Enhanced adsorption of Direct Orange 26 dye in aqueous solutions by modified halloysite

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Abstract: The usefulness of untreated (H-NM) as well as modified by sodium benzoate (H-SB) and sulfuric acid (H-SA1 and H-SA2) halloysites as low-cost adsorbent for the removal of Direct Orange 26 azo dye from aqueous solutions was investigated. The kinetic data were evaluated in terms of the pseudo-first order and pseudo-second order kinetic models, while the equilibrium adsorption data were analyzed by the Freundlich and Langmuir isotherm equations. The data follows the pseudo-second order kinetic and Langmuir adsorption models. The DO26 adsorption capacities were 64.93, 74.07, 303.0, and 384.4 µmol/g for the H-NM, H-SB, H-SA1, and H-SA2, respectively. Adsorption of the dye was strongly pH dependent; no effect of ionic strength was observed. The study revealed that halloysites, especially acid-activated halloysites, could be used as an effective and low-cost adsorbents.

Keywords: halloysite, azo dye, Direct Orange 26, adsorption

1. Introduction

Halloysite is a natural clay mineral described as dioctahedral, which contains gibbsite octahedral sheet $(Al(OH)_3)$, and modified by siloxane groups at the outer surface (Duarte et al., 2012). Halloysite consists of hollow cylinder formed by multiple rolled layers. Layered halloysite occurs mainly in two different polymorphs: the hydrated form $(Al_2Si_2O_5(OH)_4 \cdot 2H_2O)$ and the anhydrous form $(Al_2Si_2O_5(OH)_4)$ (Massaro et al., 2017). Halloysite is mainly used as nanocontainer for the controlled release of several chemicals (e.g. drugs and various macromolecules), for hydrogen storage, catalytic conversion of hydrocarbons, and remediation of various environmental pollutants, especially *via* adsorption (Rawtani and Agrawal, 2012; Matusik, 2016; Yu et al., 2016; Anastopoulos et al., 2018).

As an adsorbent, halloysite is cheap, available in Poland on a large scale; it can also be modified to adjust adsorption properties of the mineral for a specific contaminant (Matusik, 2016; Yu et al., 2016; Wierzbicka et al., 2019; Kołodziejczak-Radzimska and Jesionowski, 2019). The features that determine its adsorption activity are its chemical structure, highly developed specific surface area and the presence of pores in the structure (Duarte et al., 2012; Aidong et al., 2016).

In recent years, numerous papers have described adsorption of many pollutants on raw and modified halloysites, including metal ions (Matusik, 2016; Yu et al., 2016), chlorophenols (Sahnoun et al. 2016), chloroanilines (Szczepanik et al., 2014; Szczepanik et al., 2017), pharmaceuticals (Jiang et al., 2016), and some dyes (Zhao and Liu, 2008; Luo et al., 2010; Kiani et al., 2011; Liu et al., 2011; Belkassa et al., 2013; Zhao et al., 2013; Bessaha et al., 2016). The latter authors chose different dyes belonging to different classes and groups of coloring substances as model water pollutants.

In our paper we chose azo dye Direct Orange 26 (DO26) as an example dye. This compound belongs to one of the most important group of dyes (azo dyes), which constitute between 60-70% of global production of synthetic dyes (Drumond Chequer et al., 2013.) In this work the halloysite modified by various types of chemical compounds was obtained. Sodium benzoate and sulfuric acid were selected as modifying substances. This choice was due to the following reasons. Halloysite modified by sodium

benzoate was previously used as a sorbent of free monomer during the preparation of phenol-formaldehyde resins. High efficiency this additive was observed in this process. Acid treatment, in turn, is commonly used to activate clay materials. Halloysite activated by sulfuric acid displays increases in specific surface area, porosity, and adsorption capacity. Modified halloysite complies with two functions: a chemical sorbent of free monomer – effect of reaction between dyes and functional groups present on the surface of modified halloysite and a physical sorbent – effect of highly developed specific surface area. The first modification stage of the treatment of the mineral with ultrasounds was performed for the purpose of the generation of structural defects on the crystallographic surface. It is assumed that the formed defects will be active centers for coupling of organic compounds used for surface modification. As a result of this interaction, an organic layer is formed on the surface of the layer leading to the formation of the hybrid structure.

