

## Role of Different Bleaching Earths for Sunflower Oil in a Pilot Plant Bleaching System

Mustafa Topkafa<sup>1,\*</sup>, H. Filiz Ayyildiz<sup>1</sup>, Fatma Nur Arslan<sup>2</sup>,  
Semahat Kucukkolbasi<sup>1</sup>, Fatih Durmaz<sup>1</sup>, Seyit Sen<sup>3</sup>, Huseyin Kara<sup>4</sup>

<sup>1</sup>Selcuk University, Faculty of Science, Department of Chemistry, 42075 Campus, Konya, Turkey

<sup>2</sup>Karamanoglu Mehmetbey University, Faculty of Science, Department of Chemistry, 70010 Campus, Karaman, Turkey

<sup>3</sup>Helvacizade Edible Oil Company, Konya, Turkey

<sup>4</sup>Konya Necmettin Erbakan University, Faculty of Science, Department of Biotechnology, Konya, Turkey

Key words: adsorption isotherms, bleaching earth material, chlorophyll,  $\beta$ -carotene, pilot system, red colour, sunflower oil

The purpose of present study is to investigate the efficiency of different kinds of Turkish commercial bleaching earth materials for changes in different colour pigment concentrations in neutralized sunflower oils. The bleaching experiments were performed in a pilot system under at stable vacuum (50 mmHg) and temperature (100°C) for 30 min. By examining the changes in chlorophyll,  $\beta$ -carotene and red colour, bleaching process parameters such as type and dosage of the bleaching material were optimised. The sorption characteristics of colour pigments were evaluated using common adsorption isotherms and Scatchard plot analysis. Ads-3 acid-activated earth material at 1% (w/w) per samples was found to be the most appropriate sorbent and the amount of sorbed pigments was calculated as  $1.01 \times 10^{-4}$  mmol/g ads. for chlorophyll,  $1.15 \times 10^{-3}$  mmol/g ads. for carotene and 1.70 red on Lovibond colour scale. The procedure indicated that this system can be easily adapted to the actual oil refining systems.

### INTRODUCTION

Crude edible oil contains undesirable substances such as free -fatty acids, gummy materials and colouring matters. Colouring matters are due to the presence of pigments passing to the oil with the crushing extraction or pressing treatments and could not be removed sufficiently during refining steps of crude edible oils. These pigments consist of carotenoids, chlorophyll, gossypol and related compounds [Erten, 2004; Reddy *et al.*, 2001]. Besides, crude edible oil contains soap residues, phosphatides and metals at trace concentrations and mentioned substances affect the quality of the end-product by alteration of its taste and colour, the process efficiency and also affect its market value. These impurities from crude oils are removed in the bleaching step by using the materials, with a strong adsorption power, are called bleaching earths which are usually activated bentonites [Erten, 2004; Boukerroui *et al.*, 2002].

Bleaching is a technological process, whereby the clay adsorbents are mixed with the oil under specified conditions to remove unwanted colour bodies and other contaminants and cannot be discussed without consideration of other processes during refining, such as degumming, neutralisation and deodorisation [Zschau, 2001].

The general bleaching process is carried out at contact temperature in the range of 80–120°C and contact time ranging from 20–40 min under vacuum. The dosage of bleaching earth can vary depending on oil type and 0.5–2% bleaching earth material is usually used in refining process [Erten, 2004; Diaz *et al.*, 2001]. These materials with low adsorption capacities are needed to keep activation treatment in order to increase their sorption capacities. Activation treatment was generally applied to the natural bleaching earth materials by heating with and without strong acids or microwave irradiation [Kaynak *et al.*, 2004; Didi *et al.*, 2009], resulting in strongly protonated clay mineral surface and increased specific surface area from an original 40–60 to about 200 m<sup>2</sup> per gram of dry clay [Didi *et al.*, 2009; Hymore, 1996]. The acidity of bleaching clays generally depends on the degree of activation: the higher the degree of activation, the higher the degree of cation substitution (Ca, Mg, Al, Fe) in the clay structure interlamellar layer by the H<sup>+</sup> ions of the acid used for the treatment [Rossi *et al.*, 2003].

There are a multitude of different physical and chemical mechanisms such as adsorption, ion-exchange, acidity and complexation to explain the sorption of undesired impurities onto bleaching earth materials. In each of these mechanisms there is available an equilibrium between the sorbed/unsorbed impurity concentrations and the amount of sorbed material in relation to the amount of bleaching earth material (g/100 g). Common adsorption isotherms are used to determine the amount of sorbed materials.

\* Corresponding Author:  
E-mail: m.topkafa@gmail.com (M. Topkafa)

TABLE 1. Physical and chemical properties of oils.

Specification	Oil 1	Oil 2	Oil 3	Oil 4
Colour of red	3.8	4.6	5.5	3.5
Chlorophyll (ppb)	403	1021	953	885
Carotene (ppb)	1692	2273	2803	2516
Peroxide (meq/kgO <sub>2</sub> )	15	7	10	12

TABLE 2. Physical and chemical properties of the adsorbents.

Specification	Ads 1	Ads 2	Ads 3
pH (10% suspension)	9.4	9.7	3.5
Cation exchange capacity (meq/100 g)	75.24	75.24	95
Adsorption of oil (%)	40	35	24
Combustion loss (1000°C/1 h)	7.0	0.6	6.7
Grain size (% over 200 mesh)	12	15	97

The aim of this study was to investigate the sorption performances of three kinds of commercial Turkish bleaching earth materials for the removal of main colour pigments (chlorophyll,  $\beta$ -carotene and red colour) from neutralised sunflower oils. In the bleaching experiments performed in a pilot system various parameters such as type and dosage of the bleaching earth material were optimised. In order to evaluate the sorption characteristics of colour pigments Freundlich, Langmuir, and Dubinin–Radushkevich (D-R) adsorption isotherms were used and the characteristics of binding sites were evaluated by using Scatchard plot analysis.

