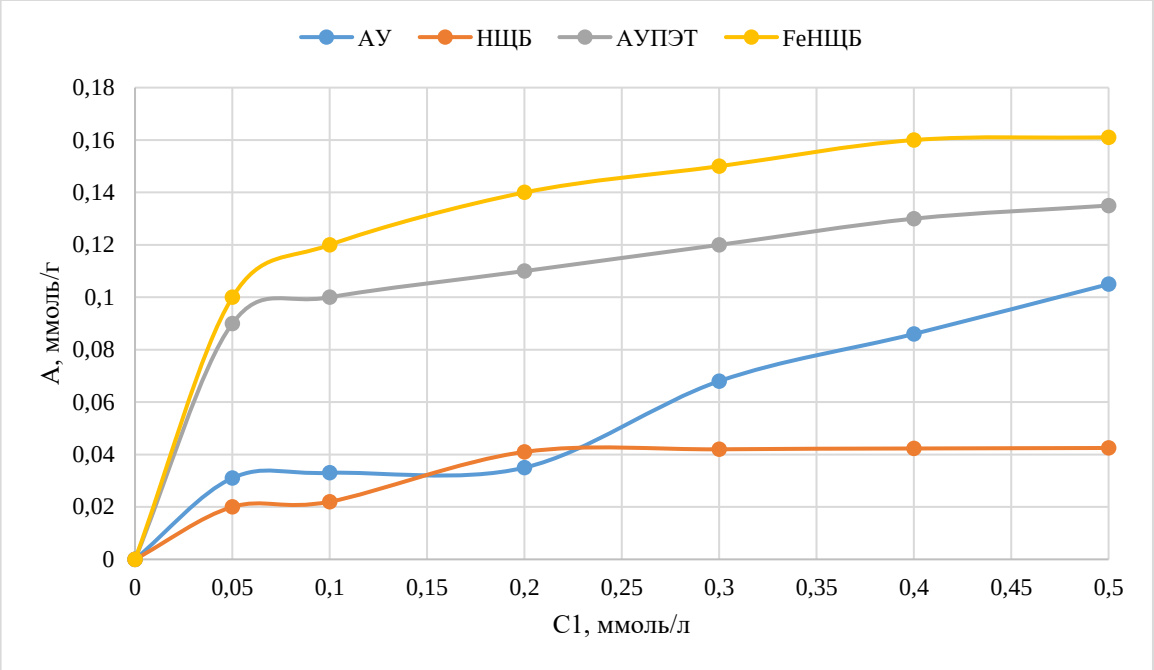

Fig. 1. Adsorption isotherms of CC on the studied objects

The adsorbent AU shows a sharp saturation of adsorption sites already at a relatively low concentration of C1, which is evident from the rapid saturation of the curve. This may indicate high adsorption activity at low concentrations, but limited overall capacity due to possible saturation of adsorption sites.

The NShB adsorbent shows a smoother increase in adsorbed substance and reaches saturation at higher C1 concentrations compared to AU. The PET waste-based adsorbent shows a moderate increase in adsorption but does not reach saturation in this concentration range, which may indicate greater accessibility of adsorption sites or a weaker adsorption bond.

The FeNShB adsorbent exhibits a constant, almost linear increase in adsorption over the entire concentration range. This may indicate the presence of a large number of available adsorption centers and an adsorption mechanism that effectively uses increasing concentration to increase adsorption.

From the analysis of isotherms it can be assumed that different adsorbents have significant differences in their adsorption characteristics, which may be due to different adsorption mechanisms, different porosity and chemical nature of the surfaces.

