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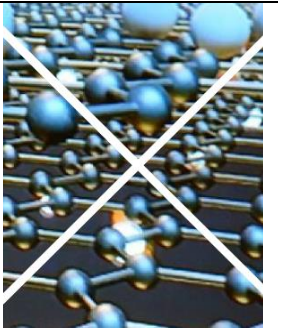

REMOVAL of DYE POLLUTION by MODIFIED HALLOYSITE as ECO-FRIENDLY ADSORBENT

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Abstract

In this study, the adsorption capacity of modified halloysite was systematically investigated with respect to temperature in a batch process. The halloysite mineral used in this work was alumina silicate mineral containing similarly structural layers. Halloysite mineral was obtained from Biga Peninsula, Western Anatolia. The characteristic properties of the modified halloysite were analyzed using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The modification process of the halloysite was achieved using a Cetyltrimethylammonium bromide (CTAB) aqueous solution. Methyl orange was used as a model dye to find out the adsorptive percentage capacity of the modified halloysite. It was found that the adsorptive capacity of clay was increased by increasing the contact time and decreasing with temperature. The thermodynamic parameters as Gibbs Free Energy (ΔG^o), Enthalpy (ΔH^o), Entropy (ΔS^o) changes were calculated and the results showed that adsorption is exothermic and spontaneous. The unmodified-clay was used to compare the adsorptive property of the modified-clay for the methyl orange adsorption. The modified halloysite showed a better adsorptive capacity than the untreated halloysite for the adsorption of methyl orange.

Keyword: Adsorption, Halloysite, Methyl orange, Isotherm

1.Introduction

Many industries such as textile, food, plastics, cosmetics and paper are a source of serious contamination as their waste materials like dyes, are often discharged directly into the environment. Dyes are highly toxic, carcinogenic and mutagenic substances and cover a significant part of the aquatic environment pollutants [1]. In addition, dyes in aqueous solutions reduce sunlight and affect the photosynthesis of the aquatic plants [1-3]. Therefore, the treatment of dyes in the contaminated water is highly important. Many conventional techniques have been used for the removal of dyes and pigments from wastewater. Precipitation, flocculation, coagulation, adsorption, oxidation, aerobic and anaerobic degradation, filtration and such are some of the techniques used to clean wastewater [4-6]. The adsorption process is commonly used for wastewater treatment because of the simplicity of design, high efficiency, low-cost investment and ease of operation. In addition, it has wider applicability in water pollution control [7]. In the adsorption process, naturally occurring materials, some waste substances are preferably used as adsorbents [8-10]. There are various works on the use of low-cost materials like clays, fly ash, agricultural wastes [4,9,10]. Clays are modified by using different methods such as acid and heat treatment [11], organic or inorganic modification [12,13] and mixing with suitable polymers [14] in order to improve their adsorptive properties which are then called organoclays. Labastida and co-workers studied on organically modified clays and their composites to change the surface properties for optimized performance for the removal of anionic dyes from aqueous solutions using the adsorption technique [12]. Chen and coworkers used modified bentonite to remove methyl orange and some metal ions removal from water [15]. Kang et al., prepared an adsorbent from montmorillonite to investigate the adsorption of methyl orange as an anionic dye, in the single and binary system with methylene blue. The effects of pH value, initial dye concentration and contact time on the adsorption were conducted to estimate the adsorption capacity of methyl orange on the adsorbent [16]. Halloysite formed within the melting cavities of the clayey limestones is a silicate group clay mineral. These are created by the alteration of the magmatic depth, magmatic and metamorphic rocks. They include some minerals such as mica and feldspar. Halloysite is chemically similar to kaolin and has a hollow tubular structure like nanotubes as well as large surface area, therefore, it is suitable to be used in adsorption processess as adsorbent [17,18]. It has excellent physical and chemical properties and it is a suitable mineral to be mixed with polymers. Furthermore, halloysite is easily modified to further increase its adsorptive capacity. There are many review articles that discuss for the usage of halloysite-based materials to remove dyes, heavy metals, and other pollutants from wastewater [2,19,20].

The purpose of the present study was to assess the adsorption capacity of halloysite clay before and after modification for the removal of methyl orange dye from aqueous solutions. The adsorption capacity of the halloysite was increased by an easy and simple modification process. The adsorption capacities of the modified and unmodified halloysite during the adsorption of methyl orange were also compared with respect to temperature and time. The adsorption capacity of modified halloysite increases with time and decreases with temperature in a batch process. The characteristic properties of the unmodified and modified halloysite were analyzed using XRD and FTIR.