2. Materials and methods

2.1. Chemicals and materials

Direct Orange 26 azo dye ($C_{33}H_{22}N_6Na_2O_9S_2$, molecular weight: 756.67 g/mol, CAS number: 3626-36-6) was received from a Boruta-Zachem Kolor (Zgierz, Poland). The structure is shown in Fig. 1. All other analytical grade chemicals and reagents were from Avantor Performance Materials (Gliwice, Poland). Halloysite was obtained from Dunino mine (Intermark Company, Legnica Poland).
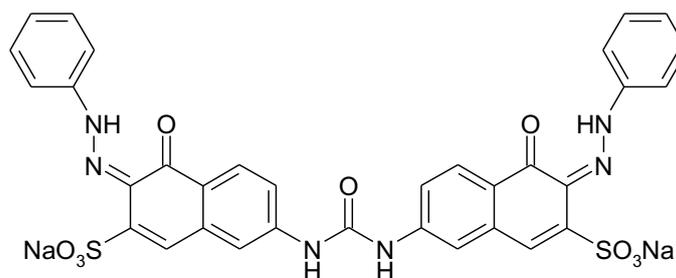
Fig. 1. Chemical structure of Direct Orange 26 azo dye

2.2. Halloysites modification and characterization

In this study, unmodified halloysite (H-NM), halloysite modified with sodium benzoate (H-SB) and sulfuric acid treated halloysites under two different conditions (H-SA1 and H-SA2) were used. The first stage involved the preliminary treatment of virgin halloysite fraction with ultrasounds of frequency 30 kHz for 2-4 h in an ultrasounds bath IS-7S (Intersonic S.C., Poland). The amount of a modifying compound used for halloysite modification was derived through numerous preliminary experiments. Modified halloysite materials were obtained by mixing a modifying compound and halloysite in room temperature in a solvent (demineralized water) by using stirrer and ultrasounds. The obtained product was separated from unreacted reagent to obtain the final modified halloysite. The names of the obtained modified materials are presented in Table 1.

Table 1. Name of modified halloysite materials and used modifying compounds

Material	H-SB	H-SA1	H-SA2
Halloysite (g)	90	92	80
Sulfuric acid (98%) (g)	-	8	20
Sodium benzoate (g)	10	-	-
Solvent (g)	200	200	200

The Brunauer-Emmett-Teller (BET) specific surface areas as well as micro- and mesopore volumes of the halloysite materials were calculated on the basis of measured low temperature nitrogen adsorption isotherms using a TriStar II 3020 V1.03 (Micromeritics Company, USA). Measurements of

their surface chemical compositions were carried out using JSM–6490LV (JEOL Company, USA) scanning microscope coupled with an energy dispersive X-ray spectrometer (EDS).

2.3. Adsorption procedure

The adsorption experiments were carried out by shaking 0.02 g of halloysite (raw or modified) with 20 cm^3 of adsorbate solution of known concentration (from 20 to 100 µmol/dm^3) in Erlenmeyer flasks. The samples were shaken under constant conditions (200 rpm, temp. 25°C) until equilibrium was reached. In the kinetic studies, the mixing time was 5, 10, 15, 20, 30, 45, 60, 90, 120, 180 and 240 minutes and the initial concentration of DO26 was 50 µmol/dm^3. The resulting mixtures were filtered through a filter paper and the filtrates were analyzed. A Carry 3E UV-Vis spectrophotometer (Varian, USA) was used to quantify the dye concentrations before and after the adsorption experiments (λ = 495 nm). The adsorbed amount of DO26 was calculated by taking the difference of initial concentration and final dye concentration in the filtrate to the equations:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

$$q_t = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where: q_t and q_e are the amounts of dye adsorbed onto adsorbent at time t and at equilibrium (µmol/g); C_0, C_t and C_e are the initial adsorbate concentration, concentration at time t and equilibrium concentration (µmol/dm^3); V is the volume of the solution (dm^3); m is the mass of the adsorbent (g).

