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Effect of ultrasound on the dispersion of kaolinite and sepiolite suspensions with and without sodium silicate

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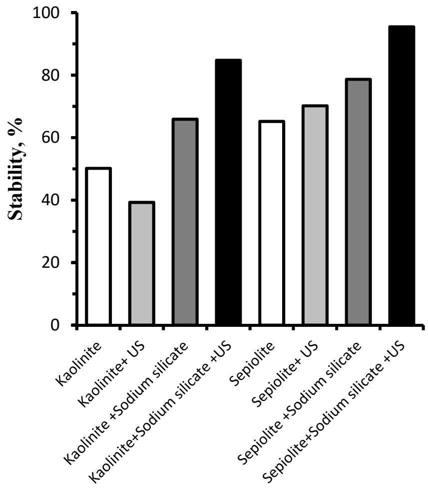
HIGHLIGHTS

- The effect of ultrasound process on the dispersion of kaolinite and sepiolite suspensions was studied.
- The ultrasonic had no effect on the isoelectric point of clay minerals.
- The ultrasonic treatment improved the dispersion of kaolinite and sepiolite with sodium silicate.
- The ultrasonic treatment led to more negative zeta potentials for kaolinite and sepiolite.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the effect of the ultrasound process on the dispersion of kaolinite and sepiolite suspensions in the absence and presence of sodium silicate was investigated. The effects of ultrasonic device-dependent parameters such as power, treatment time, and application method (batch and continuous) on the dispersion of kaolinite and sepiolite suspensions were determined. Results of the studies carried out without sodium silicate showed the suspension stability values of kaolinite and sepiolite minerals presented some differences. While the stability of the kaolinite suspension decreased at high power ultrasonic values, it increased slightly for the mineral sepiolite. Also, the stability of the kaolinite suspension decreased, while the stability of sepiolite increased with a prolonged ultrasonic treatment time. It was also found that the application of ultrasound did not affect the isoelectric point (iep) of these clay minerals. In the presence of sodium silicate as a dispersant, the dispersion of these mineral suspensions increased depending on ultrasonic power and treatment time. Moreover, higher suspension stability values were obtained with the ultrasound application. In addition, the negative zeta potential values of clays after ultrasonic treatment were higher than those without ultrasound. The findings obtained showed that kaolinite and sepiolite suspensions were more successfully dispersed by ultrasonic treatment.

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1. Introduction

When dispersion is created, the main problem is its protection. Generally, the most practical way to protect dispersion is to use chemicals called dispersants [1]. Sodium silicate is the most commonly used among inorganic substances in the dispersion of clay minerals [2,3]. The dispersion can be achieved by electrostatic stabilization, steric stabilization, or using both of these effects together. The electrostatic stabilization process is carried out by electrically repelling particles from each other by increasing the particles surface charges. In steric stabilization, a physical barrier is built between particles. Steric stabilization is caused by the adsorption of surfactants or polymers on the surface of the particles. Steric stabilization, in other words, is based on the use of the structure of adsorbed chemicals to prevent the particles from approaching each other [1].

The crystal structure of kaolinite consists of silica tetrahedral and alumina octahedral layers, and the unit cell has the composition of $Si_2Al_2O_5(OH)_4$. Sepiolite is a natural clay mineral belonging to a group of layered silicates. It has a fibrous structure formed by stacking tetrahedral and octahedral oxide layers. Kaolinite and sepiolite, which are industrial clay minerals, are used in many fields such as ceramics, paper, medicine, chemical industry, and removal of heavy metals from water [4,5]. In many of these areas, clays are used as a suspension (or sludge), and the dispersion (stability) conditions of this suspension directly affect the final product property [6,7].

Ultrasound is a three-dimensional pressure wave consisting of successive compression and rarefaction cycles. The rarefaction cycle has negative pressure, and the following compression cycle has positive pressure. The rarefaction cycle overcomes the intermolecular forces binding liquid, resulting in the formation of microbubbles, and then the compression cycle instantaneously causes a localized burst of energy. This phenomenon, known as cavitation, imposes a significant effect on any solid phase within the liquid [8,9]. Although ultrasonic vibration is commonly used to characterize the physical properties of materials, it is also used in medical designs, material testing methods, cleaning processes, welding (smelting) processes, and in many industries to provide particle stability in emulsions [10,11]. Studies in mineral processing have recently focused on determining the effects of ultrasound on the flotation of minerals [12-17]. However, only limited studies have been conducted to determine the effects of ultrasound on sedimentation. In these studies, it was stated that the positive and negative effects of ultrasound application generally varied depending on the operating parameters [8,17,18].