2. Materials and Methods

Halloysite mineral was gathered from Biga, Çanakkale Province, in Turkey. The cation-exchange capacity (CEC) of the halloysite is 1 meq/10g. The cetyltrimethylammonium bromide (CTAB) was 99% in purity and supplied from Sigma Company. Methyl orange was purchased from Merck and used as received.

Preparation of Adsorbents

The clay was first washed with distilled water to remove the water-soluble impurities and it was cleaned from dust. The wet clay was dried in an oven at 115-120 °C until constant weight. They were first grounded and sieved through a sieve (80 mesh). After the sieving process, the clay samples were stored in a desiccator for later use as an adsorbent (unmodified halloysite). To prepare the modified halloysite, 2 grams of unmodified halloysite were dispersed in 1mmol CTAB solution. The resultant solution was continuously stirred for 5h at 25°C.

Then the solution was centrifugated to remove the solid particles after settling down. The centrifuged product was then washed with distilled water and dried in an oven at 115-120 °C until unchanged of its weight.

Characterization

The main mineral phase composition of the halloysite was determined by X-ray Diffraction (XRD). The comparable XRD patterns are shown in Fig.1 (a) and Fig.1 (b), for unmodified halloysite and modified halloysite, respectively. XRD measurements of the halloysite samples were examined by X-ray powder diffraction (Philips diffractometer with a PW-1730 at 36 kV and 30 mA, using Ni-filtered CuK α-radiation). The scanning speed was 1°/min. The clay samples were first saturated with ethylene-glycol vapor at 55 ºC for 18 h and then X-rayed immediately. The Fourier transformed infrared spectra (FTIR) of the samples (Fig.2) were detected by the ThermoNicolet 380 FT model spectrometer.

Batch Experiments

Adsorption of methyl orange from aqueous solution was followed by the batch process. The effect of temperature and contact time on the adsorption were studied at 4 different temperatures as, 25°C, 40°C, 50°C 60°C. The initial concentration of methyl orange was 60 ppm prepared in distilled water. During the adsorption studies, the adsorbent weight/solution volume was used as 0.5g/50mL. The pH values of the solutions were adjusted to 6.5 with HCl or NaOH solutions. The changes in the concentration of methyl orange were followed by a UV-vis spectrometer (T-80, PG Instruments) at λ_{max} = 464 nm. The uptake percent values of dye solutions were calculated using Eq. 1.

$$\%\,Uptake = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

The amount of adsorbed dye/unit mass of the adsorbent (q_t) was estimated by the following equation.

$$q_t = \frac{C_o - C_t}{W} \times V \qquad (2)$$

where C_o and C_t (in mg/L) are the concentration of dye at initial time and at the time t, respectively. The C_t value turns to C_e at equilibrium which indicates the equilibrium concentration of dye.

3. Results and Discussion

Characterization of unmodified and modified Halloysite

The comparable X-Ray Diffraction patterns of the unmodified (Fig.1(a)) and modified halloysite (Fig.1(b)) showed that the distances between the layers in the modified halloysite have changed compared to the unmodified clay. As seen in Fig.1, the shifting of the peaks and decreasing in intensities in the modified clay indicate that the modification process was successful. These results are in agreement with the study conducted by Mahrez et. al [21].