## MATERIALS AND METHODS

### Chemicals and reagents

All chemicals and solvents were of analytical or HPLC grade and obtained from commercial sources (Merck, Fluka). Neutralised and dried sunflower oils were obtained from Helvacizade Edible Oil Company in Türkiye. Physical and chemical properties of these oils are presented in Table 1. In the bleaching tests, three different commercially available bleaching earth materials (Ads-1, Ads-2 and Ads-3) were used as sorbents. Among these, Ads-3 was acid-activated, while others were not subjected to any treatment. The properties of the sorbents are presented in Table 2.

### Bleaching process in pilot system

Bleaching process was performed in a pilot system located at Helvacizade Edible Oil Company and this pilot plant was connected to a vacuum system capable of achieving 50 mmHg vacuum. Neutralised and dried sunflower oil were bleached through the following steps:

- *Pre-heating*: 10 L of oil was placed into mixing tank for 3–5 min under the vacuum at 70°C.
- *Mixing with bleaching earth material*: Pre-treated oil was put into the bleaching tank and mixed with 1% bleaching earth by means of steam at 11 bar for 30 min under the vacuum at 100°C.
- *Filtration*: Bleached oil was separated from bleaching earth material by using special filter cloth and filtered oil collected for the analysis.

The pilot system used in the bleaching process is shown in Scheme 1.

### Oil analysis

The bleached oil samples taken from pilot system were analysed to determine chlorophyll and  $\beta$ -carotene contents and colour intensity.

### Chlorophyll content

To determine the amount of chlorophyll pigment, AOCS Official Method Cc 13e-92 were used [AOCS, 1998]. According to this method, the oil samples was put into a 10-mm cuvette without any dilution and the total content of chlorophyll and related pigments (pheophytins) was determined by UV-Vis spectrophotometer (Model UV-1601, Shimadzu Corporation, Japan) at 630, 670 and 710 nm and calculated as chlorophyll A from the following equation [AOCS, 1998]:

$$C_{\text{chlorophyll}} = \frac{A_{630}[A_{630} + A_{710}]/2}{0.0964 \times L}$$

where: C = chlorophyll pigments, A = absorbance, and L = cell length (cm).

### $\beta$ -Carotene content

Carotenoid concentrations were determined spectrophotometrically as  $\beta$ -carotene content according to the Alfa-Laval ALS Method, 4031 E 162 [Alfa Laval Separation AB, 1995]. Specific absorbance measurements were conducted on a UV-visible spectrophotometer (Model UV-1601, Shimadzu Corporation, Japan). According to this method, 1 g of oil put into 25-mL volumetric flask was dissolved in isooctane and filled up to the dimension line with isooctane. The maximum absorbance in the region 440–455 nm was registered and  $\beta$ -carotene concentration was calculated from the following equation [Alfa Laval Separation AB, 1995]:

$$C_{\beta\text{carotene}} = \frac{A \times v}{W \times 0.261}$$

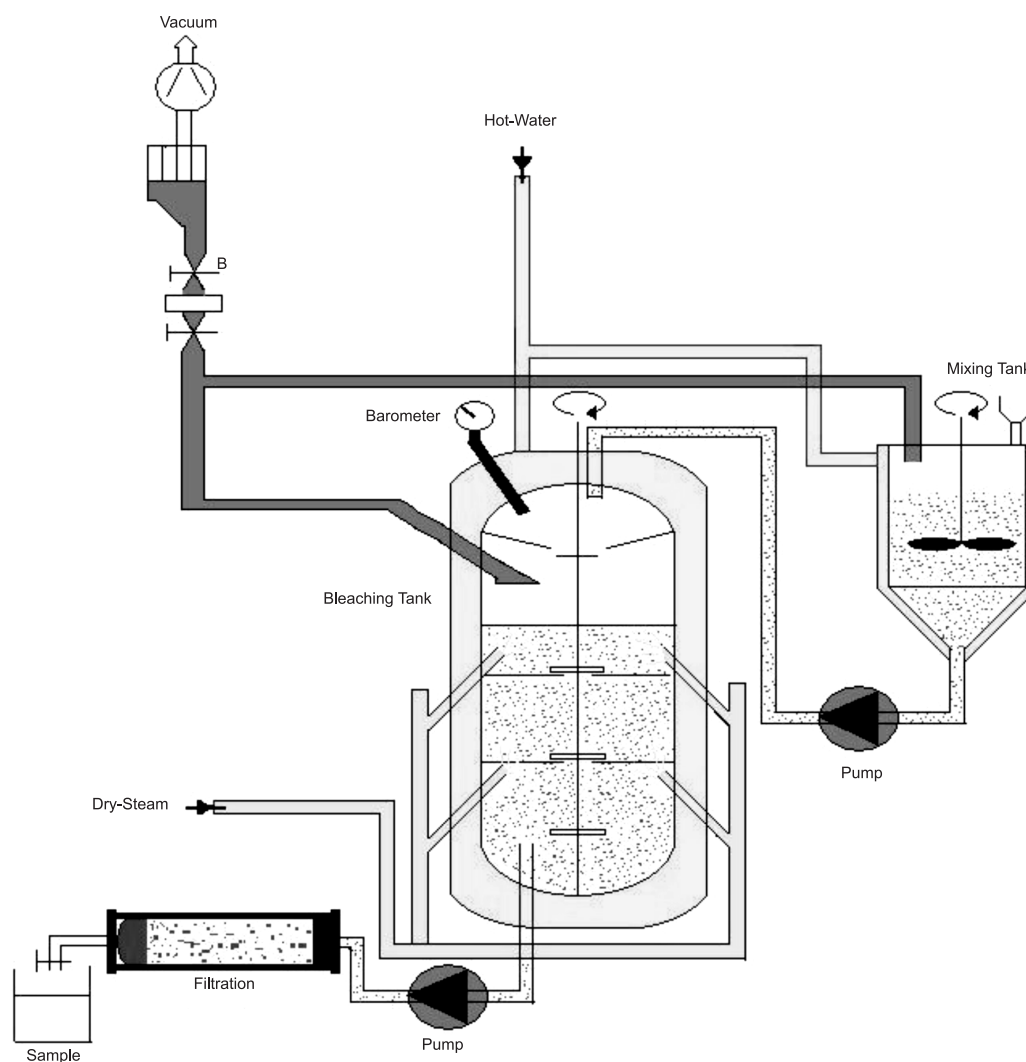
where: A = absorbance, v = volume of the solution (mL), and W = weight of the sample (g).

