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Bleaching of Crude Glycerol by Organobentonite

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ABSTRACT

As an alternative to fossil fuel, production of biodiesel is very attractive but limited supply of raw materials, capital and production costs make the process less economically feasible. Because the process economics is improved by the supplementary utilization of glycerole, refinery of the crude glycerole is of importance even it means the additional cost affecting the sale of glycerole in addition to its quality. In this work, use of organo-bentonites is proposed for bleaching. It was found that the mixture of 1% of activated carbon and %1 of microwave dried organoclay is effective as 3% of activated carbon for 50°C and 1 hour contact time. Thus, a 60% reduction obtained in the amount of activated carbon points that the method proposed has the potentialities to evaluate a more feasible process economics.

Key Words: *Biodiesel, Bleaching, Glycerole, Activated Carbon, Organobentonite.*

1.INTRODUCTION

Due to the limited capacity of fossil fuels and their environmental impacts, the production of renewable and environmentally friendly fuels is an active area of research. Although they are about 2.3 times more expensive than the fossil fuels at the moment [1], the use of sustainable raw materials, vegetable oils and animal fats, and their lower emissions [2] make the biofuels the alternatives to the classical fuels. The ratio of raw material prices is 80% in the total production cost [1]. When the raw materials are considered, the production of biofuels in community scale farmers seems very advantageous. However, the other factors such as capital costs, electricity costs, supplementary utilization of by products and waste appreciable affect the production costs [3]. In this respect, the large scale production becomes more economically feasible than the small scale production.

Catalytic reaction of triglycerides with an alcohol of lower molecular weights namely transesterification, yields biodiesel and glycerol. The reaction is rather simple and has high rate of reaction but the process has several drawbacks: such as an intensive energy use, difficulties in the recovery of glycerol, alkaline waste water treatment requirement etc. Additionally, the soap formation reduces the biodiesel yield and also causes significant difficulty in product separation and purification. Thus, the technology development necessity for the separation, purification and transformation of it into biochemicals and bio fuels is the major limiting factor for the use of biomass [4]. Therefore the research

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[♠]Corresponding author, e-mail: saadet.yapar@ege.edu.tr on the separation techniques is very common and all the parameters are considered to improve the separation process. The difficulties in the removal of homogeneous catalyst [5] tried to overcome by the use heterogenous catalysis [6] or enzymatic methanolysis was offered for this aim [4]. However, the high cost of the lipases catalyst was the major problem in this technique and enzyme immobilization was introduced for easy of recovery and reused [7]. Nevertheless, the industrial use of this technology is not proper in terms of feasibility aspects and technical challenges [4]. The effect of oil to alcohol ratio and existence of water during the transesterification were also studied. Demirbaş [7] reported that the existence of water will reduce the methyl ester conversion from vegetable oil even the amount is around 0.1%. As widely considered and mostly adopted to commercial biodiesel production transesterification involves the washing step to remove free glycerol, soap, excess alcohol and residual catalyst. This stage performed using a large amount of water creates additional waste water.

Besides, biodiesel like other biofuels is not economically competitive with the fossil fuels as mentioned previously and technological development is also needed to bring the production cost of biodiesel down. Because the process economy is greatly affected by the sale of glycerole, a right-sized biodiesel plant will win with more feasible project economics by the sale of this product. Therefore, the biodiesel manufacturers should also consider glycerole quality even it means additional cost. The use of activated carbon is one of the factors affecting the economy of this step due to the high cost of adsorbent. Besides, the adsorption of the large molecules blinds the macroporous space and thus renders the adsorbent ineffective in the systems having high molecular weight organics [8]. Due to the existence of pseudo organic layer on their surfaces and adjustable swelling capacities, organoclays have potentialities for the solution of this problem. The structure of organic layer could be altered through the modification to obtain a suitable surface structure for a certain application. Generally the chain length and/or the amount of hydrocarbon are changed to alter the surface structure. The use of the amounts corresponding to different percentage of cation exchange capacity, CEC, is generally followed procedure in the modification.