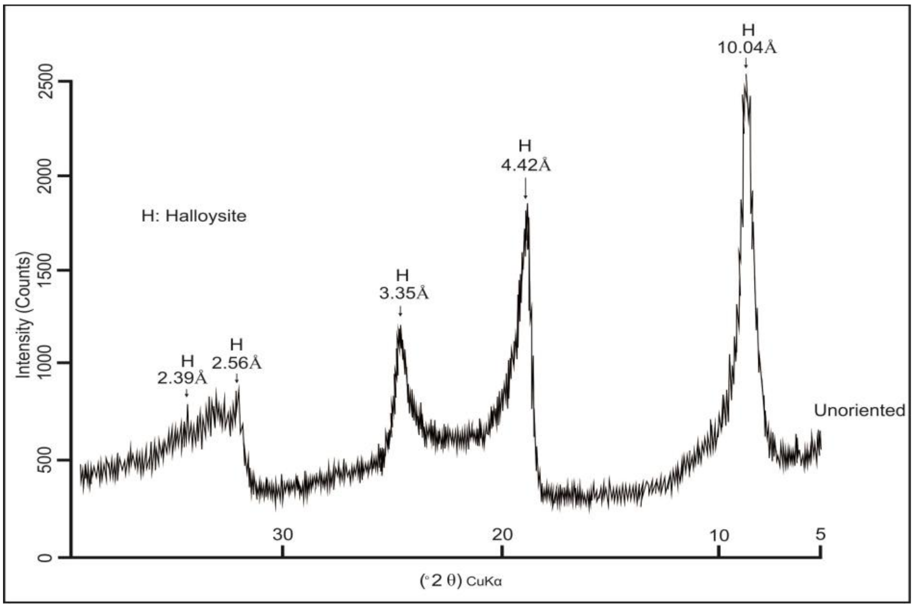

Figure 1 (a): XRD patterns of Unmodified Halloysite.

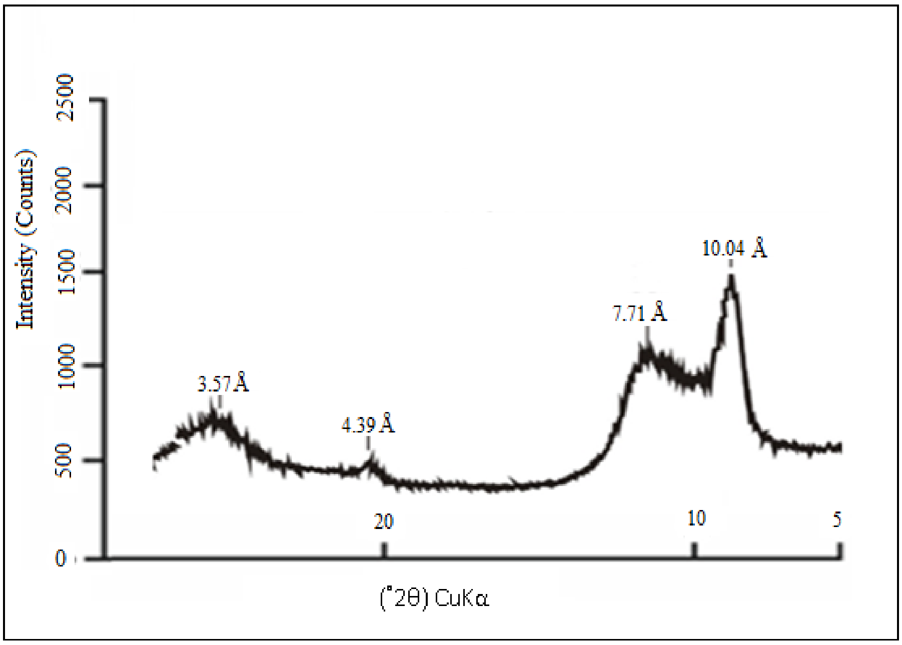

Figure 1 (b): XRD patterns of Modified Halloysite.

Fig 2 indicates the FTIR results of the unmodified and modified samples. The absorption peaks at 3695.5 cm^{-1} and 3617.6 cm^{-1} are referred to as the stretching vibrations of Al–OH bonds. Al–OH bending vibration, peaks can be observed at 1032.5 cm^{-1} and 910.2 cm^{-1} represent. Si–O stretching vibration peak is observed at 690.5 cm^{-1}. Modified Halloysite is shown to lose its outer hydroxyls, as evidenced by an intensity loss of the ~3695.5 cm^{-1} peak and shifted to 3635 cm^{-1}. Successful modification of the halloysite is further evidenced by the appearance of two peaks at 2935.4 cm^{-1} and 2863 cm^{-1}, and disappearance of the broad peak at 3472.4 cm^{-1} [22].