### Colour density

Colour measurement is based on matching the colour of the light transmitted through a specific depth of liquid oil to the colour of light originating from the same source, transmitted through glass colour standards [AOCS, 1998]. Colour measurements were made by means of a Lovibond Tintometer by using 5/4 cuvette (AOCS Official Method Cc 13e-92).

## RESULTS AND DISCUSSION

As known, in sorption process, the degree of mass transfer between fluid and solid phases is fairly affected by influent concentration that provides an important driving force for sorption [Gezici *et al.*, 2007]. The reason for this movement of substances from high to low concentration, from liquid to solid phase, is a dynamic balance. This balance depends on several



SCHEME 1. Pilot plant developed for bleaching process.

parameters such as temperature, contact time, the amount of adsorbent and type and colour of the material.

### Selection of the bleaching earth material

Bleaching earths possess a large surface that has a more or less specific affinity for colour pigment-types, thus removing them from oil without damaging the oil itself. A lot of adsorbent materials are being used in vegetable oil industry for example: acid-activated bleaching earth, natural bleaching earth, activated carbon and synthetic silicates. Among of these materials, the activated bleaching earths are more effective in the removal of the colour pigments due to the acidity properties and sorb the target ions according to adsorption, complexation and ion-exchange mechanisms. During the sorption procedure, some minor compounds (tocopherols, tocotrienols, etc.) assuring the stability and quality of the oil may also be removed while some undesired compounds (trans fatty acids, polar and polymeric compounds, aldehydes, ketones, etc.) occurred [Arslan, 2009]. This situation is related to the dosage and type of the bleaching earth material, by increasing of dosage and acidic character of the earth the amount of sorbed species is increased.

In order to select the suitable bleaching earth material for the removal of colour pigments, three different earths, two of them (*Ads-1*, *Ads-2*) are natural and another is (*Ads-3*) acid-activated, were used in a pilot system using the oil samples in different colour pigment content and the most appropriate type and dosage were determined. The effect of bleaching earth dosage and type on the removal of colour, chlorophyll and carotene is given in Figure 1.

As it can be seen from Figure 1, the amounts of chlorophyll, carotene and colour sorbed by *Ads-3* were considerably higher than the other sorbents. This result is based on the *Ads-3* having greater surface area in comparison with the other sorbents due to the acid activation treatment resulting in pH decrease. For this reason, *Ads-3* was found to be appropriate sorbent and its dosage was determined as 1% per gram of oil sample.

### The bleaching process of sunflower oils

Bleaching experiments in the pilot system were performed by using *Ads-3* bleaching earth material in constant temperature (105°C), pressure (50 mm Hg) and bleaching earth dosage (1% per oil sample).