Clay minerals, which are found as the main gang mineral in many mineralization processes, create problems at all stages of mineral processing. The presence of clay minerals causes problems of excessive reactive consumption and problems such as slam coating. Clay minerals cause high viscosity in grinding and blockages in crushers. For this reason, it is important to ensure the stability (dispersion) of clays. Several published studies successfully use ultrasound for dispersion and homogenization of other materials, such as nanosized silica and alümina, nano-alumina, and cement grout [19-21]. The studies showed that the effect of ultrasonication can depend on the material. In studies on clays, ultrasound processing has mostly been used to reduce the size of clays [22,23]. As noted in these studies, ultrasound treatment caused a change in the surface load of clays. The dispersion of clays directly depends on the zeta potential of the particles. Therefore, knowledge of the zeta potential plays an important role in the dispersion of a clay suspension [24].

In this study, the effect of an ultrasonic process on the suspension stability of kaolinite and sepiolite minerals was investigated depending on various operating conditions. Also, the effect of ultrasound on the zeta potential of these minerals was determined in the absence and presence of sodium silicate. It is hoped that the findings will benefit the dispersion process of clay minerals in flotation and flocculation processes.

2. Materials and Methods

2.1. Materials

Kaolinite and sepiolite samples used in the experimental studies were obtained from the Eskisehir and Bilecik regions in Turkey, respectively. The XRD analysis of the Kaolinite and sepiolite are given in Fig. 1. The samples were dry-ground for 3 hours in a ceramic ball mill. The particle size analysis was performed using a Malvern Mastersizer 2000 device, and the particle size distributions of the ground samples are shown in Fig. 2. As can be seen, 80 % of the ground

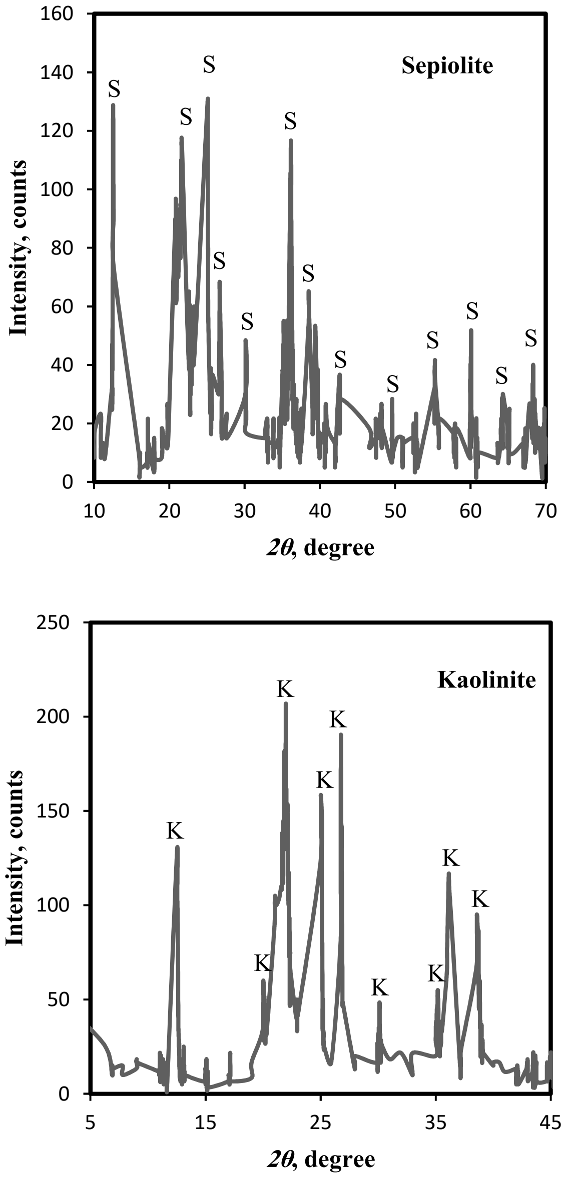


Fig. 1. X-ray diffraction pattern of the clay samples.

samples of kaolinite and sepiolite are finer than 78 and 39 µm, respectively. Sodium silicate (Na_2SiO_3) (Merck) was used as a dispersant for these clay minerals. Sodium hydroxide and hydrochloric acid were used to adjust the pH values in the zeta potential measurements. Ultrasonic treatment was conducted using an ultrasonic homogenizer (Bandelin HD 3200) and a titanium probe (horn-type equipment). The device has a constant frequency of 20 kHz, and its highest ultrasound output power value is 200 W.