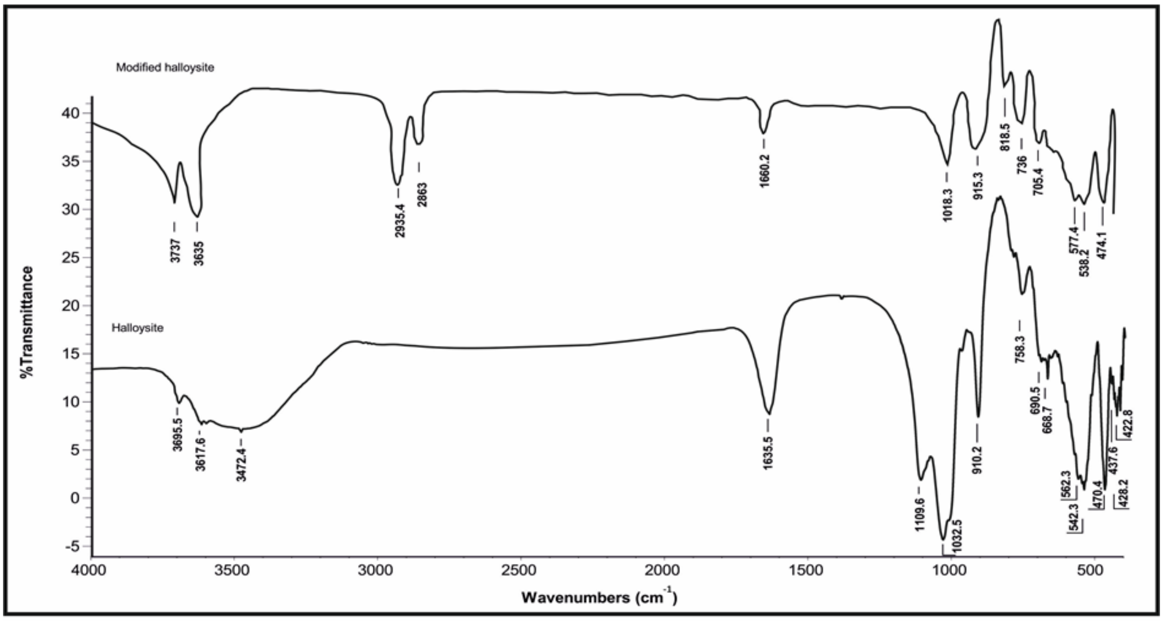

Figure 2. FTIR results of the unmodified halloysite and modified halloysite.

Effect of modification on adsorption

The adsorptive percentage capacities of the unmodified and modified halloysites can be seen in Fig. 3. The maximum adsorption (%) values were found as 45% and 83% for both the unmodified and modified halloysites, at 25°C, respectively (Fig.3). It can be seen that the modification process is effective on adsorption of methyl orange.

Effect of temperature on adsorption

The effect of temperature on the methyl orange adsorption was investigated at a constant dye concentration. The concentration of methyl orange was chosen as 60 ppm. The adsorption process was studied at 4 different temperatures as, 25°C, 40°C, 50°C 60°C to find the temperature effect on modified halloysite (Fig.4).