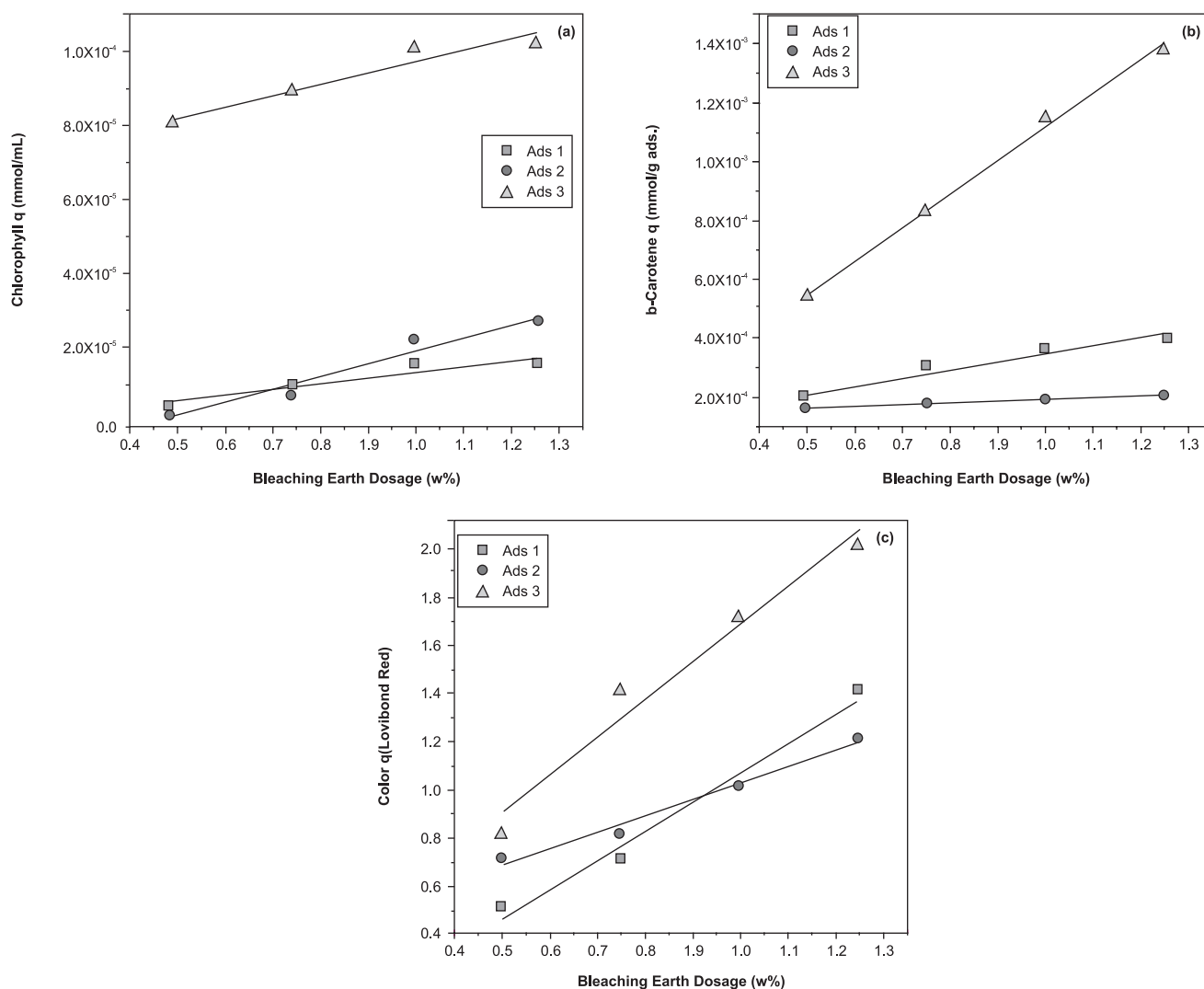


FIGURE 1. Adsorption curves for pilot plant experiments carried out to investigate the effect of the dosage on (a) chlorophyll; (b) carotene; (c) and colour.

Four sunflower oil samples in different concentrations of colour (3.5–5.5 lovibond red), chlorophyll ( $4.91 \times 10^{-4}$ – $1.08 \times 10^{-3}$  mmol/mL) and carotene ( $3.27 \times 10^{-3}$ – $5.68 \times 10^{-3}$  mmol/mL) were used in this process. The obtained results showed that the amount of sorbed pigments and total sorption capacity of Ads-3 were increased with the increasing of initial concentrations (see Table 3), since the dynamic equilibrium may be reached more easily at the higher concentrations.

### Adsorption isotherms

The distribution of colour materials between the liquid phase and adsorbent is a measure of equilibrium position in the sorption process and can generally be expressed by one or more series of isotherms [Kaynak *et al.*, 2004]. In this study, the sorption characteristics of colour, chlorophyll and carotene pigments onto the Ads-3 are mainly discussed on the basis of Freundlich, Langmuir, Dubinin–Radushkevich (D-R) adsorption isotherms, as well as Scatchard plot analysis.

The Freundlich isotherm model is:

$$\ln q = \ln k + \frac{1}{n} \ln C$$

where:  $q$  is the amount of the sorbed analyte per unit weight of the solid phase at the equilibrium concentration,  $C$ ; the Freundlich constant,  $k$ , is related to the sorption capacity; and  $1/n$  is related to the sorption intensity of a sorbent [Kara *et al.*, 2008]. The bleaching capacity of an adsorbent and its characteristic manner of adsorption may be described, respectively, by the  $k$  and  $n$  parameters defined by Freundlich [Rossi *et al.*, 2003]. The  $k$  constant is a rough measure of the surface area of the adsorbent [Achife *et al.*, 1989]. The  $1/n$  value ranges between 0 and 1, and if the numerical value of  $1/n$  is less than 1, it indicates a favourable sorption [Gezici *et al.*, 2007; Ahmaruzzaman *et al.*, 2005]. Furthermore, the  $k$ ,  $n$  and  $R^2$  values were calculated from the linearized Freundlich isotherm and listed in Table 4. Freundlich isotherm for all colour pigments can be seen from Figure 2.

It was deduced that the Freundlich isotherms exhibited linear plots with a high correlation coefficient for the sorption of chlorophyll ( $R^2 = 0.9966$ ), carotene ( $R^2 = 0.9989$ ) and colour ( $R^2 = 0.9973$ ) pigments. It can be concluded that the physical interactions were more effective in comparison to the chemical interactions.

TABLE. 3 Effect of the different oils on (a) chlorophyll; (b) carotene; and (c) colour sorption.

Specification	Chlorophyll		Carotene		Colour	
	C	q	C	q	C	q
Oil 1	4.91x10 <sup>-4</sup>	1.01x10 <sup>-4</sup>	3.27x10 <sup>-3</sup>	9.88x10 <sup>-4</sup>	3.8	1.7
Oil 2	1.24x10 <sup>-3</sup>	5.92x10 <sup>-4</sup>	4.61x10 <sup>-3</sup>	1.71x10 <sup>-3</sup>	4.6	2.2
Oil 3	1.16x10 <sup>-3</sup>	4.80x10 <sup>-4</sup>	5.68x10 <sup>-3</sup>	2.20x10 <sup>-3</sup>	5.5	2.7
Oil 4	1.08x10 <sup>-3</sup>	4.08x10 <sup>-4</sup>	5.10x10 <sup>-3</sup>	1.90x10 <sup>-3</sup>	3.5	1.5

TABLE. 4. Some parameters calculated from isotherms and Scatchard plots.