In this work, HDTMA-bentonite was used as adsorbent for the bleaching of crude glycerine instead of activated carbon, which is highly expensive in comparison to organo bentonites. The bentonite was synthesized by using hexadecyltrimethylammonium bromide (HDTMA) in an amount equal to 100 % of the cation exchange capacity. In addition to the use of different percentages of CEC, the type drying is also a factor causing changes in the surface conditions and thus the adsorption efficiency. Especially, freeze drying causes lyophilization of the surface. Therefore, the modified clays dried under the different drying conditions were used to see the effect of surface structure and conditions to the adsorption efficiencies in this work. The adsorption experiments were carried out by using crude glycerine obtained from a local biodiesel plant. The effect of time, temperature and the amount of adsorbent were investigated. Because the improvement in the process economy is targeted, the range of the these parameters were determined by considering the real bleaching process conditions, namely temperature interval was chosen as 30°C -70°C, time interval 5-120 min and amount 0.5-2.0g. The bleaching efficiencies (BEs) were defined depending on the changes both in redness and yellowness of the crude glycerole. All the experiments were repeated by using activated carbon, crude clay and a commercial organoclay to compare the efficiency of HDTMA bentonite synthesized in our laboratory. It was determined that crude clay has the lowest bleaching efficiency and the efficiency of commercial organoclay is close to that of the freeze dried samples. On the other hand, the bleaching efficiencies of microwave and oven dried organoclays are approximately same in both scale and the freeze dried samples have less BE values. The bleaching efficiencies of activated carbon were found to be 98.7% in red and 99% in yellow scale for 3%wt of the adsorbent, 50°C and 45 minutes contact time. Whereas the BEs of microwave dried organoclay were 50.6% in red and 50.8% in yellow scale for 1%wt of the adsorbent and same temperature and contact time. However the mixture of 1% wt of activated carbon and 1% wt of microwave dried organo clay gave 95% BE in red and 98.7% BE in yellow scales. Additionally the measurements of soap content before and after adsorption showed that the relatively high amount of soap was also removed by the organo clays. Therefore, it was concluded that it is possible to reduce the operational cost by using the organoclays and thus to evaluate of the process economics.

2.EXPERIMENTAL

2.1. Materials Used

Organobentonite was synthesized according to the method described in an earlier work [9] by using HDTMA in amounts equal to 100 % of CEC. Five hundred milliliters of surfactant solution was added into the dispersion of 10% (w/w) bentonite. After mixing, the dispersion was put into microwave oven for 5 min at 360W. At the end of the irradiation period, solid and liquid phases were separated and solid phase was washed several times with 1:1 ethanol-water mixture and distilled water. The modified bentonite was dried by using oven, freeze and microwave drying methods to see the effect of drying conditions to the adsorption efficiency.

Crude glycerole was obtained from a local biodiesel plant. Specifications of glycerole are shown at Table 1. Commercial organoclay Viscobent SB-I was produced by Bensan (Enez, Turkey). It is a dimethyldodecylamine (DMDA) montmorillonite having 43.6m^2/g specific surface area and 0.14 cm^3/g specific mesopore volume [10].

Before the experiments all the samples were subjected to XRD analysis. The analyses were carried out in a Siemens-AXS X-Ray diffractometer D5000, Bragg-Brentano-geometry, equipped with graphite primary monochromator and scintillation counter.

Table 1. Properties of Glycerole.

Specifications	**Value (%)**
Average Molecular Weight (g/mol)	92.05
Glycerine Content (%)	Min. 99
Specific Gravity (g/cm^3) @ 25°C	Min. 1.26
Ash Content (%)	Max. 0.01
NaCl (%)	Max. 0.01
Sulphates (%)	Max. 0.1
Arsenic (ppm)	Max. 0.01

2.2. Adsorption Experiments

Since the aim of this work is the evaluation of a new method that helps to reduce the cost of refinery, the maximum values for the parameters affecting the adsorption efficiency were assigned by considering the operating conditions in the local plant. Experiments were carried out by using batch equilibration technique in three groups to see the effect of temperature, amount of adsorbent and time. In these groups, the time interval was 5-120 min, temperature 30°C-70°C and amount of adsorbent 0.5-5%wt. The same experimental procedure was followed in each group of experiments, the adsorbents were added to glycerole heated to a predetermined temperature and the dispersion was vigorously stirred for a certain time. At the end of stirring period, the oil was filtered and the final color of glycerole was determined by using a Lovibond PFX880 Tintometer with a 5.25-inch column. Color was read in red and yellow scales.