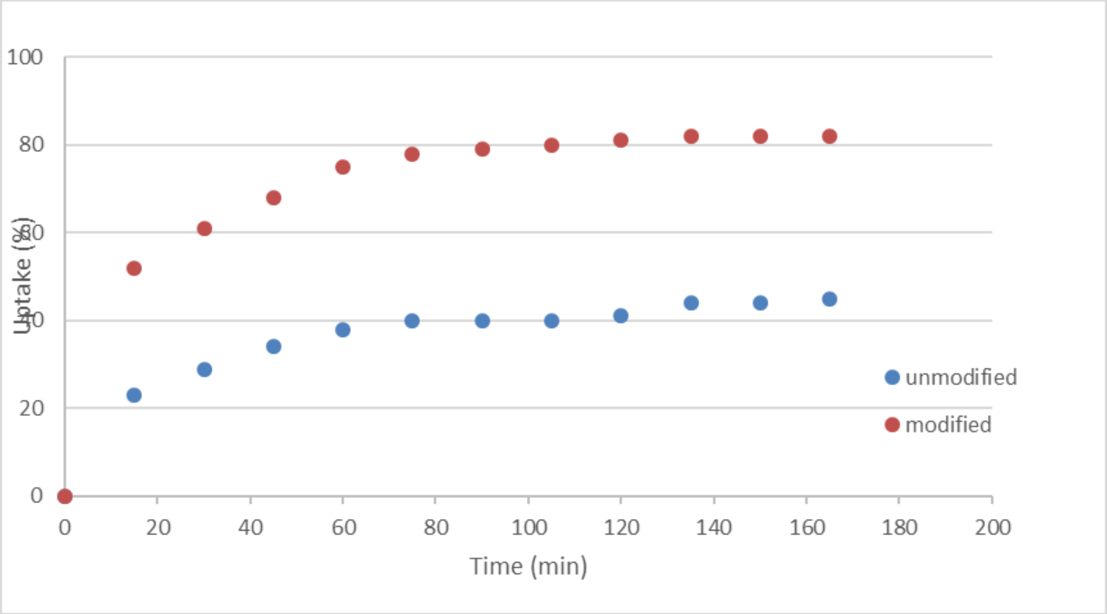

Figure 3. The adsorption (%) of Methyl Orange on modified halloysite, 60 ppm at 25°C.

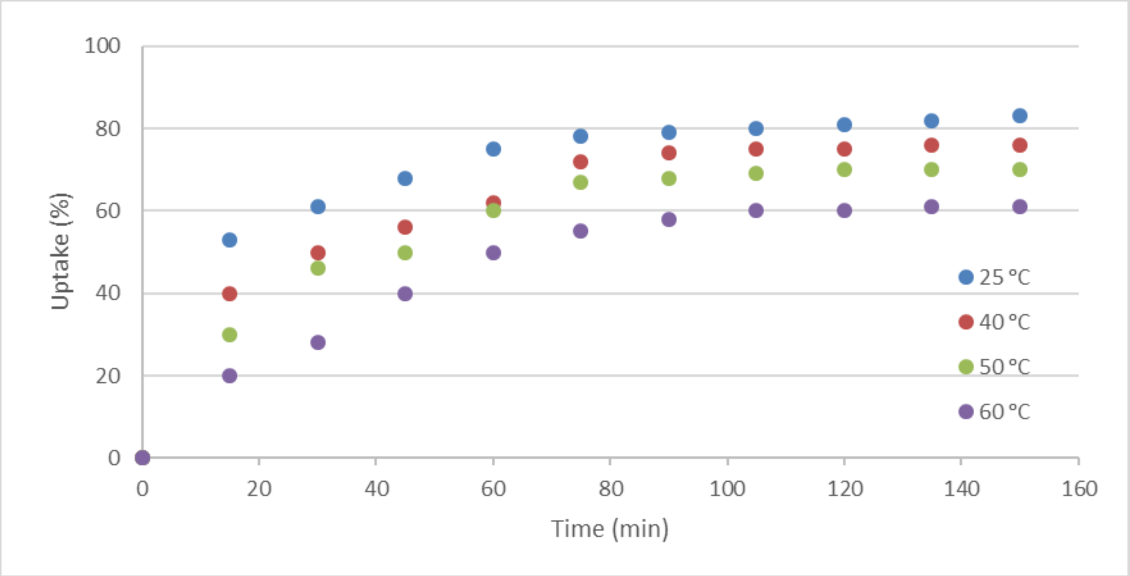

Figure 4. MO adsorption at different temperatures on modified halloysite, 60 ppm.

According to Fig.4 the percentage of adsorption at 25^{o}C was obtained 83%, while it was found 61% at 60 ^{o}C. These results indicate the exothermic nature of the adsorption process.

Thermodynamic study

In order to clearly understand the nature of adsorption, the thermodynamic parameters play an important role. The Gibbs free energy (ΔG^{o}) was estimated using the following equation,

$$\Delta G^o = -RTln(K) \tag{3}$$

The enthalpy (ΔH^o) and entropy changes (ΔS^o) were evaluated by using van't Hoff equation given below,

$$ln(K) = -\Delta G^o/RT = -\Delta H^o/RT + \Delta S^o/R \tag{4}$$

where, R is universal gas constant (8.314 J/molK), T(K) is the absolute temperature. K is equilibrium constant which is known as, distribution coefficient of the adsorbate and equals to the following equation. [23]

$$K = C_{ads}/C_e \tag{5}$$

Where C_{ads} (mg/L) denotes the amount of methyl orange adsorbed on the adsorbent at the equilibrium time (min) and Ce (mg/L) is the equilibrium concentration of dyes adsorbed. The plot of lnK against 1/T gave a straight line from which enthalpy and entropy changes were estimated from the slop and intercept, respectively (Fig.5). The thermodynamic parameters obtained at different temperatures investigated for methyl orange (60 ppm) were given in Table 1.