Specification	Chlorophyll			Carotene			Colour		
	k	n	R <sup>2</sup>	k	n	R <sup>2</sup>	k	n	R <sup>2</sup>
Freundlich Isotherm	0.001	0.542	0.997	0.042	0.781	0.999	0.298	0.77	0.997
Langmuir Isotherm	K <sub>b</sub> (L mol <sup>-1</sup> )	q <sub>m</sub> (mmol/g Ads.)	R <sup>2</sup>	K <sub>b</sub> (L mol <sup>-1</sup> )	q <sub>m</sub> (mmol/g Ads.)	R <sup>2</sup>	K <sub>b</sub> (L mol <sup>-1</sup> )	q <sub>m</sub> (mmol/g Ads.)	R <sup>2</sup>
	0.0007	222	0.9992	0.0001	2500	0.9541	0.0515	6.935	0.9138
Scatchard Plot Analysis	K <sub>b</sub> (L mol <sup>-1</sup> )	q <sub>m</sub> (mmol/g Ads.)	R <sup>2</sup>	K <sub>b</sub> (L mol <sup>-1</sup> )	q <sub>m</sub> (mmol/g Ads.)	R <sup>2</sup>	K <sub>b</sub> (L mol <sup>-1</sup> )	q <sub>m</sub> (mmol/g Ads.)	R <sup>2</sup>
	0.0007	215.8571	0.9997	0.0001	2810	0.9702	0.0515	6.932	0.9465
D-R Isotherm	k (mol <sup>2</sup> kJ <sup>2</sup> )	E (kJ mol <sup>-1</sup> )	q <sub>m</sub> (mmol/g Ads.)	k (mol <sup>2</sup> kJ <sup>2</sup> )	E (kJ mol <sup>-1</sup> )	q <sub>m</sub> (mmol/g Ads.)	k (mol <sup>2</sup> kJ <sup>2</sup> )	E (kJ mol <sup>-1</sup> )	q <sub>m</sub> (mmol/g Ads.)
	179.41	1.16	86000	437.67	0.93	842000	1.05	0.69	208000

The Langmuir model assumes uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface [Kara *et al.*, 2008]. The most important model of monolayer adsorption came from the work of Langmuir [Tor *et al.*, 2006; Langmuir, 1916]. The linear form of the Langmuir adsorption isotherm is often expressed as:

$$\frac{C}{q} = \frac{1}{q_m K_b} + \frac{C}{q_m}$$

where C is the colour equilibrium concentration, the parameters K<sub>b</sub> and q<sub>m</sub> are the adsorption binding constant (L/mmol) and the maximum sorption of sorbent, respectively [Kaynak *et al.*, 2004].

Langmuir isotherm for all colour pigments was given in Figure 3. In turn, the K<sub>b</sub>, q<sub>m</sub> and R<sup>2</sup> calculated values from the linearized Langmuir isotherm are listed in Table 4. It can be concluded that while the sorption characteristics of carotene and colour pigments do not fit to Langmuir model, the sorption characteristics of chlorophyll are compatible with this model (R<sup>2</sup> = 0.9992).

Dubinin and Radushkevich put forward the D-R isotherm, based on the development of the Polanyi's potential theory of adsorption and have proved successful in describing the adsorption isotherms of micropore adsorbents. The D-R equation relates pore filling to the free energy of adsorption. This isotherm is more general than the Langmuir, BET

and Redke-Prusnitz isotherms, because it does not assume a homogeneous surface or constant adsorption potential [Rey *et al.*, 1998].

The D-R equation is given by the following relationship:

$$\ln q_e = \ln q_m + K \varepsilon^2$$

where: q<sub>e</sub> is the amount of the analyte sorbed at the equilibrium, K is the constant related to the mean free energy of sorption, q<sub>m</sub> is the theoretical saturation capacity, and ε is the Polanyi potential, equal to RT ln[1 + (1/C<sub>e</sub>)]. The values of q<sub>m</sub> and K were deduced by plotting ln q<sub>e</sub> versus ε<sup>2</sup> [Kara *et al.*, 2008]. DR isotherm obtained from the "K" value using to the mean free energy of adsorption energy (E) can be calculated from the following formula:

$$E = (2K)^{-1/2}$$

D-R isotherm for all colour pigments can be seen from Figure 4. The typical range of bonding energy for ion-exchange mechanisms is 8–16 kJ mol<sup>-1</sup>, indicating that chemisorptions may play a significant role in the sorption process [Gezici *et al.*, 2005; Ho *et al.*, 2002; Helferrich, 1962]. The E, K and q<sub>m</sub> were calculated from the linearized D-R isotherm and listed in Table 4. The results were found to be lower than the typical free energy attributed to an chemisorption mechanism and so the multilayer sorption behaviour of chlorophyll, carotene and colour were also proven by the D-R isotherm.

