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Utilization of Seashells and Sand Powders as Natural Material for Bleaching Crude Soybean Oil

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THIS study was carried out to use the seashells and sand powders as natural materials to reduce color of crude soybean oil compared with synthetic bleaching earth during its refining process. Some chemical properties, *e.g.* acid, peroxide and thiobarbituric acid values as well as effect of bleaching earth, sand and seashell treatments on fatty acid profiles of crude soybean oil were studied. The color of crude soybean oil was determined and the percentage of removal of red color was calculated. The results showed that removal of red color of crude soybean oil treated with seashells and sand powders was higher than bleaching earth and the highest removal was observed using seashell powder. The addition of seashells and sand powders to soybean oil during itsbleaching process retarded the red color of soybean oil.Seashells and sand powders a significant ($P \leq 0.05$) enhanced the acid, peroxide and thiobarbituric acid values of crude soybean oil.

Keywords: Bleaching process, Color, Acid, Peroxide and thiobarbituric acid values, Fatty acid profiles, Crude soybean oil.

Introduction

Soybean oil is a globally largely used edible plant oil, with a worldwide production (Quadros and Giudici, 2016). Process of oil refining is important to improve oil characteristics for different applications. This process include degumming and neutralization followed by bleaching, decolourisation and dewaxing (Manjula and Subramanian, 2009; Yu et al., 2013; More and Gogate, 2018). Bleaching is one of the four stages of oil refining and the optimal bleaching efficiency was achieved with 4% of clay at 99.83 ℃ for 40 min in refining of palm oil (Egbuna et al., 2015 and Gurdeep Singh et al., 2017).

Many varieties of activation clays are used for process of bleaching. Bleaching clay acid was used for bleaching process at 80–120 °C for 20–40 min by concentration of 2–5% (Valenzuela Diaz & Souza Santos, 2001 and Abedi et al., 2016). Moreover many studies have reported that acid activation caused some undesirable and disadvantagous components including: a) free fatty acid enhancement, b) breakage of oxidation products, c)formation of cyclic polymer, d) color fixation and free fatty acid enhancement, e) oil separation from clay take a long time, f) clay causes oil loss during oil retention of bleaching, g) the acidity of oil increases due to acidity of activated bleaching clay convert triglycerides to free fatty acids during bleaching process, h) the bleaching clay cost is very high and i) clay causes environmental problems as a waste remnants (Morgan et al., 1985; Taylor and Ungermann, 1991; Proctor and Brook, 2005; Didi et al., 2009; Gunawan et al., 2010; Hussin, Aroua and Daud, 2011).

Peroxide value is very important so it refers the hydroperoxides formed due to primary oxidation present in oil (GurdeepSingh et al., 2017). Zhang et al. (2018) reported that peroxide and acid values of oil extracted from raw soybean were 3.42 meq/kg and 4.51 mg KOH/g, respectively. Moreover Chou et al. (2018) studied the acid, peroxid and thiobarbituric acid values in four experimental oils (Camellia, soybean, palm and blended oils) and reported that these values were 0.15 ± 0.02 mg KOH/g , 4.23 ± 0.39 meq/kg and 0.32 ± 0.03 for soybean oil, respectively.

Bleaching process includes the removal of the undesirable components such as, oil-soluble, solids and non-triglyceride components from stream of the oil by changing these components from the liquid to the solid state by adsorbing it onto the surface of the bleaching earth particles added to the oil during the refining process and removing it by filtration (Proctor and Brooks, 2005).

Recent studies have reported bleaching clays have high cost and caused increasing in acidity of oil due to converting triacylglycerols to free fatty acids. Moreeover, many researches are concerned in the reduction of bleaching clay due to the same mentioned reasons (Taylor and Ungermann, 1991, Hussin et al., 2011 and Abedi et al., 2016).The present work aimed to use seashell and sand powders as natural powders for developing the bleaching process of oil which can possibly be considerably economic in addition to their effects on fatty acid composition, acid, peroxide and thiobarbituric acid values of soybean oil.

Materials and Methods

Materials

The commercially extracted crude neutralized soybean oil and Clay (bleaching earth) obtained from Tanta Company for oils and soaps, Benha branch, Egypt. Chemicals purchased from Sigma-Aldrich Company. Seashells and sand were obtained from the local market in Egypt.