2.2. Ultrasonic treatment and dispersion experiments

The experiments were conducted in a 400 cm^3 cylindrical beaker with four baffles using 1 g of the clay sample and 300 cm^3 of distilled water. In

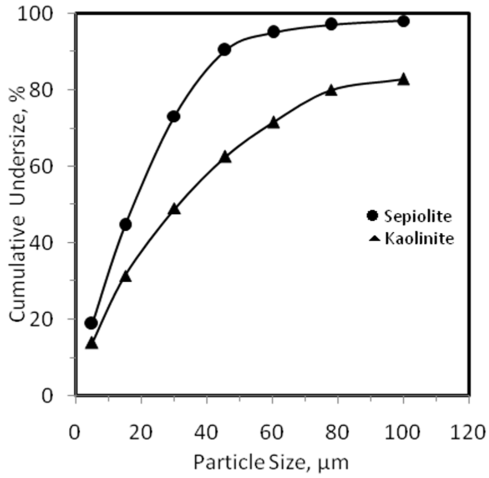


Fig. 2. The particle size distribution of the clay samples used in the experiments.

the experiments without ultrasound, the dispersed suspension was conditioned with a magnetic stirrer at a rotation speed of 500 rpm for 2 min at the natural pH. Then, sodium silicate was added to the suspension, and the suspension was conditioned with a magnetic stirrer for 2 min. After that, the system was stopped, 1 min settling time was allowed for the suspension, and then 20 cm^3 of the sample was taken out at a fixed distance of 5 cm below the air-liquid interface for turbidity measurements. In the experiments with ultrasound, after adding the dispersant, the suspension was treated with the ultrasound device for 2 min. A digital turbidimeter (Velp Scientifica) was used to measure the turbidity of the taken sample. The stability of suspension was determined using the formula given below in Eq. (1).

$$stability,\% = (T_f / T_0) \times 100 \quad (1)$$

where T_0 is the turbidity (nephelometric turbidity unit) of the original suspensions of clays and T_f is the turbidity of the taken sample when dispersion occurs.

The experiments were conducted at the natural pH (8.5) of kaolinite and sepiolite suspensions. Experimental studies were conducted at an ultrasonic power of 150 W and by adjusting the immersion depth of the ultrasonic probe to 2 cm. The ultrasonic treatment was performed as a batch regime, i.e., sequential pulsation on for 5 sec and pulsation off for 10 sec.

2.3. Zeta potential measurements

A ZetaPlus apparatus from Brookhaven was used for the zeta potential measurements. A 1 g sample was taken for zeta potential measurements; it was mixed for 3 min in 300 cm^3 distilled water at the natural pH, and then sodium silicate was added, and the suspension was treated with ultrasound for 2 min (the suspension was mixed with the magnetic stirrer for 2 min in the experiments without ultrasound). Thereafter, the system was stopped and paused for 2 min to allow the coarser particles to precipitate. Then, a sample of the supernatant was taken out and placed in a cell made of plastic. Twelve runs were measured for the zeta potential of each sample, and the average values were reported.

3. Results and discussion

3.1. Effect of ultrasonic treatment on the stability of clay suspensions

The effect of ultrasonic treatment on the zeta potential of kaolinite and sepiolite at different pH values is presented in Fig. 3. As shown in Fig. 3, the isoelectric point (iep) of kaolinite in the measurements without ultrasound was found to be pH = 4.4. From the literature, we know that the iep value of kaolinite varies in the pH range of 2 - 4.5 [24]. In the zeta potential measurements with ultrasound, the iep of kaolinite was found to be the same value, meaning that the ultrasound did not have an important effect on the iep. In addition, the iep of sepiolite occurred at pH 4.2, and again, the ultrasonic treatment did not cause a change in the iep of sepiolite. This iep is very close to the value stated by Sabah *et al.* [25]. On the other hand, the ultrasonic treatment increased the negative surface charge of both clay minerals at pH values higher than the iep.