The effects of pH and ionic strength on the dye adsorption were studied for initial DO26 concentration of 50 µmol/dm^3 according to the similar procedure. The effect of initial solution pH was investigated in the range pH 2.5-10.0, while the effect of ionic strength was studied for several NaCl concentrations (0-0.2 mol/dm^3). All the experiments were carried out in duplicate and the mean values were reported.

3.   Results and discussion

3.1. Halloysites characterization

Table 2 summarizes the surface areas (S_{BET}), total (V_t), micro- (V_{mi}) and mesopore (V_{me}) volume data for the materials. To determine the total pore volume as well as micro- and mesopore volumes Barrett-Joyner-Halenda and t-plot methods were used. Surface area values increase in order of H-NM < H-SB < H-SA1 < H-SA2. The mesopore volumes are significantly higher than micropore volumes in the case of each sample. Modification of halloysite by sodium benzoate led to a slight increase in the specific surface area, while the acid-activation gives the halloysite samples a significantly increased specific surface areas as well as the mesopore volumes. The H-SA2, modified under more drastic conditions than the H-SA1 (longer activation time and higher acid concentration), exhibits well-developed pore structure and higher specific surface area. The S_{BET} of H-SA2 is over three times higher than the specific surface area of non-modified halloysite (H-NM). These observations are consistent with the results obtained by other authors (Zhang et al., 2012; Belkassa et al., 2013; Szczepanik et al., 2014; Saklar and Yorukoglu, 2015; Garcia-Garcia et al., 2017; Szczepanik et al., 2017), who studied in detail the effect of time and concentration of acid on the halloysite activation.

Table 2. Textural properties of the halloysite samples

Adsorbent	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)
H-NM	53	0.217	0.019	0.198
H-SB	55	0.232	0.020	0.212
H-SA1	155	0.411	0.084	0.327
H-SA2	180	0.452	0.097	0.355

The composition of the surface of the halloysite samples from EDS is listed in Table 3. The chemical composition of halloysite samples surface shows considerable similarity except for H-SB. This difference

(presence of 28.5 %wt. C) is the result of modification with sodium benzoate. Modification of halloysite with sulfuric acid does not cause significant changes in the content of O, Al, Si, Fe.

Table 3. The EDS analysis results of the halloysite samples

Adsorbent	C	O	Al	Si	Fe
			wt. %		
H-NM	-	63.6	16.0	18.5	1.9
H-SB	28.5	31.3	21.1	18.0	1.1
H-SA1	-	63.1	15.8	19.2	1.9
H-SA2	-	64.3	15.9	17.9	1.9

3.2. Adsorption study

3.2.1. Adsorption kinetics

Fig. 2 shows the effect of contact time on the adsorption of DO26 from aqueous solution on all of the halloysites for initial adsorbate concentrations of 50 $\mu mol/dm^3$. The dye was fast adsorbed during the first 15 min and then more slowly until equilibrium was reached (around 60 min).
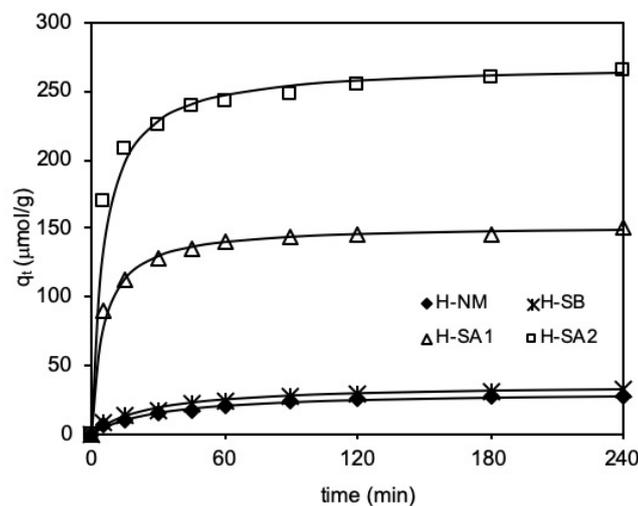
Fig. 2. Adsorption kinetics of Direct Orange 26 on the halloysites