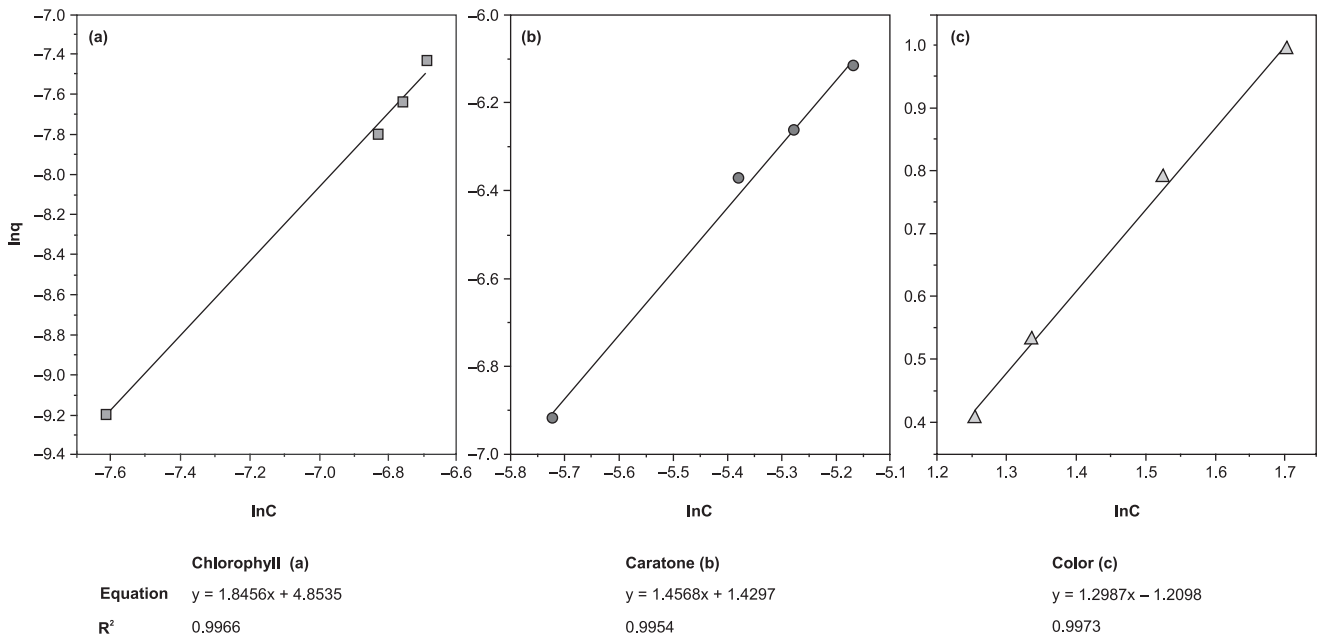


FIGURE 2. Freundlich isotherms for (a) chlorophyll; (b) carotene; and (c) colour.

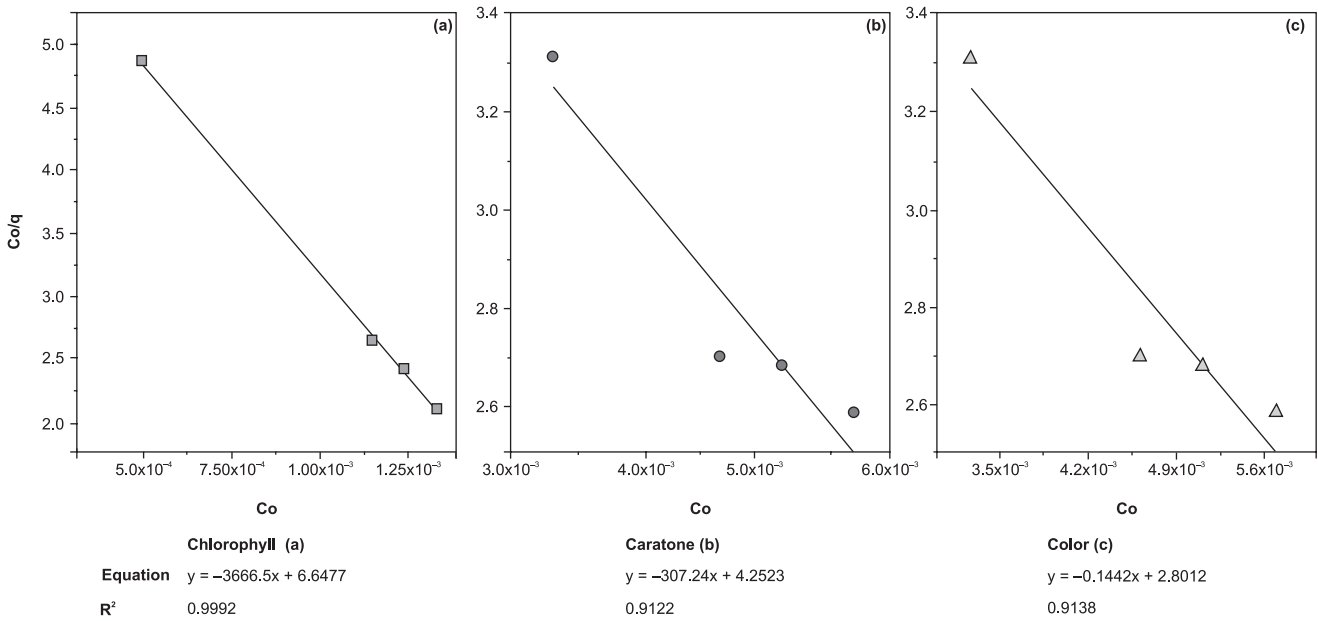


FIGURE 3. Langmuir isotherms for (a) chlorophyll; (b) carotene; and (c) colour.

The Scatchard plot analysis is one of the techniques for characteristics of the major events on the adsorption process [Gezici *et al.*, 2005]. Especially, it gives important information about the binding sites with low affinity and high affinity related to the single or multi-layer case of sorption.

The Scatchard equation is represented as follows:

$$\frac{q}{C} = q_m K_b + q K_b$$

where:  $q$  and  $C$  are the equilibrium analyte adsorption capacity of the resin and the equilibrium analyte concentration in the aqueous solution, respectively, and  $q_m$  and  $K_b$

are the adsorption isotherm parameters [Kara *et al.*, 2008]. Scatchard plot for all colour pigments can be seen from Figure 5.

When the Scatchard plot exhibits a deviation from linearity, greater emphasis is placed on the analysis of the adsorption data in terms of the Freundlich model, in order to construct the adsorption isotherms of the sorbent at particular concentration(s) in solutions [Gezici *et al.*, 2005; Ozdere *et al.*, 2003]. If the Scatchard plot is linear with a negative slope, it is related to the interaction between the analyte and the binding sites that follows the Langmuir model [Kara *et al.*, 2008]. The  $K_b$ ,  $q_m$  and  $R^2$  were calculated from the linearized Scatchard pilot and listed in Table 4. As