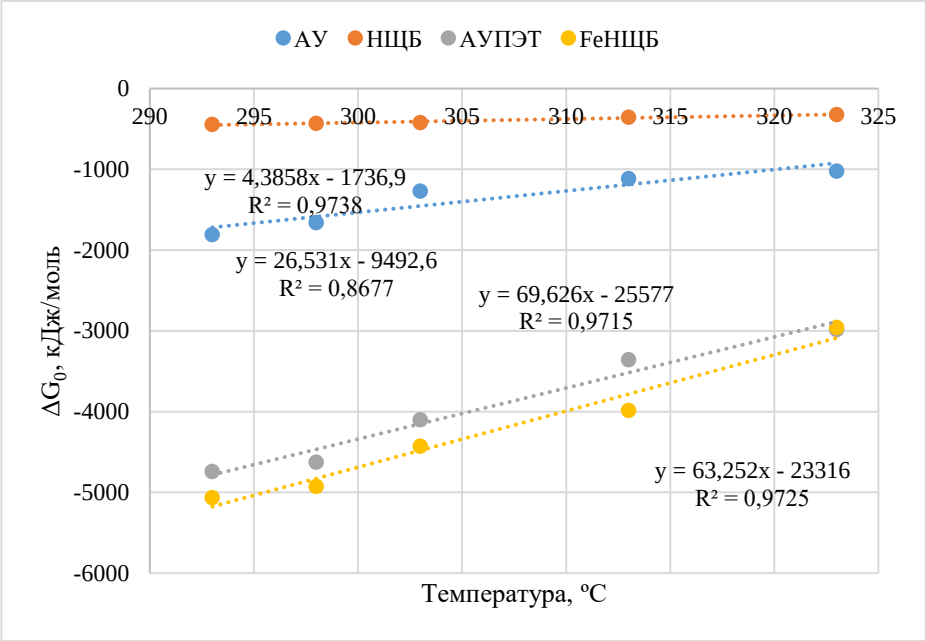

Fig. 2. Change in the Gibbs energy of the adsorption process of CC on the studied objects.

The graph shows that for all adsorbents ΔG_0 decreases (becomes more negative) with increasing temperature, which indicates an increase in the spontaneity of adsorption with increasing temperature. The ΔG_0 values for all adsorbents are in the negative region, which confirms the spontaneous nature of adsorption processes at all measured temperatures.

By analyzing the regression equations, one can notice differences in the slopes and intercept values with the Y axis, which indicates a different degree of dependence of the change in ΔG_0 on temperature for each adsorbent. For example, the adsorbents AUPET and FeNSHB show a significantly greater decrease in ΔG_0 with increasing temperature compared to AU and NShB, which may indicate their higher thermal sensitivity in the context of adsorption processes.

The determination coefficient R2 for all lines is high, which indicates a good approximation of the experimental data by the proposed linear models. Such a model allows one to reliably predict the behavior of ΔG0 when the temperature changes in the studied range.

Table 1. Thermodynamic parameters of adsorption of CC on samples

Sample	ΔH^0, kDj/mol	ΔS^0, kDj/mol
AU	1,7369	-4,3558
NSHB	8,677	-26,531
AUPET	25,577	-69,626
FeNSHB	23,316	-63,252

Table 1 presents the thermodynamic parameters of Congo red dye adsorption on different adsorbent samples. It is evident from the table that all adsorbents demonstrate endothermic adsorption, which indicates the consumption of thermal energy during adsorption. The smallest value of enthalpy change (ΔH^0) for AC indicates relatively weak interactions between the adsorbent and the dye, probably limited by physical adsorption. In contrast, AUPET and FeNSHB show significantly higher ΔH^0 values, which may indicate strong chemical bonds or more complex interactions facilitating more intensive energy absorption.

An important aspect is that dyes, having polar and non-polar parts in the molecules, can be adsorbed through various mechanisms. Electrostatic interactions between positively charged dye molecules and the negatively charged adsorbent surface, as well as the formation of hydrogen bonds and water bridges between the amino or azo groups of the dye and the hydroxyl groups on the adsorbent surface, contribute to closer adsorption.

Negative values of entropy change (ΔS^0) indicate an increase in the ordering of the system, which reflects a more structured interaction of the adsorbate with the adsorption centers on the adsorbent surface, which is not accompanied by significant changes in the internal structure of aluminosilicates. This is especially noticeable for AUPET and FeNSHB, where a large decrease in entropy may reflect a significant decrease in the degree of freedom of the adsorbed dye molecules as a result of their close and specific interaction with the active centers of the adsorbents. It is interesting to note that adsorption on Fe-intercalated bentonite and carbon based on PET waste shows higher ΔS^0 values, which may indicate strong chemical interactions. In the case of FeNSHB, the addition of Fe ions can promote the formation of additional bonds with the amino or azo groups of the dye, enhancing adsorption due to chemical sorption.