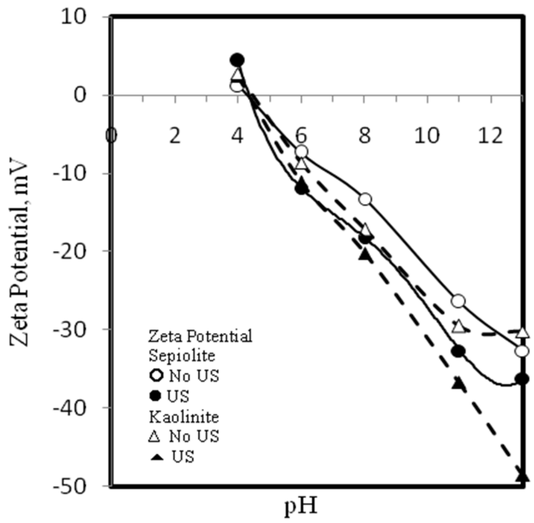


Fig. 3. The effect of ultrasonic treatment on the zeta potential of clays at different pH values.

Fig. 4(a) illustrates the stability of kaolinite and sepiolite suspensions depending on the ultrasonic power (batch application). As seen in Fig. 4(a), while the stability of kaolinite suspension decreased with increasing ultrasonic power, the stability of sepiolite suspension slightly increased at high ultrasonic power values. Fig. 4(b) also presents the effect of ultrasonic treatment time on the suspension stability of these minerals. The stability of the sepiolite suspension increased depending on treatment time; however, the stability of the kaolinite suspension showed a decreasing trend. Chen *et al.* [26] examined the effect of the ultrasonic process on montmorillonite suspension and stated that ultrasonic treatment decreased turbidity values of a montmorillonite suspension with increasing treatment time. Clays have different crystal structures; therefore, the application of ultrasound may be said to show different effects on the suspension stability of clay minerals.

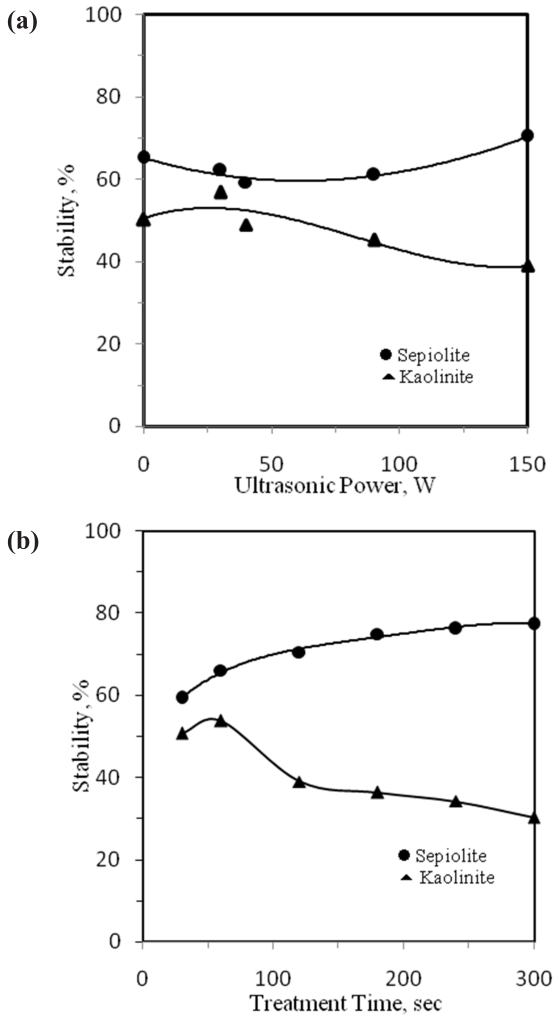


Fig. 4. The stability of clay suspensions depending on (a) ultrasound power and (b) treatment time.

The effect of batch and continuous ultrasonic treatment on the stability of kaolinite and sepiolite suspensions is presented in Fig. 5. The treatment regime of ultrasonication also significantly affected the suspension stability. For both clay minerals, the continuous ultrasound treatment led to higher suspension stability values. In other words, the continuous application was more effective in achieving more successful dispersions of clay minerals, especially sepiolite.

