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Investigation of Nanocarbon Bleaching Capacity in Sunflower Oil with Adsorption Isotherms

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Abstract

In this article, various adsorbents were applied to the bleaching process of sunflower oil and determined that nanocarbon has highest adsorption properties among them. As a result of the analyzes made before and after the bleaching process, isotherms have been established and Freundlich isotherm has been found to be more suitable for these processes. It was determined that n and K_f values changed depend on temperature, time and dosage. 1/n values were less than 1 and greater than zero indicating favorable adsorption with nanocarbon. In addition, nanocarbon showed the highest adsorption at 80°C, while the other adsorbents showed same result at 100°C temperature. 1% of adsorbent A1, 80°C temperature and 30 minutes contact time are optimal values in sunflower oil bleaching process. Thus, these values indicate that the adsorption of unwanted color pigmentsand other residues from sunflower oil using nanocarbon can be attributed to physico-chemical adsorption process.

Keywords: Adsorbtion isotherms; Freundlich isotherms; Nanocarbon; Bleaching earth; Activated carbon

Abbreviations: CVD: Chemical Vapor Deposition; AOCS: American Oil Chemists' Society

Introduction

The process of purifying the vegetable oilis a vital issue for our health. Contaminations must be removed carefully by oil refining process. Refining process consists of several stages and bleaching stage has particular importance among these. Because, compounds which serve in vegetable oil as a bad taste, odor and dark color are removed from impure crude oilin bleaching stage. This process also improves the appearance of final product and enhance shelf life. In addition, metal oxides, oxidation products and soap particles in vegetable oil are eliminated at this stage. Another benefit, bleaching stage is increase heat resistance of oil before deodorization step [1,2]. Removing of pollutants from vegetable oil are divided into three types, which are significant in the selection process of adsorbent. Main pollutants are oil soluble proteins, sterols, tocopherols, hydrocarbons and natural pigments. Organic compounds such as free fatty acids, peroxides, ketones and aldehydes are characterized as a secondary pollutants. Heavy metals, soaps, phosphates, citric acidare include in the third type of pollutants [3,4].

Bleaching process is implemented by various methods such as chemical oxidation, hydrogenation, acid neutralization, heating and adsorption. Some pigments, such as carotenoids, turn into colorless state while heating at a certain temperature. However, these pigments break down at high temperatures which affects adversely the quality of oil. Therefore, bleachingvia heating method is rarely used in industry. It is possible to transform into completely colorless state or lighten the color of some pigments (carotenoids) by chemical oxidation method. This method is only used for technical oil production because it affects glycerides and destroys natural oxidizers. The major bleaching method in the vegetable oil industry is the adsorption-based bleaching method. This process is carried out with intermittent or continuous bleaching method. The difference between these systems is that vegetable oil are less exposed to oxidation in the constant bleaching than intermittent bleaching. Generally, bleaching is performedunder vacuum between 20-40 minutes at a temperature of 80-120°C. The amount of bleaching material is determined by the type of oil. Bleaching material is typically used in the chemical refining processranged between 0.5% and 2%. However, dosage can be increased up to 4% due to coloring demand [5-8].

Mathematically, the bleaching process is based on adsorption isotherms. Adsorption isotherms are based on the equilibrium relationship between the concentration of adsorbent particles and the concentration in liquid phase at certain temperatures. The most commonly used isotherms are Langmuir and Freundlich isotherms. Freundlich isotherm is more suitable for adsorption liquid contaminant. This type of isotherm is also used for bleaching oils. The Freundlich equation for bleaching is as follows:

$$q_e = K_f C_e^{1/n} \quad (1)$$

Ce: concentration of residual material in solution after adsorption (mg/l)
qe: Amount of adsorbed material on adsorbent (mg/g)
K_f: experimentally calculated adsorption capacity
n: Adsorption density.
Freundlich equation is associated with a specific adsorption, that is, the amount of material adsorbed in each unit of the adsorbent weight is equivalent to the concentration of concentrate in the above equation. The equation of 2 can also be expressed in logarithmic form as follows:

$$\log q_e = \log K_f + \log \frac{1}{n} C_e \quad (2)$$

If a dependency matrix is established between log q_e and log c_e, a straight-line graph is obtained. The values of the Freundlich constant k and n were obtained from plots of log q_e against log C_e. The vertical intercept (k) and slopes of the linear graphs (n) characterize the bleaching power of adsorbent and the highest bleaching rate of the adsorbent materialrespectively. The adsorbent with higher kvalue bleached better than one with smaller k. The value of the Freundlich constant n is used to determine the range of decolourisation with in which the adsorbent is most effective. Also, k and 1/n values depend on the type of adsorbent and the conditions which the bleaching process takes place [9,10].