Methods

Preperation and addition of seashells and sand powders

Seashells and sand were cleaned from any extraneous matter and washed by tab water, then dried at an air-oven at 40 ºC for 24 hr and then crushed into fine powder. Crude soybean oil was divided into three parts. The first part was mixed with 0.5% seashell powder and the second part was mixed with 0.5% sand powder while the third part was mixed with 0.5% bleaching earth (Clay) as a control sample. Samples of crude soybean oils kept under vacuum for 5, 10, 15, 20, 25, 30 min. and at different temperature (30,40,50,60,70,80,90 and 100 °C) then the oil samples were filtered and packed into bottles (Dark brown) without any purification and kept until analysis (AOAC, 2000).

Determination of color of crude soybean oil

Color of crude soybean oil was determined by the AOAC (2000) using Lovibond Tentometer, model F, and a 5.25-inch cell.% Removal of red color can be calculated using following equation:

$$\% \text{ Removal} = [(A_0 - A_t) / A_0] \times 100$$

Where, A_0 is the red color of the control crude soybean oil (None treated) and A_t is the red color of the crude soybean oils treated.

Chemical properties of soybean oils

Acid, peroxide and iodine values of soybean oil were analyzed by AOAC (2000). While thiobarbituric acid (T.B.A.) value was determined according to the method described by Sidwell, et al. (1954).

Fatty acid composition determination

The fatty acids compositions of soybean oil were determined according to the method described by Stahl (1969).

Statistical analysis

The statistical analysis calculated by Bezerra et al. (2008).

Results and Discussion

The red color adsorption from crude soybean oil using seashell, sand and bleaching earth

The effect of time and temperature on red color adsorption of seashell and sand powders have been studied and compared with bleaching earth powder.

Effect of time contact on color of soybean oil

The data in Table 1 and Fig.1 showed that the red color removal (%) using seashell and sand powders increased rapidly until it reached 39.3%, 41.6% and 43.8%, respectively in 30 min. The percentage of removal values (%) remained constant for 60 min. It remained almost unchanged due to the active sites saturation of the adsorbent of the equilibrium state.The optimum contact time was 30 min for the colors removal of crude soybean oil. It can explain the adsorption mechanism, the adsorption of bleaching earth, sand and seashell molecules have three successive stages, a) first stage (film diffusion), b) second (intraparticle diffusion) and c) third stage (adsorption) and the adsorption rate is usually controlled by the first two stages (Srivastava et al., 2015 and Nassar et al., 2017).

Effect of temperature on color of soybean oil

The effect of temperature on the removal process of red color of crude soybean oil was studied. The results showed that the efficiency of adsorption increased gradually with raising the temperature of the adsorption media, as reveled in Table 2 and Fig.2. The percentage of red color removal increased from 1.12% to 43.82%, 12.36% to 48.31% and 19.10% to 49.44% for crude soybean oils treated with bleaching earth, sand and seashell powders at 30 and 100°C, respectively. The increase in the rate of adsorption with increasing the temperature may be due to the decrease in the viscosity of crude soybean oil molecules led to a great ability to being adsorbed at higher temperatures.Ustra et al. (2013) mentioned that the temperature increasing caused

TABLE 1. Effect of contact time on color of crude soybean oil treated with seashells, sand and bleaching earth powders.

Color of soybean oils Treatments		Contact time (Min.)							
		5	10	15	20	30	40	50	60
Seashells	Yellow	35	35	35	35	35	35	35	35
	Blue	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Red	6.6	6.2	5.8	5.1	5.0	5.0	5.0	5.0
	Removal of red color (%)	25.9	30.3	34.8	42.7	43.8	43.8	43.8	43.8
Sand	Yellow	35	35	35	35	35	35	35	35
	Blue	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Red	6.7	6.3	6.0	5.3	5.2	5.2	5.2	5.2
	Removal of red color (%)	24.7	29.2	32.6	40.5	41.6	41.6	41.6	41.6
Bleaching earth	Yellow	35	35	35	35	35	35	35	35
	Blue	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Red	6.8	6.4	6.0	5.5	5.4	5.4	5.4	5.4
	Removal of red color (%)	23.7	28.1	32.6	38.2	39.3	39.3	39.3	39.3