3.2. Effect of ultrasonic process on the dispersion of clays with sodium silicate

The stability of kaolinite and sepiolite suspensions depending on the ultrasonic power (continuous application) in the presence of sodium silicate (0.4 $g.dm^{-3}$) is shown in Fig. 6(a). As can be seen, the stability of both clay suspensions sharply increased until a certain power value and thereafter only slightly increased. Fig. 6(b) illustrates the effect of ultrasonic treatment time on suspension stability. The stability of the sepiolite suspension increased with increasing treatment time, while the stability of the kaolinite suspension increased towards a certain treatment time and then showed a slight decrease.

The effect of batch and continuous ultrasonic treatment on the dispersion of kaolinite and sepiolite suspensions is presented in Fig. 7. The continuous application of ultrasound resulted in higher stability values of both mineral suspensions with sodium silicate. That is, the continuous application of ultrasound provided more successful dispersions of these clays with dispersant.

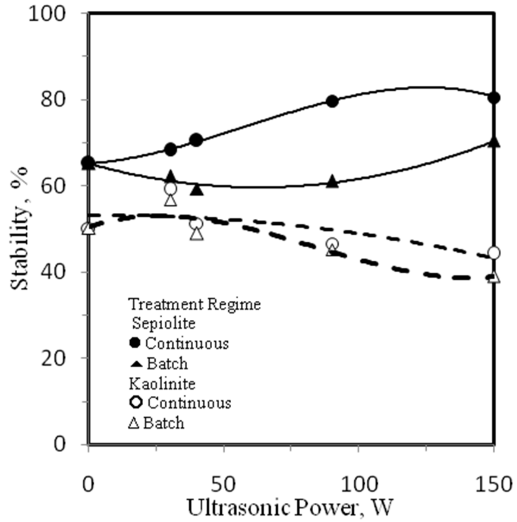


Fig. 5. The effect of the treatment regime of ultrasonic on the stability of clay suspensions.

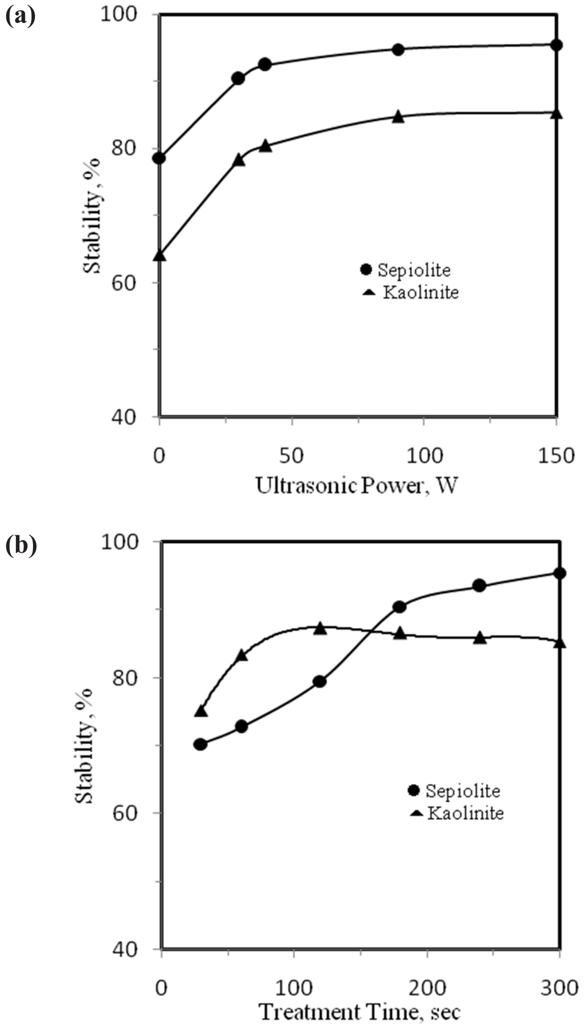


Fig. 6. The effect of (a) ultrasonic power and (b) treatment time on the dispersion of clay suspensions.