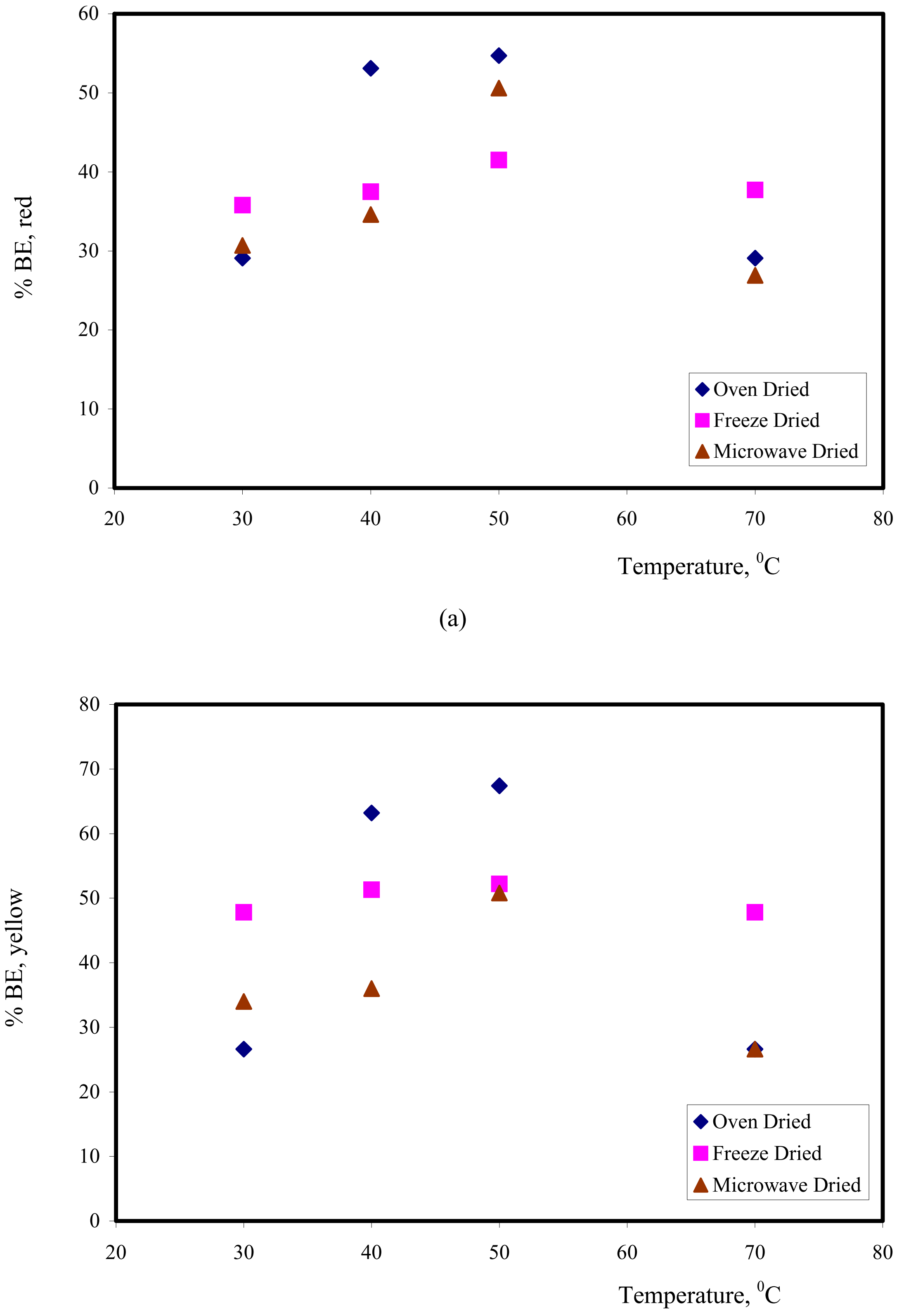
The bleaching efficiency was calculated by using the following equation,

$$\%\mathrm{BE} = \frac{\text{Initial Color} - \text{Final Color}}{\text{Initial Color}} \qquad (1)$$

The experiments were also repeated by using activated carbon for comparison.