Materıals and Methods

Materials

Nanocarbon sample (A1) was obtained from liquid products of pyrolysis at the Institute of Petrochemical Processes named after Y. Mammadaliyev. For obtaining nanocarbon (A1), C5 fraction has been used as a raw material, which consist of 63.9% unsaturated hydrocarbons. Then, C5 fraction pyrolysed on the ferrocene catalyst and MgO carrier at 920^{0}C temperature during 20 minutes in an argon atmosphere in CVD unit. Commercial activated carbon sample (A2) and bleaching earth sample (A3) were obtained from different companies. Winterized and neutralized sunflower oil has been obtained from the Baku Oil Factory. All chemicals and solvents are in analytical purity and purchased from Merck (Merck, Germany) [11,12].

Methods

The bleaching effect of adsorbents were carried out according to the AOCS Official Method Cc 8f-91 at the Azersun Holding Central Laboratory. Initially, the appropriate amount (0.1, 0.3, 0.5, 0.7 and 1 gram) of adsorbents were weighed. These samples were labelled in sequence and stored for use. Then, 100gram neutralized sunflower oil was poured into 500ml flask and heated at a set temperature with stirring continuously. The desired temperature is set by the thermometer. Firstly, 0.1g of adsorbentwas added to the flask. These processes were carried out with the addition of 0.3, 0.5, 0.7 and 1g of adsorbents to determine the effectivity of the adsorbent amount. The effectiveness of contact time was determined at 20, 25, 30, 35 and 40 minutes. The effect of temperature were studied at 20, 40, 60, 80 and 100°C. All procedures were carried out under vacuum. Finally, oil and adsorbent mixtures were filtered using Whatman filter paper No. 4 and the bleached oil samples were collected after filtration. Then, bleaching efficiency of adsorbents were determined by measuring the color of bleached oil. The color of the sunflower oil is measured by the Lovibond Tintometer Model F in accordance with the

AOCS Official Method Cc 13e-92. The oil sample was poured into a 51/4 cuvette and measured [13].

Results and Discussions

Bleaching process were carried out with using three adsorbents and due to color differencies adsorbtion isoterms were studied. The difference between bleached and unbleached oil are clearly seen by adsorption isotherms. The purpose of this study is observing the result of bleaching process with Freundlich isotherm. Thus, the bleaching process was carried out using various amounts of adsorbentsat 20-100°C temperatures and at a result 1/n, K_f and R^2 values were found. It has been found that, increasing temperature and amount affects the process positively.

Bleaching process was performed at various temperatures, color analysis results were collected before and after bleaching and adsorption isotherms were set up on the basis of these results. As a result of adsorption at 1 g/l concentration at 20, 40, 60, 80, 100°C and after 30 minute contact, isotherms were established and isotherm ratios were calculated on the basis of red color alteration. Based on the result of oil analysis bleached with nanocarbon, formed of linear shape between log qe and log Ce and obtain value of 1/n between 0 and 1 is an indicative of excellence process flow.

As shown on Table 1, adsorption is unfavorable between 20-60 ºC temperatures, because 1/n value is too small. On the contrary, adsorption is feasible at 80 and 100 ºC, because 1/n value is between 0.5 and 1. If we compare K_f values, the highest value is obtained at a 80 ºC. The values of the constant K_f rise in accordance with the temperature increase, shows increasing access to adsorption sites. In addition, the highest correlation coefficient (R^2) is also obtained at 80 ºC.

Temperature, °C	Nanocarbon		
	1/n	K_f	R^2
20	0.07	3.75	0.6751
40	0.12	3.46	0.9876
60	0.23	2.94	0.9833
80	0.81	5.36	0.9942
100	0.85	4.51	0.9854

Table 1: Comparison of Freundlich isotherm constants after bleaching with nanocarbon at different temperatures.

From Figure 1, it is clearly seen that the highest correlation coefficient (R^2 = 0.9942) is obtained at 80 ºC in bleaching process with nanocarbon. Moreover, we can see that 1/n value is less than 1 (0.81), that is, nanocarbon has a strong absorption. At 20 °C, due to the low correlation coefficient (R^2 = 0.6751), the system is not coincidence toFreundlich isotherm. In addition, 40 and 60 °C temperatures 1/n value is much smaller than 1 and it is not coincidence to Freundlich isotherm. It is determined that, when compared nanocarbon with other adsorbents, adsorption effectivity decreased in sequence of nanocarbon (1/n = 0.85), activated carbon (1/n = 0.73) and bleaching earth (1/n = 0.67) [14,15].