A_0 (Red color) = 8.9

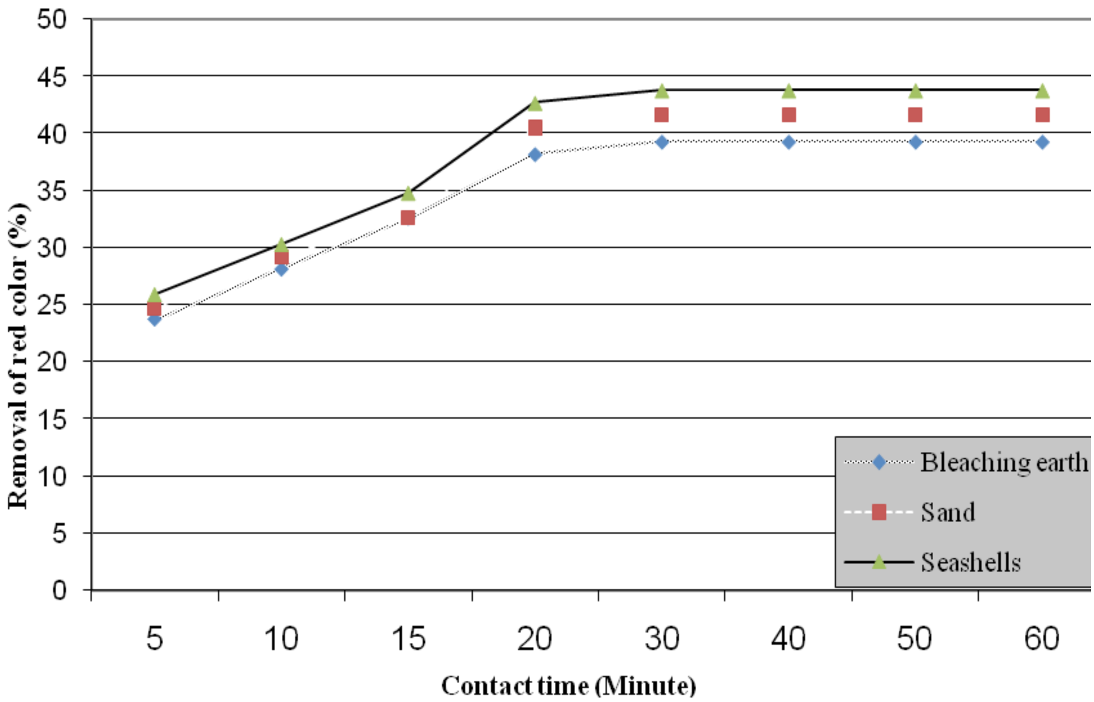

Fig.1. Effect of contact time on removal of red color (%)of crude soybean oil treated with seashells, sand and bleaching earth powders .

TABLE 2. Effect of temperature on color of crude soybean oils treated with seashells, sand and bleaching earth powders.

Temperature (°C)	Treatments											
	Seashells				Sand				Bleaching earth			
	Yellow	Blue	Red	Removal of red color (%)	Yellow	Blue	Red	Removal of red color (%)	Yellow	Blue	Red	Removal of red color (%)
30	35	0.1	7.2	19.10	35	0.1	7.8	12.36	35	0.1	8.8	1.12
40	35	0.1	7.1	20.22	35	0.1	7.7	13.49	35	0.1	8.7	2.25
50	35	0.1	7	21.35	35	0.1	7.1	20.22	35	0.1	8.1	8.99
60	35	0.1	6.9	22.47	35	0.1	6.5	26.97	35	0.1	7.8	12.36
70	35	0.1	6.7	24.72	35	0.1	6.8	23.60	35	0.1	7.5	15.73
80	35	0.1	6.3	29.22	35	0.1	6.4	28.09	35	0.1	7	21.35
90	35	0.1	4.6	48.32	35	0.1	6.3	29.21	35	0.1	6	32.58
100	35	0.1	4.5	49.44	35	0.1	4.6	48.31	35	0.1	5	43.82