3.RESULTS AND DISCUSSION

In this work an improval in the biodiesel economics was targeted. For this aim, the use of organoclay in bleaching of glycerol was studied. In the first step of the work, the effect of temperature on the BEs was determined. Although the cost of heating is also a factor to be considered in the process economy, the high viscosity of crude glycerole requires relatively high temperatures. Thus, the minimum temperature was chosen as 30°C and the experiments were conducted over the temperature range from 30°C to 70 °C. As shown in Figure 1, the maximum values in BEs are observed at around 50°C in both scales and thus the experiments placed in the other two groups were conducted at this temperature.



(a)

(b)

Figure 1. Effect of temperature on BEs.

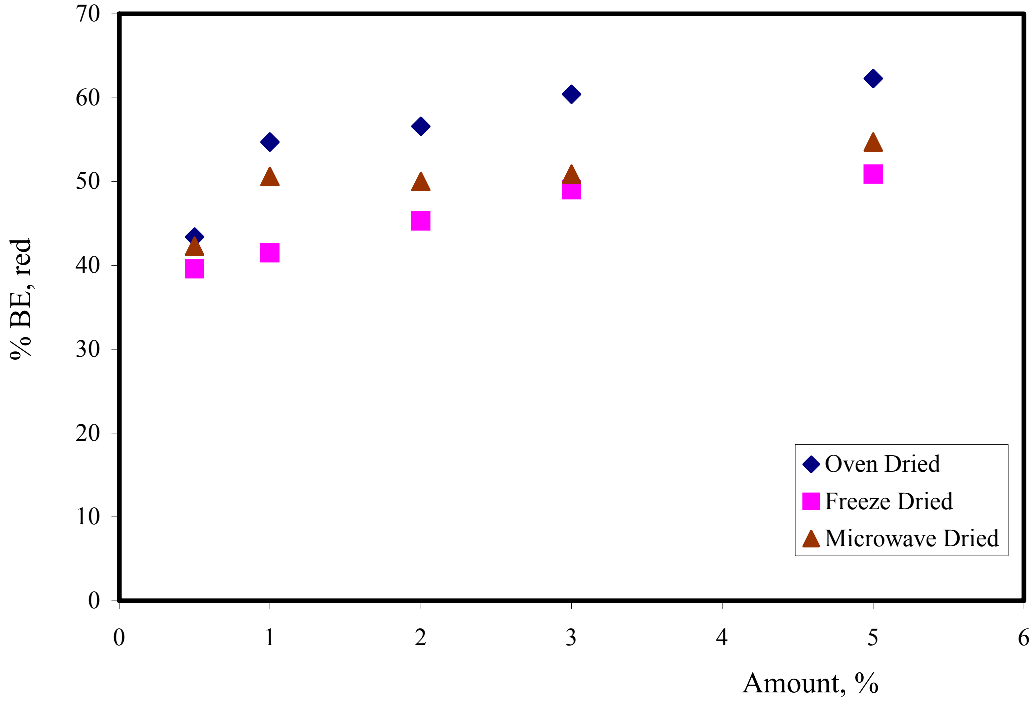
After the determination of the temperature at which the maximum BEs were obtained the effect of adsorbent amount was studied. By considering the difficulties arising from the increase in apparent viscosity depending on the increase in amount of solid, the maximum amount was taken as 3% wt. The results of these groups of experiments are given in Figure 2. As shown in the figure, the bleaching efficiencies increase with increasing amounts for all type of adsorbents but this increase is very smooth for the amounts exceeding 1% wt and it approaches a certain value. The same phenomenon was also reported by Al-Malah et al. [11] and Al-Asheh et al. [12] for CTAB-bentonite and by Yapar et al. [13], for the removal of phenol by using hexadecyl trimethyl ammonium-bentonite and they attributed this behavior to the effect of intra particle interactions. Therefore, the amount of adsorbent was limited at 1% wt for the kinetic experiments.