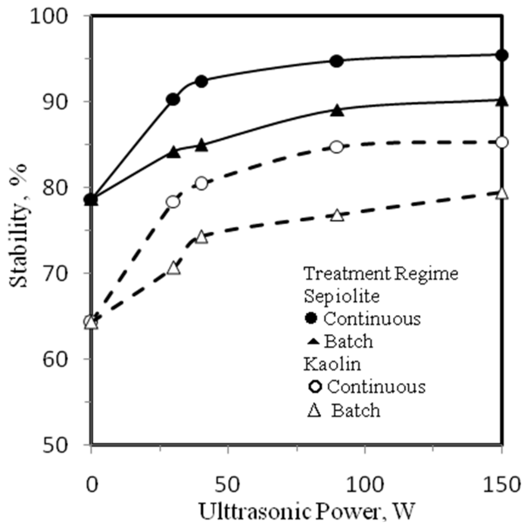


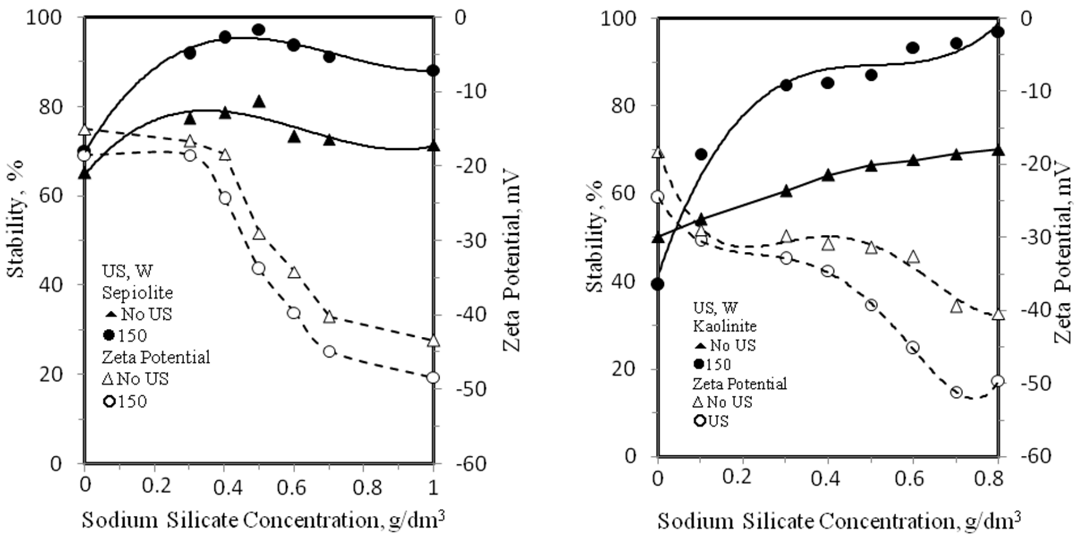
Fig. 7. The effect of the treatment regime of ultrasound on the dispersion of clay suspensions.

The effect of ultrasound at different sodium silicate concentrations on the stability and zeta potential of sepiolite and kaolinite is given in Fig. 8. The stability of the sepiolite suspension increased up to a particular concentration of sodium silicate, while the dispersion of kaolinite suspension improved with increasing dispersant concentration. Moreover, the stability values obtained with ultrasonic treatment for both clay minerals were higher than those obtained without ultrasound. The reason ultrasound application is more effective could be that the ultrasound process improves the effect of dispersant by providing a more uniform distribution in the suspension. On the other hand, the negative zeta potential of sepiolite and kaolinite increased depending on the dispersant concentration. Also, the ultrasonic treatment led to more negative zeta potentials for both clays. As it is known, the formation of dispersion processes in the suspension of solid particles is related to the surface charge of minerals. As stated in the literature, the dispersion process usually occurs at surface charges above ±15 mV [27]. When the suspension stability and zeta potential values of these minerals were examined, we found that the dispersion of clay suspensions improved with increasing surface charge, especially for the kaolinite mineral. The negative potential increase showed that electrostatic stabilization took place, and thus the particles repelled each other, providing a stronger dispersion [28,29]. Parsonage *et al.* also stated that sodium silicate is adsorbed by multiple weak bonds to generate hydrated layers on the mineral surface [30]. Consequently, dispersion is provided by both increased negative surface charges and hydrated layers. Andreola *et al.* proposed that the polymeric species of sodium disilicate may precipitate on the surfaces of kaolinite [31]. However, Ma suggested that sodium silicate kaolinite interactions are purely electrostatic [32]. Mekhamer also investigated the effect of ultrasound on bentonite suspension and stated that ultrasound treatment increased the zeta potential of bentonite and had a positive effect on suspension stability [33].