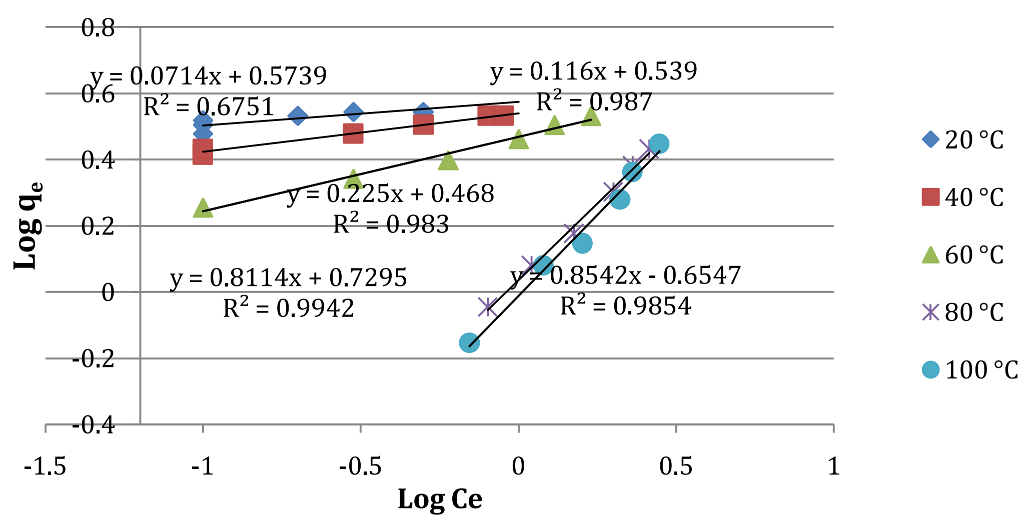

Figure 1: Freundlich isotherms for the bleached sunflower oil at 20, 40, 60, 80, 100 ⁰C temperatures, 30 min contact time and using 1 gram nanocarbon (A1).

According to Figure 2, the bleaching process is implemented at various contact times (within 20-40 minutes). Freundlich isotherms is set based on the red color alteration before and after bleaching and the isotherm constantsis found via these isoterms. It is obviously seen according to Figure 2 that the highest correlation coefficient (R^2 = 0.963) is occured with nanocarbon. However, 1/n value is defined to be less than value 1 (nanocarbon-0.78, activated carbon-0.64, bleaching earth-0.46) in all three adsorbents. When it comes to K_f value, it is defines thatsequence of bleaching earth-3.06, activated carbon-3.57 and nanocarbon-4.23 has increased. The results show that, the advancement of adsorption process is related with adsorption time period. The highest adsorption took place during 30 minutes mixture period with using nanocarbon and 35 minutes mixture period with using activated carbon and bleaching earth [16,17].