The bleaching efficiencies of the adsorbents were compared with those of crude and commercial organoclays in Table 2. As shown in the table, the existence of organic layer causes an increase in bleaching efficiencies in both red yellow scales. This behavior is attributed to the increase in the interaction between the colorful components of glycerol and clay surface due to the existance of organic layer. In contrary of the negatively charged clay surface rendering less interaction between the surface and nonionic organic compounds, organic layer on the surface supplies a medium increasing the adsorbent - adsorbate interaction. A close examination of the table reveals that the type of drying has also a considerable effect in the BEs and highest values were obtained in the case of ovendried organoclay.

Table 2. BEs of Adsorbents.

Adsorbent	**Maximum BE, %**	
	Redness	**Yellowness**
Crude Clay	33.3	40.3
OD Organoclay	54.7	67.4
FD Organoclay	47.2	56.5
MWD Organoclay	54.0	57.0
Commercial Organoclay	47.3	51.2

When the efficiencies of synthesized organoclays were compared that of a commercial organoclay as in Table 2, it was determined that the oven and microwave dried organoclays has higher efficiencies than commercial organoclay. As shown in Table 3, commercial organoclay has higher basal spacing than the synthesized organoclays. According to the model developped by Lagaly and Weiss[14], d_{001} values of synthesized organoclay corresponds a bilayer arrangement of flat lying molecules [9], whereas the d_{001} value of commercial organoclay indicates the existance of a pseudo triple layer configuration. This difference is attributed to the use of different organic molecule in the modification. Because surface structure is closely related to the type of organic molecule used in the modification, commercial organo clay has the different surface structure and dependently different adsorption behavior.



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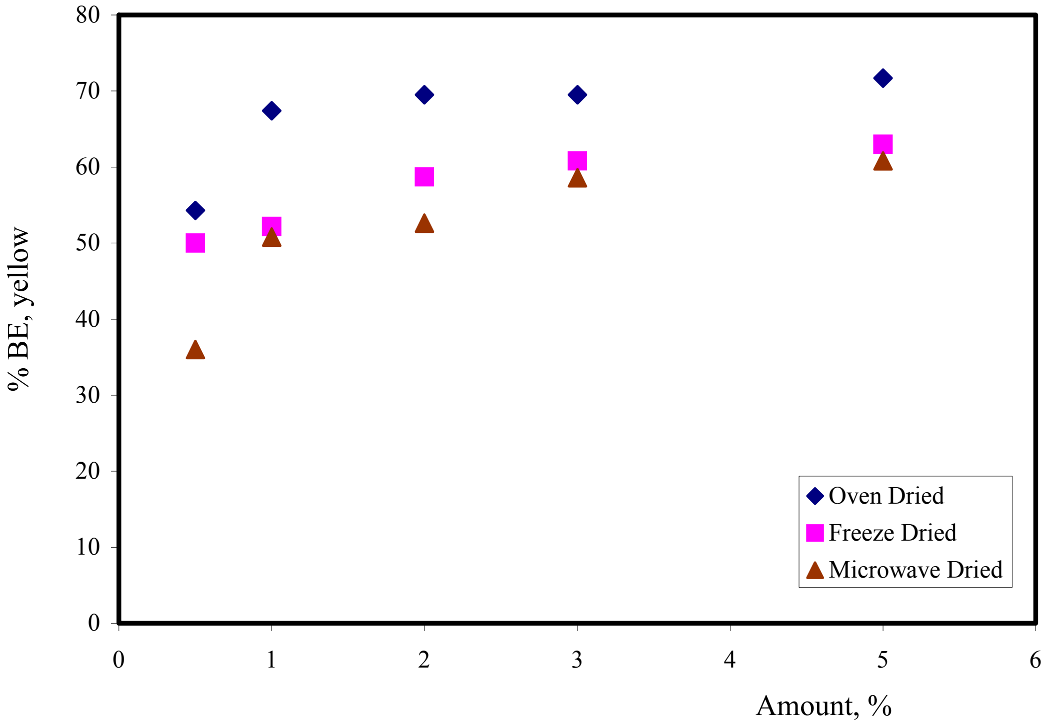