The effects of ultrasound treatment on the suspension stability and zeta potential of kaolinite and sepiolite in the absence and presence of sodium silicate (0.4 g.dm^{-3}) are summarized in Fig. 9. As can be seen, the dispersion of kaolinite and sepiolite suspensions with sodium silicate was significantly improved by the application of ultrasound. In addition, the negative zeta potential of these clays with dispersant was increased by ultrasound, resulting in stronger dispersion of kaolinite and sepiolite suspensions.

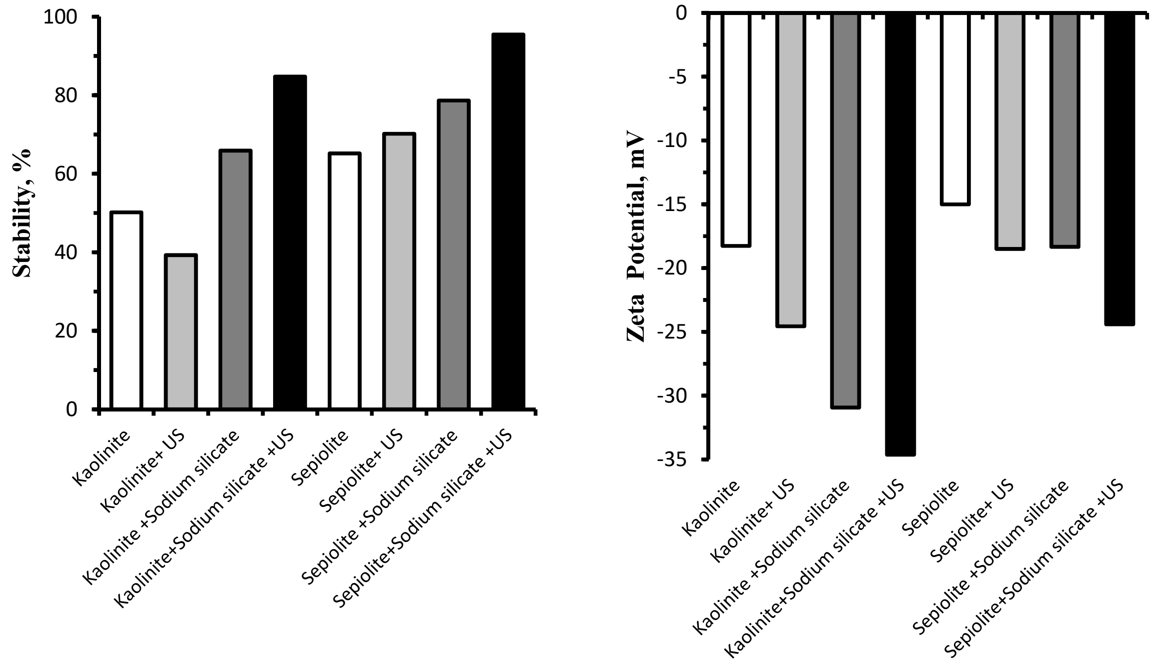
4. Conclusions

The ultrasonic power value, application regime (batch and continuous), and treatment time of ultrasound affected the dispersion of sepiolite and kaolinite suspensions. Some differences were observed in the behavior of these clay suspensions in the experiments carried out without dispersant. While the stability values of sepiolite slightly increased depending on the ultrasonic power, the stabilityf the kaolinite suspension decreased relatively. Also, the stability of the kaolinite suspension decreased, while the stability of the sepiolite increased with the prolongation of the ultrasonic treatment. On



(a) **(b)**

Fig. 8. The effect of ultrasonic process on the dispersion and zeta potential of clays depending on sodium silicate concentration.



(a) (b)

Fig. 9. The effect of ultrasonic treatment on the (a) suspension stability and (b) zeta potential of clays.

the other hand, the ultrasonic treatment did not change the isoelectric point of the clay; however, it increased the zeta potential negativity of the clays at pH values higher than the iep. In the presence of sodium silicate, the use of ultrasonic treatment significantly enhanced the dispersion of kaolinite and sepiolite suspensions. In addition, the negative zeta potential of sepiolite and kaolinite increased with increasing sodium silicate concentration. Furthermore, the ultrasonic treatment caused more negative zeta potential values for both clay minerals with dispersant, resulting in more powerful dispersion of kaolinite and sepiolite suspensions.

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