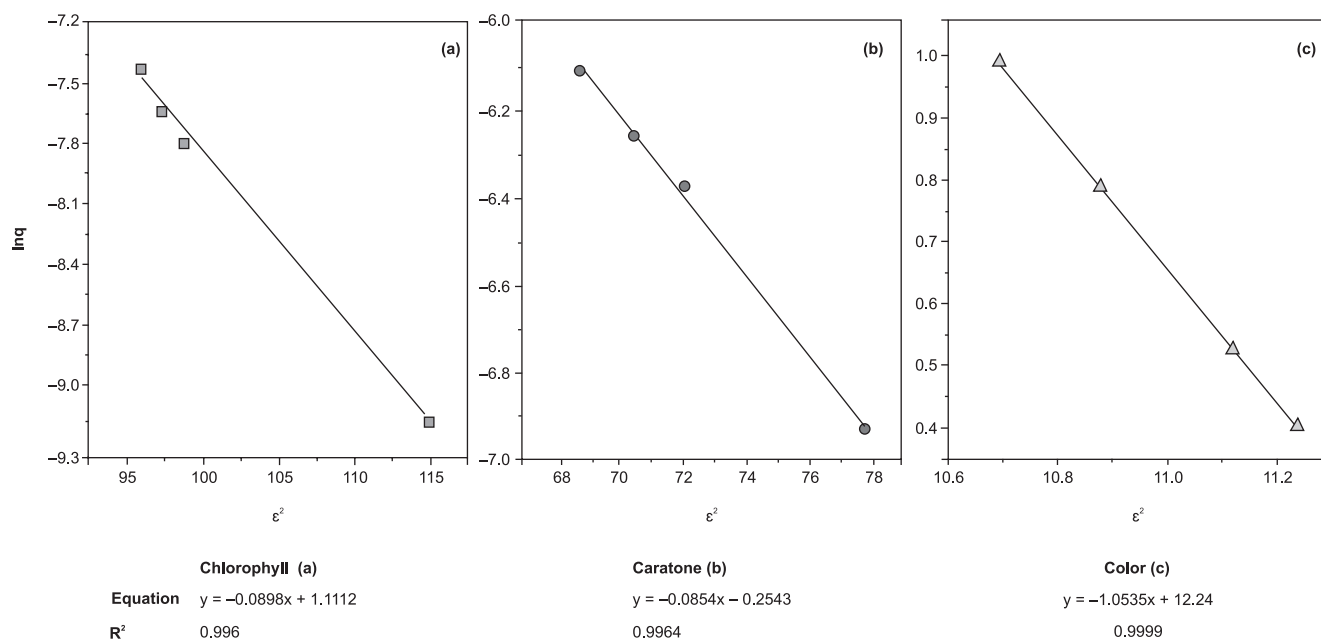


FIGURE 4. D-R isotherms for (a) chlorophyll; (b) carotene; (c) and colour.

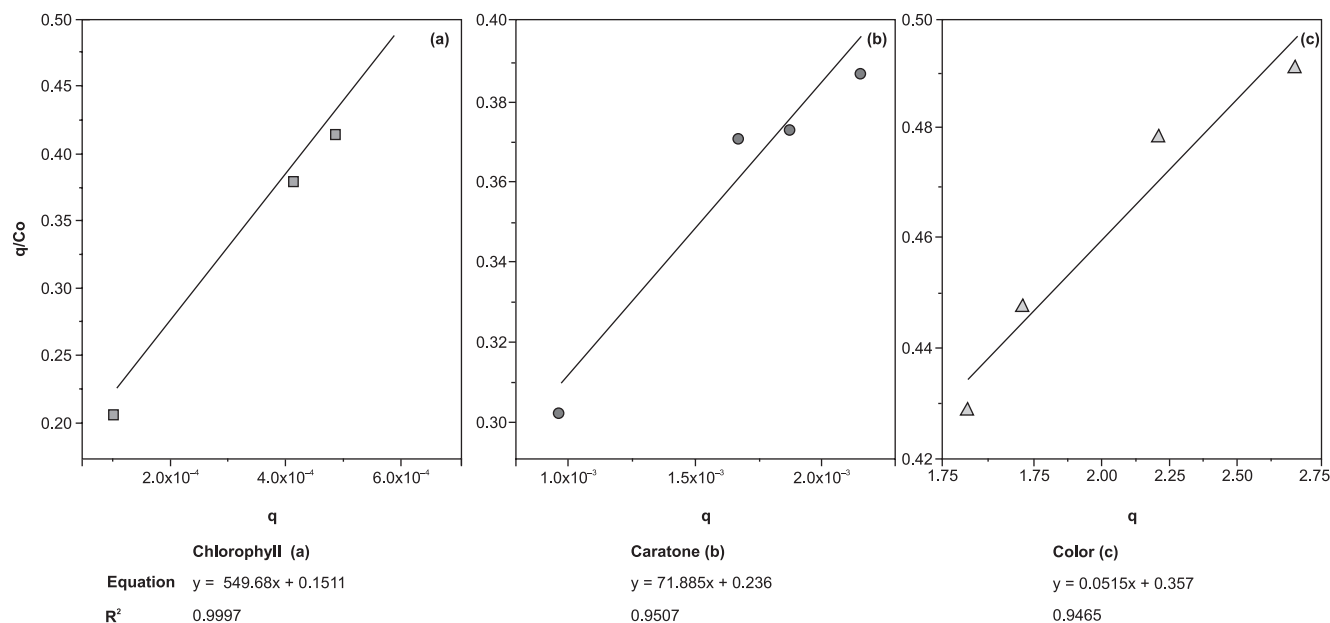


FIGURE 5. Scatchard plot analysis for (a) chlorophyll; (b) carotene; (c) and colour.

it can be seen also from Table 4, while  $K_b$  values were lined up as  $Kb_{\text{carotene}} < Kb_{\text{chlorophyll}} < Kb_{\text{colour}}$ , the amount of sorbed colour pigments could be ordered thusly;  $qm_{\text{colour}} < qm_{\text{chlorophyll}} < qm_{\text{carotene}}$ . The order of the amount of colour pigment is caused by the amount of carotene pigments in edible oils is more than other pigments.