A_0 (Red color) = 8.9

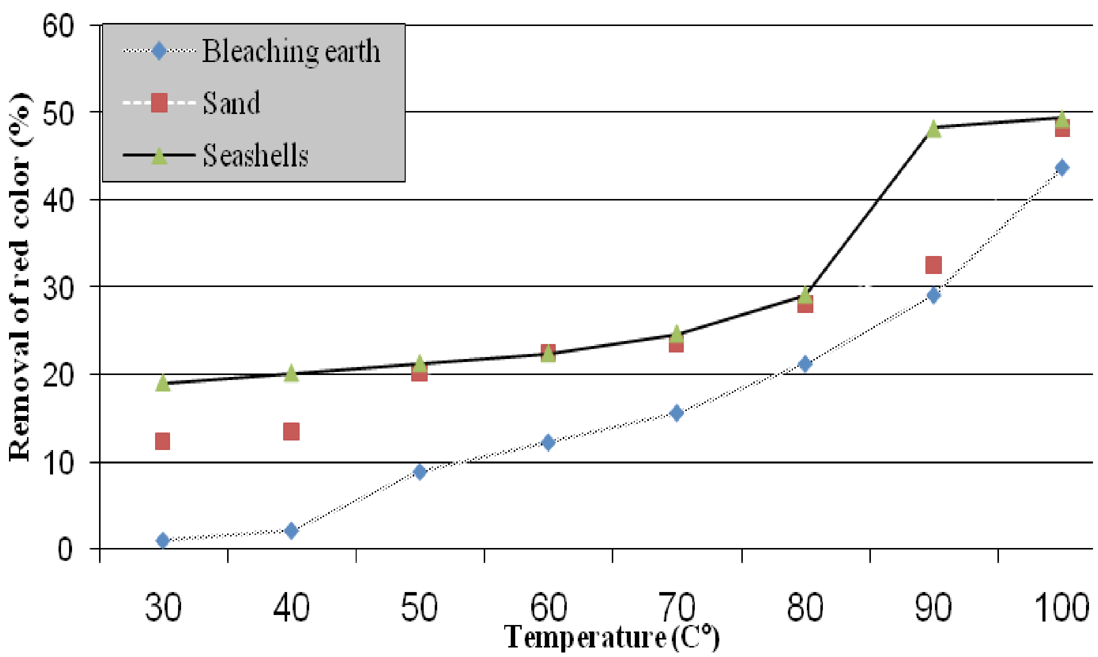

Fig. 2. Effect of Temperature (°C) on removal of red color (%) of crude soybean oil treated with seashells, sand and bleaching earth powders.

a decrease in viscosity for fatty acid methyl esters from soybeanoil.Hence, the results indicated that the best treatment for bleaching crude soybean oil was seashell powder followed by sand powder compared with bleaching earth powder.

Effect of seashell, sand and bleaching earth powders treatments onsome chemical properties of crude soybean oils

Table 3 and Fig.3 exhibit the influence of bleaching earth, sand and seashell powders on some chemical properties of crude soybean oils. The acid value of crude soybean oil before bleaching process which was 0.17mg.KOH/g. oil, and this value a significant ($P \leq 0.05$) increased to 0.48mg.KOH/goil after bleaching process with bleaching earth powder. While utilization of seashell and sand powders as natural bleaching earth has no effect on the acid values of soybean oils which recorded 0.18 and 0.17mg.KOH/goil, respectively. The same manner for peroxide and thiobarbituric acid values which were 2.7 meq/kg oil and 0.13mg MDA/kg oil before bleaching process, respectively. These results are consistent with the published data reported by GurdeepSingh et al. (2017) and Chou et al. (2018). Bleaching

TABLE 3. Effect of seashells, sand and bleaching earth powders treatments on some chemical properties of crude soybean oil .

Some chemical properties	Crude soybean oils treatments				LSD
	Before bleaching	After bleaching			
		Seashell	Sand	Bleaching earth	
Acid value (mgKOH/g)	0.172 [a] ±0.02	0.166[a] ±0.01	0.18 [a] ±0.01	0.477 [b] ±0.11	0.103
Peroxide value(meq /kg oil)	2.800 [a] ±0.10	2.700 [a] ±0.15	2.733 [a] ±0.10	3.800 [b] ±0.26	0.317
T. B. A. * (mg MDA/kg oil)	0.130 [a] ±0.01	0.133 [a] ±0.01	0.137 [a] ±0.01	0.410 [b] ±0.01	0.018

*Thiobarbituric acid (absorbance D. at 530 nm). Values are means of three replicates ± stander deviation. LSD: Least significant differences. Data were analyzed by ANOVA (Single factor $P \leq 0.05$)