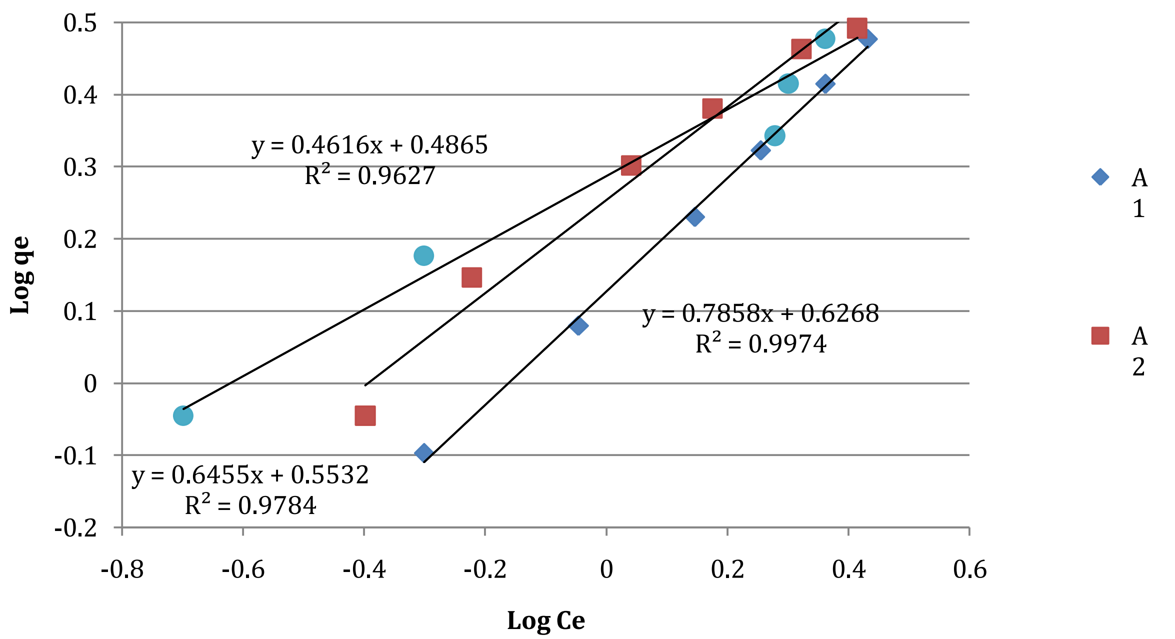

Figure 2: Freundlich isotherms for the bleached sunflower oil at 20, 25, 30, 35 and 40 min of contact time, 100 ºC temperature and using 1 gram nanocarbon (A1).

Bleaching process of sunflower oil was performed with using various amount of adsorbent, color analysis results were collected before and after bleaching and adsorption isotherms were set up according to these results. Isotherms were established and isotherm ratios were calculated accourding to 0.1, 0.3, 0.5, 0.7 və 1 g/l concentrated mixtures exposed to bleaching process during 30 minute contact time at 80^{0}C.

It is clear to see from Figure 3 that the highest correlation coefficient (R^2 = 0.993) is obtained with nanocarbon. Activated carbon and bleaching earth have approximately same correlation coefficient. It is determined that 1/n value is less than value one (A1 - 0.879, A2 - 0758, A3 - 0.717) bleaching with all three adsorbents. In terms of K_f value, there is an increasein sequence of bleaching earth (5.06), activated carbon (6.7) and nanocarbon (7.4). The results show that, the advancement of adsorption process is related with amount of adsorption [18,19]. The highest adsorption is achieved with using 1gram of nanocarbon.This outcome is obtained with using 1.5gram of bleaching earth and activated carbon. According to these results it can be stated that nanocarbon is more effective adsorbent than bleaching earth and activated carbon.

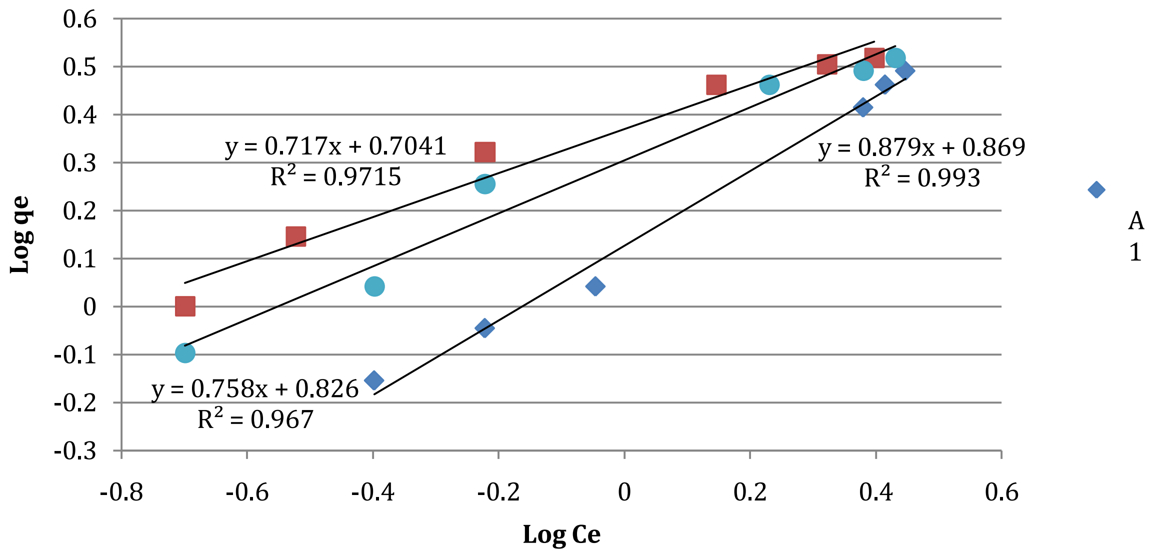

Figure 3: Freundlich isotherms for the bleached sunflower oil during 30 min contact time, at 80 ºC temperature and using 0.1, 0.3, 0.5, 0.7 and 1 g/l adsorbents.