**CONCLUSION**

The removal of the main colour pigments (chlorophyll, β-carotene and red colour) in neutralised sunflower oils with different type of commercial bleaching earth materials has been examined in a pilot system in constant temperature

(105°C), pressure (50 mmHg) and bleaching earth dosage. In the present study, the following conclusions can be drawn:

- Among the used sorbents, Ads-3 was more effective and assured higher sorption performance to removal of the colour pigments due to the acid-activated treatment resulting in higher surface area compared with the other sorbents.
- Although the amount of sorbed species was increased by increasing of the bleaching earth dosage, the most appropriate dosage of Ads-3 was found to be as 1% per gram of oil samples.
- Evaluating of the adsorption isotherm, the Freundlich isotherms exhibited linear plots with a high correla-

tion coefficient for the sorption of chlorophyll, carotene, and colour pigments. This result showed that the physical interactions were mainly responsible for chlorophyll, carotene and colour sorption's comparison to the chemical interactions. E values obtained from D-R isotherm proved also that the physical sorption mechanism was more effective for colour pigments sorption.

- Scatchard Plot Analysis provided information about the binding side's affinity of the sorbent and the binding constant and capacity varying according to the diversity of the sorbed species.
- The procedure indicating of such a pilot plant system can be easily adapted to the actual oil refining systems.

#### ACKNOWLEDGEMENTS

The authors are grateful for kind financial support provided by The Scientific and Technological Research Council of Turkey (TUBITAK) in Technology and Innovation Funding Programs Directorate (TEYDEB), Project Number: 3060009. The authors thank to Helvacizade Edible Oil Company for administrative support and guidance.

#### REFERENCES

1. Achife E.C., Ibemesi J.A., Applicability of the Freundlich and Langmuir adsorption isotherms in the bleaching of rubber and melon seed oils. *J. Am. Chem. Soc.*, 1989, 66, 247–252.
2. Ahmaruzzaman M., Sharma D.K., Adsorption of phenols from wastewater. *J. Colloid Interf. Sci.*, 2005, 287, 14–24.
3. Alfa Laval Separation AB, Methods for Analysis Application General Manual MA 0901. Alfa Laval Separation AB, 1995, Tumba, Sweden.
4. AOCS, Official Methods and Recommended Practices of the American Oil Chemists' Society. 1998, 4th edition, Champaign, IL: AOCS Press.
5. Arslan F.N., Increasing of Usage Efficiencies Of Cottonseed Oils Produced in Our Country by Improving Their Refinery Process. 2009, M. Sc. Thesis. Selçuk University Institute of the Natural and Applied Sciences, Turkey.
6. Boukerroui A., Ouali M.S., Edible oil bleaching with a bentonite activated by microwave irradiation. *Ann. Chim.-Sci. Mat.*, 2002, 27, 73–81.
7. Diaz F.R.V., Santoz P.S., Studies on the acid activation of Brazilian smectitic clays. *Quim Nova*, 2001, 24, 345–353.
8. Didi M.A., Makhoukhi B., Azzouz A., Villemin D., Colza oil bleaching through optimized acid activation of bentonite. A comparative study. *Appl. Clay Sci.*, 2009, 42, 336–344.
9. Erten Y., Use of Domestic Minerals for Vegetable Oil Bleaching. 2004, Master Thesis, İzmir Institute of Technology, İzmir, Turkey.
10. Gezici O., Kara H., Ersoz M., Abali Y., The sorption behavior of a nickel-insolubilized humic acid system in a column arrangement. *J. Colloid Interf. Sci.*, 2005, 292, 381–391.
11. Gezici O., Kara H., Ayar A., Topkafa M., Sorption behavior of Cu(II) ions on insolubilized humic acid under acidic conditions: An application of Scatchard plot analysis in evaluating the pH dependence of specific and nonspecific bindings. *Sep. Purif. Technol.*, 2007, 55, 132–139.
12. Helferrich F., Ion Exchange, 1962, McGraw-Hill, New York.
13. Ho Y.S., Porter J.F., McKay G., Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems. *Water Air Soil Poll.*, 2002, 141, 1–33.
14. Hymore F.K., Effects of some additives on the performance of acid-activated clays in the bleaching of palm oil. *Appl. Clay Sci.*, 1996, 10, 379–385.
15. Kara H., Ayyildiz H.F., Topkafa M., Use of aminopropyl silica-immobilized humic acid for Cu(II) ions removal from aqueous solution by using a continuously monitored solid phase extraction technique in a column arrangement. *Colloid Surface A*, 2008, 312, 62–72.
16. Kaynak G., Ersoz M., Kara H., Investigation of the properties of oil at the bleaching unit of an oil refinery. *J. Colloid Interf. Sci.*, 2004, 280, 131–138.
17. Langmuir I., The constitution and fundamental properties of solids and liquids. Part I. Solids. *J. Am. Chem. Soc.*, 1916, 38, 2221–2295.
18. Ozdere G., Kurt G., Mercimek B., Ayar A., Ligand adsorption of adenine and adenosine on poly(vinyl chloride) bound cobalt(II)-carboxylated diaminoethyl complex. *Colloid Surface A*, 2003, 223, 287–293.
19. Reddy K.K., Subramanian R., Kawakatsu T., Nakajima M., Decolorization of vegetable oils by membrane processing. *Eur. Food Res. Technol.*, 2001, 213, 212–218.
20. Rey F., Calle E., Casado J., Study of the effects of concentration and pH on the dissociation kinetics of Fe(II)-fulvic acid complexes. *Int. J. Chem. Kinet.*, 1997, 30, 63–67.
21. Rossi M., Gianazza M., Alamprese C., Stanga F., The role of bleaching clays and synthetic silica in palm oil physical refining. *Food Chem.*, 2003, 82, 291–296.
22. Tor A., Cengeloglu Y., Aydin M.E., Ersoz M., Removal of phenol from aqueous phase by using neutralized red mud. *J. Colloid Interf. Sci.*, 2006, 300, 498–503.
23. Zschau W., Bleaching of edible fats and oils. *Eur. J. Lipid Sci. Tech.*, 2001, 103, 505–508.

Submitted: 28 March 2012. Revised: 19 November 2012. Accepted: 11 December 2012. Published on-line: 31 July 2013.