Table 1: The thermodynamic parameters for the adsorption of methyl orange onto modified Halloysite.

ΔH^o (J/mol)	ΔS^o (J/mol)	ΔG^o (J/mol)			
		298K	313K	323K	333K
-26375	-75	-3928.5	-2999.6	-2275	-1238.4

The negative values of ΔG^o mean that the adsorption is feasible and spontaneous when the temperature increases from 298K to 333K. The absolute magnitude of the ΔG^o value between 20 and 0 kJ/mol is assumed as physicsorption [24]. Therefore, ΔG^o values in Table 1 indicated that the adsorption of methyl orange on modified halloysite is physisorption. The negative value of enthalpy ΔH^o is confirmed the exothermic nature of the adsorption process. The negative value of entropy relates to the decreases randonmess between adsorbate-adsorbent interface during the adsorption process.

In addition, the high uptake percentage value of methyl orange at low temperature indicated that it is appropriate process in order to remove the methyl orange from aqueous solution with less energy consumption. Similar results obtained by S. Gamoudi and Srasra, in their study on the adsorption of methyl orange by Tunisian modified clay support the results in this work [25]. Unmodified-clay was used to compare the adsorptive property of the modified-clay during the adsorption process. The modified halloysite performed better capacity as an adsorbent than untreated clay for the adsorption of methyl orange.

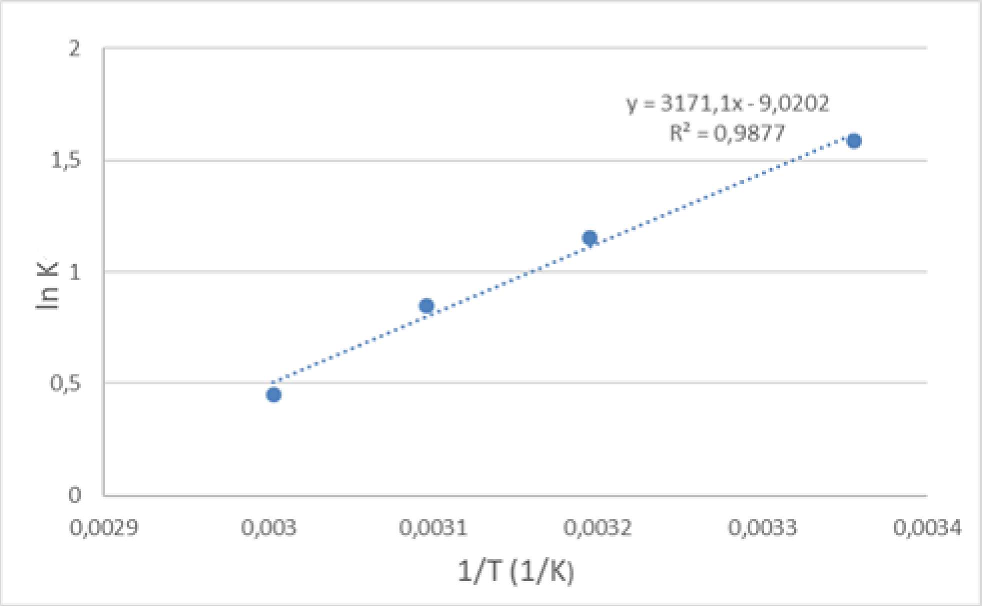

Figure 5. Plots ln K versus 1/T for adsorption of methyl orange on modified halloysite (50 mL solution, 60 ppm MO)

4. Conclusions

The adsorbing capacity of the methyl orange dye on modified halloysite as eco-friendly adsorbent was studied and the effect of temperature was discussed. The temperature effect showed that the adsorption of methyl orange on modified halloysite were an exothermic process in nature and mainly controlled by physical adsorption mechanism. The adsorption percentage of methyl orange on the unmodified halloysite indicated low uptake percentage comparing with the modified clay. The Gibbs energy (ΔG°) and entropy (ΔS°) were calculated and the results showed that adsorption process was spontaneous and feasible at low temperature. Negative enthalpy value (ΔH°) indicates that adsorption process is exothermic nature. The modified halloysite could be used as a low-cost and eco-friendly adsorbent for the removal of methyl orange anionic dye.

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