Conclusion. In this study, the adsorption properties of four different adsorbents were analyzed: steam-activated brown coal, enriched bentonite from the Navbahor deposit, carbon based on waste polyethylene terephthalate bottles, and Fe-intercalated bentonite. The analysis of thermodynamic parameters such as enthalpy and entropy changes allowed us to better understand the adsorption mechanisms of Congo red dye and to determine the conditions under which adsorption is most effective.

The study confirmed that the adsorption process is endothermic in all cases, indicating the consumption of thermal energy during adsorption. Particularly high enthalpy change values for PET-based carbon and Fe-intercalated bentonite indicate significant chemical interactions between the adsorbent and the dye, which can be used to develop targeted adsorption materials for the removal of specific types of pollutants from wastewater.

Negative values of entropy change in all cases reflect an increase in order at the phase boundary. This indicates the formation of structured and densely packed adsorbate layers on the surface of the adsorbents, which contributes to more efficient capture of the dye.

References

1. Бондаренко, А.В. Исследование ионообменных и адсорбционных свойств катионзамещенных форм слоистых силикатов / А.В.Бондаренко, Л.И.Бельчинская, Н.С.Поляков и др. // Физико-химические процессы в конденсированном состоянии и на межфазных границах: материалы II Всерос. конф. – Воронеж, 2004 г. – Т. 2. – С. 528-529.
2. Карнаухов А.П., Адсорбция. Текстура дисперсных и пористых материалов. Новосибирск: Наука. 1999. 470 с.
3. Nomura S., Kato K., Nakagawa T., Komaki I. The effect of plastic addition on coal caking properties during carbonization // Fuel. – 2003. – V. 82. – Iss. 14. – P. 1775–1782.
4. Parra J. B., Ania C. O., Arenillas A., Rubiera F., Pis J. J. High value carbon materials from PET recycling // Applied Surface Science. – 2004. – V. 238. – Iss. (1-4). – P. 304–308.
5. R.Paygamov, M.Mexmonxonov, A.Abdikamalova, I.Eshmetov, O.Ergashev. Adsorption properties of carbon adsorbents based on wood waste E3S Web of Conferences 401, 02013 (2023) CONMECHYDRO – 2023.
6. Ramamoorthy, M.; Ragupathy, S.; Sakthi, D.; Arun, V.; Kannadasan, N. Synthesis of SnO_2 loaded on corn cob activated carbon for enhancing the photodegradation of methylene blue under sunlight irradiation. J. Environ. Chem. Eng. 2020, 8, 104331.
7. Wu, D., & Zhang, W. (2019). Evolution Mechanism of Macromolecular Structure in Coal during Heat Treatment: Based on FTIR and XRD In Situ Analysis Techniques. Journal of Spectroscopy, 2019, 1–18.
8. Дубинин, М.М. Параметры пористой структуры рационального ассортимента промышленных активных углей / Дубинин М.М., Онусайтис Б.А. //Углеродные адсорбенты и их применение в промышленности. Часть1. Сб. докл. совещания. – 1967. –С. 3-25.
9. Дубинин, М.М. Капиллярные явления и информация о пористой структуре адсорбентов // Современная теория капиллярности / Под ред. А.И. Русанова и Ф.Ч. Гудрича. – Л: Химия –1980.– С.102-125.
10. Грег, С. Адсорбция, удельная поверхность, пористость. / Грег С., Синг К. // Пер. с англ. 2-е издание. – М: Мир. – 1984.– 306 с.
11. Dubinin, M.M. Homogeneous and heterogeneous Micropore Structures in Carbonaceous Adsorbents. / Dubinin M.M., Stoeckli F.G. // Col. and Int. Sei. – 1980. – V. 75. –34 p.
12. B. Tian, Y. y. Qiao, Y. y. Tian, and Q. Liu, “Investigation on the effect of particle size and heating rate on pyrolysis characteristics of a bituminous coal by TG-FTIR,” Journal of Analytical and Applied Pyrolysis, vol. 121, pp. 376–386, 2016.

CONTENTS

PRIMARY PROCESSING OF COTTON, TEXTILE AND LIGHT INDUSTRY

GROWING, STORAGE, PROCESSING AND AGRICULTURAL PRODUCTS AND FOOD TECHNOLOGIES

CHEMICAL TECHNOLOGIES