Results

In this article, the process of bleaching sunflower oil with nanocarbon was investigated and the efficiency of adsorption process was calculated in terms of equations. According to analyses results, it can be expressed thatnanocarbon is a effective role playing material in adorsbing of colored particles. The adsorption feature is stem from suitability of nanocarbons surface, structure and characteristics. Freundlich isotherms prove that 1 gramnanocarbon is completely adsorbs coloring particlesof 1 liter sunflower oil. This proces is influenced effectually at 80°C with 30 minues contact time and as a consequence straight-line dependency was obtained. Same result was attained with using 1.5 g/l of bleaching earth and activated carbon at 100 °C temperature and 35 minutes mixture time. Compared with other adsorbents, 1/n and K_f values prove that nanocarbon is thebest adsorbent.

References

1. Zschau W (2001) Bleaching of edible fats and oils. Eur J Lipid Sci Tech 103(8): 505-551.
2. Eyup Sabah (2007) Decolorization of vegetable oil: chlorophyll adsorption by acid-activated sepolite. J Colloid Interf Sci 310(1): 1-7
3. Puah chiew wei, Choo Yuen May, MA Ahngan, Chuah Cheng Hock (2004) Degumming and Bleaching: Effect on Selected Constituents of Palm Oil. Journal of Oil Palm Research 16(2): 57-63.
4. Borner G, Hollien J, Schneider M (2003). Latest Development of Cost Savings for Bleaching Process.
5. Berbesi R (2006) Achieving optimal bleaching performance. Oil Mill Gazzetee, Volume112: 1-5.
6. Gupta M (2017) Practical Guide to Vegetable Oil Processing. (2nd edn), AOCS Press, USA.
7. Nguetnkam JP, Kamga R, Villiéras F, Ekodeck GE, Yvon J (2007) Assessing the bleaching capacity of some Camerounianclay on vegetable oils. Appl Clay Sci 39(3-4): 113-121.
8. Rossi M, Gianazza M, Alamprese C, Stanga F (2003) “The role of bleaching clays and synthetic silica in palm oil physical refining”. Food Chemistry 82(2): 291-296.
9. Huseyin T (1998) The Adsorption Isotherms of the bleaching of sunflower-seed oil. Turkish Journal of Chemistry 22(2): 143-148.
10. Achife EC, Ibemesi JA (1989) Applicability of the Freundlich and Langmuir adsorption isotherms in the bleaching of rubber and melon seed oils. J Am Oil Chem Soc 66 (2): 247-252.

11. Seyidov NI, Rustamov MI, Ibrahimov HD, Zeynalov EB, Friedrich J (2011)Two-step syntesis of nano-structured carbon phase. Materials Testing (Materials synthesis) 53(4): 211-213.

12. Zahangir ALAM, Suleyman A. MUYIBI JuriaTORAMAE (2007) Statistical optimization of adsorption processes for removal of 2, 4-dichlorophenol by activated carbon derived from oil palm empty fruit bunches. J. Environ. Sci. China 19(6): 674-677.

13. AOCS (1998) Official Methods vs Recommended Practices of the American Oil Chemists' Society. (4th edn), Champaign, IL: AOCS Press.

14. Langmaack T, Eqqers R (2002) On the bleaching kinetics of vegetable oils-experimental study and mass transfer-based interpretation. Eur J Lipid Sci Technol 104(2): 98-109.

15. Toor M, Jin B (2012) Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removal of diazo dye. Chemical Engineering Journal 187(1): 79-88.

16. Webber WJ, Morriss JC (1963) Kinetics of adsorption on carbon from solution. J Saint Eng Div Am Soc Civ Eng 89(2): 31-60.

17. Hameed BH, El-Khaiary MI (2008) Equilibrium, kinetics and mechanism of malachite green adsorption on activated carbon prepared from bamboo by K_2CO_3 activation and subsequent gasification with CO2. Journal of Hazardous Materials 157 (2-3): 344-351.

18. Usman MA, Oribayo O, Adebayo AA (2013) Bleaching of Palm Oil by Activated Local Bentonite and Kaolin Clay from Afashio, Edo-Nigeria. Chemical and Process Engineering Research 10: 1-12.

19. Shahryari Z, Goharrizi AS, Azadi M (2010) Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes. International Journal of Water Resources and Environmental Engineering 2(2): 16-28.