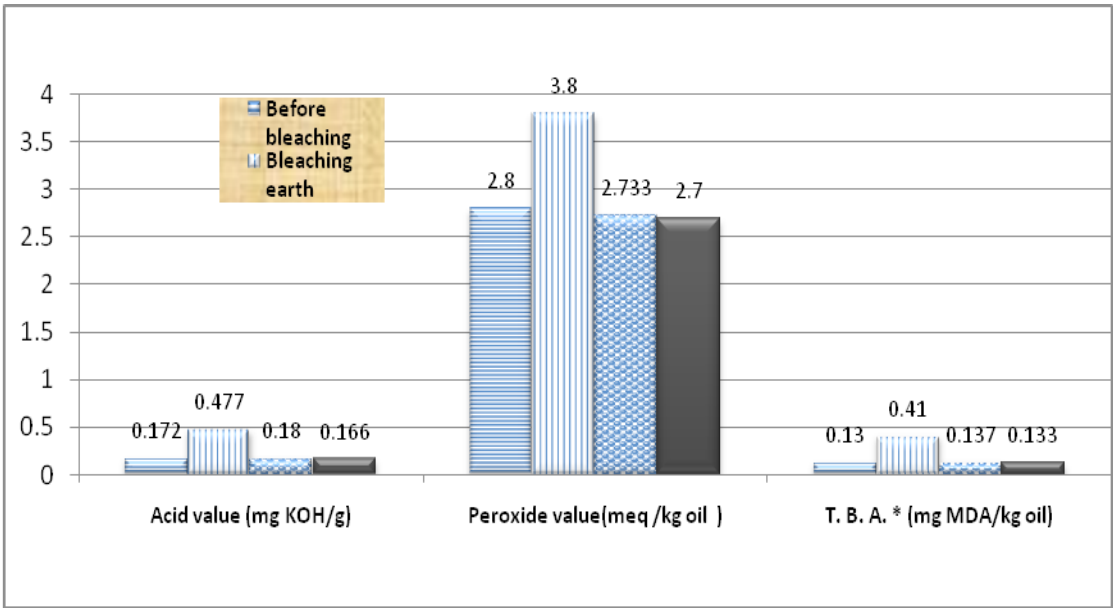

Fig.3. Effect of seashells, sand and bleaching earth powders treatments on some chemical properties of crude soybean oil .

clay treatment caused a significant increase in acid, peroxide and thiobarbituric acid values of soybean oil; this increase may be due to the effect of clay acidity on the ester bonds and liberation of free fatty acids in addition to its effects on unsaturated fatty acids.

Effect of seashell, sand and bleaching earth powders treatments on fatty acids profiles of crude soybean oil

Gas chromatographic analysis for soybean oil before and after bleaching with clay, sand and seashell powders showed that the total saturated fatty acids for their oil reached 18.978, 17.675, 15.009 and 13.238 %, while the total unsaturated fatty acids amounted to 80.942, 82.256, 84.971 and 86.731, respectively (Table 4 and Fig. 4). The palmitic and stearic were the major saturated fatty acids, while linoleic and olic constituted the major unsaturated fatty acids. Sand and seashell powders caused a decrease in the total saturated fatty acids leading to the increase in the total unsaturated fatty acids for soybean oil compared with bleaching earth powder. It can concluded

TABLE 4. Effect of seashells, sand and bleaching earth powders treatments on fatty acids profiles of crude soybean oil

Fatty acid (%)	Crude soybean oils treatments			
	Before bleaching	After bleaching		
		Seashell	Sand	Bleaching earth
Myristic (14:0)	0.190	0.201	0.270	0.314
Palmitic(16:0)	12.890	9.602	10.394	12.698
Stearic (18:0)	4.924	3.121	3.945	4.213
Arachidic (20:0)	0.265	0.314	0.400	0.450
Olic (18:1 ω9)	21.770	24.452	23.987	23.124
Linoleic(18:2 ω6)	50.344	53.854	53.142	52.012
Linolenic (18:3 ω3)	5.828	8.425	7.842	7.120
Total saturated fatty acids	18.978	13.238	15.009	17.675
Total unsaturated fatty acids	80.942	86.731	84.971	82.256