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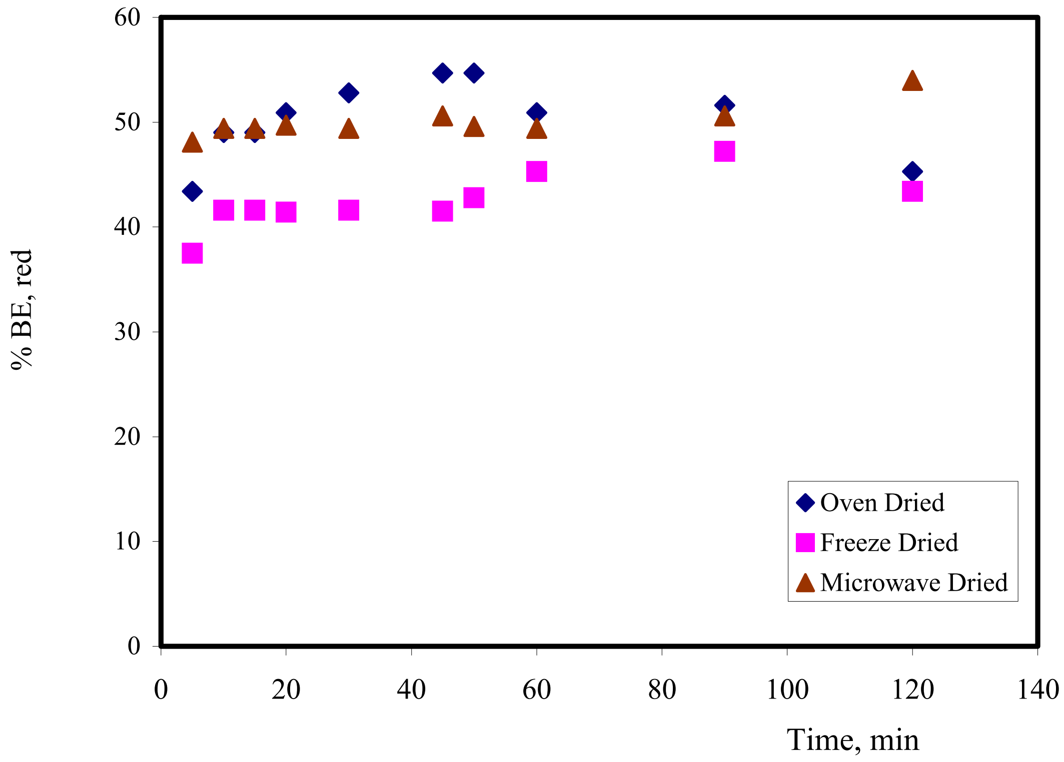
Figure 2. Effect of Amount on BEs.

Table 3. Basal Spacings of Organoclays.

Adsorbent	d_{001} (nm)
Crude Clay	1.26
OD Organoclay	1.87
FD Organoclay	1.84
MWD Organoclay	1.86
Commercial Organoclay	2.7

The effect of time to BEs is shown in Figure 3. As shown in the figure, adsorption equilibrium is almost established in 20 minutes and except the microwave dried organoclay, a slight decrease in BEs is observed for the mixing times longer than 100 minutes. During the experiments, the clay-glycerole dispersion were vigorously stirred to eliminate external mass transfer resistance, therefore adsorption is mainly controlled by the internal resistance. The very short equilibrium time namely high adsorption rate indicates low internal resistance and thus the existence of a favorable interaction between the adsorbent surface and adsorbates.