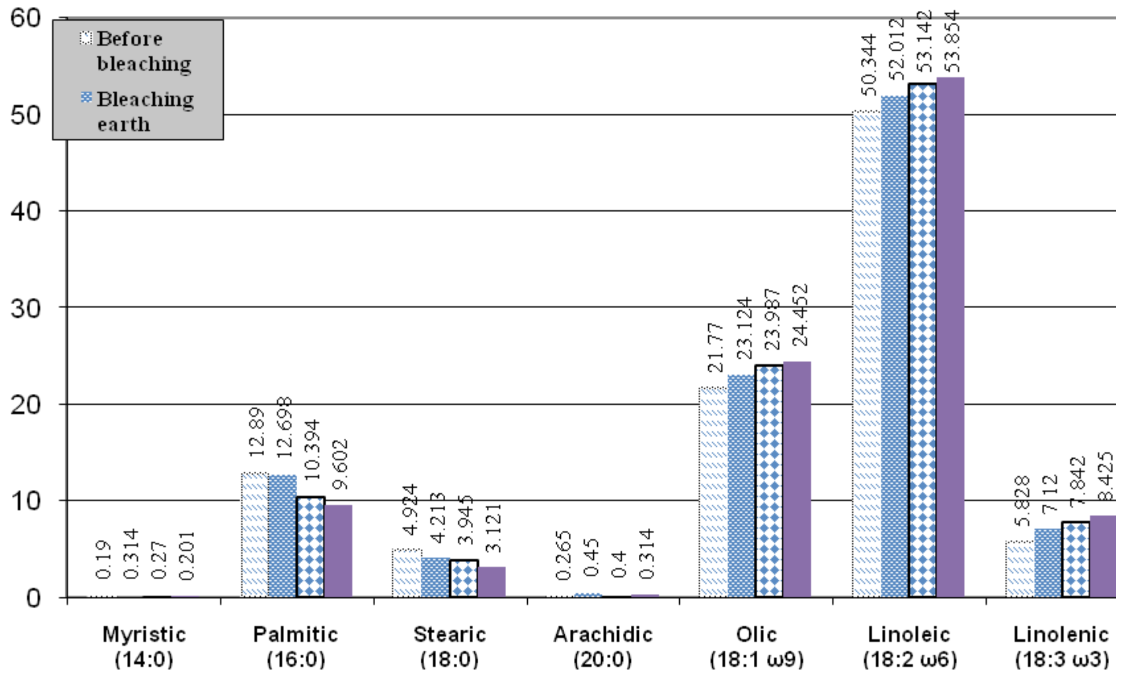

Fig.4. Effect of seashells, sand and bleaching earth powders treatments on fatty acids profiles of crude soybean oil .

that upon bleaching clay caused some undesirable and disadvantages components including free fatty acid enhancement, breakage of oxidation products and formation of cyclic polymer during bleaching process due to acidity of clay (Proctor and Brook, 2005; Didi et al., 2009; Gunawan et al., 2010; Hussin, Aroua and Daud 2011)

Conclusion

The removal of color (%) of seashell and sand powders in bleached soybean oil was higher in comparison with the bleaching earth. Furthermore, the optimum time contact and temperature for bleaching of soybean oil was 30 min and 100 °C, respectively. The seashell and sand powders bleaching technology could reduce these values compared with the clay. Consequently, sand and seashell can be used as natural bleaching powders to reduce cost in soybean oil bleaching. Therefore, it can be concluded that the optimum treatment for the bleaching of crude soybean oil without any effect on chemical properties of soybean oil were: seashell powder followed sand powder compared with bleaching earth powder.

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استخدام مسحوق صدف البحر والرمل كمواد طبيعية لتبييض زيت فول الصويا الخام

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أجريت هذه الدراسة لاستخدام الأصداف البحرية ومساحيق الرمل كمواد طبيعية لخفض لون زيت ف ول الصويا الخام مقارنة مع تراب التبييض أثناءعملية التكرير. وقد تم دراسة بعض الخصائص الكيميائية مثل دراسة قيم رقم الحمض ورقم البيروكسيد ورقم الثيوباربيوتريك وكذلك تم دراسة تأثيرتراب التبييض ومسحوق الرمل والصدف على الاحماض الدهنية لزيت فول الصويا الخام. تم تقديرلون زيت فول الصويا الخام وتم حساب النسبة المئوية لإزالة اللون الأحمر. وأوضحت النتائج أن النسبة المئوية لازالة اللون الأحمرمن زيت الصويا الخام المعالج بمساحيق الصدف والرم لكان أعلى من تراب التبييض ولوحظ أعلى إزالة للون الاحمرباستخدام مسحوق الصدف. بالاضافة الى ان مسحوق الاصداف البحرية ومسحوق الرمل ادى الى خفض اللون الاحمر اثناء عملية التبيض لزيت فول الصويا الخام فان مسحوق الصدف ومسحوق الرمل ادى الى تحسين معنوى($P \leq 0.05$) لرقم الحموضة ورقم البروكسيد ورقم حمض الثيوباربيوتريك لزيت فول الصويا الخام.