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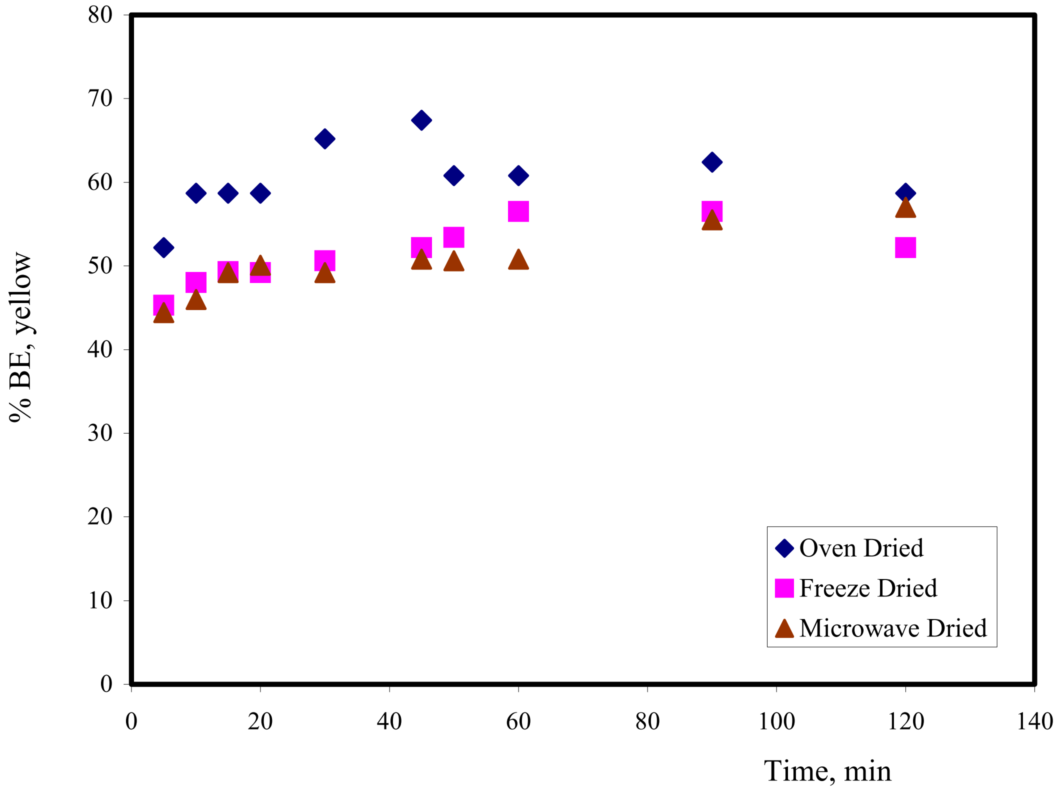

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Figure 3. Effect of Time on BEs.

Because there is no considerable increase in BEs, the mixing time was determined to be 45 minutes for other steps and the soap content was determined at 50°C, 45 minutes stirring and 1% wt of adsorbents. The results were given in Table 4.

Table 4. The change in soap content.

Adsorbent Type	Initial Soap ppm	Final Soap ppm	Percent Removal
Oven Dried	775	200	74.1
Freeze Dried	775	200	74.1
Microwave Dried	1010	305	69.8

A close examination of the table reveals that the relatively high amount of soap is removed. Oven and freeze dried organoclays are more efficient than the microwave dried adsorbent.

When the results of all experiments are considered, it is seen that the oven dried organoclay has the highest bleaching efficiency and percentage of soap removed is also high. Although it is the most effective in the removal of colorful components, the highest efficiencies are around 50% in red and 65% in yellow scales. However, oven dried organoclay was found less efficient than the activated carbon having the BE values 98.7% in red and 99% in yellow scale for the same experimental conditions. These results indicate that only certain components of crude glycerole are removed by organoclays. Since the organoclays have synergistic effect with a number of technologies [8], the mixtures of microwave dried organoclay and activated carbon were used in the bleaching. The results of those experiments are given in Table 5 in comparison with activated carbon and organoclay.

Table 5. Comparison of the efficiencies of activated carbon and microwave dried organoclay and their mixtures (Experimental conditions T: 50°C; Time 45 min).

Adsorbent	Amount, %wt	% BE, red	%BE, yellow
Organo Clay (OC)	1	50.6	50.8
Activated Carbon (AC)	3	98.7	99.0
Mixture 1	1 OC+1AC	95.0	98.7
Mixture 2	1OC+0.5AC	84.0	97.0
Mixture 3	3OC+0.5AC	87.6	97.9

As shown in the table, the activated carbon has the highest efficiency and the increase in the amount of organoclay in adsorbent mixture has little effect in the BEs. This result reveals that organoclay is functioned as coadsorbent and it is more effective in the removal of certain components in the glycerole.

4. CONCLUSION

It was concluded that the organoclays have limited efficiencies in the removal of colorful components of crude glycerole and therefore it is able to use them only as coadsorbents. However, the reduction obtained in the amount of activated carbon points that the method proposed has the potentialities to evaluate a more feasible process economics.

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