Two well-known kinetics models, the pseudo-first order (Lagergren, 1898) and pseudo-second order (Ho and McKay, 1999), were used to analyze the experimental data. The linear equations of pseudo-first order (Eq. 3) and pseudo-second order (Eq. 4) can be expressed as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (3)$$

$$\frac{t}{q_1} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (4)$$

where: k_1 (1/min) and k_2 (g /μmol·min) are the kinetic rate constants, while q_e and q_t (μmol/g) are the amounts of adsorbed DO26 at equilibrium and at time t (min), respectively. The kinetic parameters k_1 and k_2 were obtained from the plots of $\ln(q_e - q_t)$ versus t and t/q_t versus t, respectively. To determine the fit quality, the adjusted determination coefficient (R^2) as well as the root mean sum-of-squares error (RMSE) were calculated. The RMSE is expressed by equation (5):

$$RMSE = \sqrt{\frac{1}{n}\sum_{i-1}^{n}(q_{exp} - q_{cal})^2} \qquad (5)$$

where: n is the number of data points, q_{exp} is the experimental value of q_e, and q_{cal} is the predicted (calculated) q_e obtained the from Eqs. (3) and (4). The results are listed in Table 4. As can be seen, the pseudo-second order kinetic model showed higher values of R^2 and lowest values of the root-mean squared error (RMSE). Moreover, the calculated adsorption capacities (q_{cal}) for this model, are much

more close to those obtained experimentally (q_{exp}) compared to the pseudo-first order model. All this suggests that adsorption of DO26 on all of the halloysites follows the pseudo-second order model.

Table 4. Constant parameters obtained from kinetic models for the adsorption of DO26 on halloystie samples

Kinetic model	Adsorbent			
	H-NM	H-SB	H-SA1	H-SA2
q_{exp} (µmol/g)	27.90	32.02	150.07	265.19
pseudo-first order model				
k_1 (1/min)	0.0175	0.0188	0.0251	0.0281
q_{cal} (µmol/g)	24.11	26.26	66.20	128.80
R^2	0.985	0.974	0.902	0.909
RMSE	6.35	10.64	68.01	60.02
pseudo-second order model				
k_2 (g/µmol·min)	0.901×10^{-3}	0.934×10^{-3}	1.266×10^{-3}	1.405×10^{-3}
q_{cal} (µmol/g)	29.01	35.21	151.51	270.27
R^2	0.997	0.997	0.996	0.997
RMSE	2.45	3.08	9.15	8.58

The DO26 was adsorbed faster on the modified materials than on the non-modified halloysite. The values of k_2 adsorption rate constants increased in the order: H-NM < H-SB < H-SA1 < H-SA2. It implies that the adsorption rate of the DO26 is closely related to the mesopore volume of the adsorbents (Table 2). The mesopores play the role of transporting "arteries" (Lorenc-Grabowska et al., 2016), thus the increase in the mesopore volume of the adsorbents corresponds to their faster uptake of adsorbate molecules from aqueous solution.

3.2.2. Adsorption isotherms

Adsorption isotherms of DO26 from aqueous solutions on the halloysites are shown in Fig. 3.

The Freundlich (1906) and Langmuir (1916) theoretical isotherms were used to identify the adsorbent-adsorbate interactions. The Freundlich isotherm model is related to the assumption that multilayer adsorption occurs on the heterogeneous adsorbent surface, while the Langmuir isotherm assumes that the adsorption happens on a homogeneous surface by monolayer adsorption without interaction between the adsorbate molecules. The Freundlich and Langmuir isotherm models are represented by the following linearized equations:

$$\log(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e) \tag{6}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{q_m b} \tag{7}$$
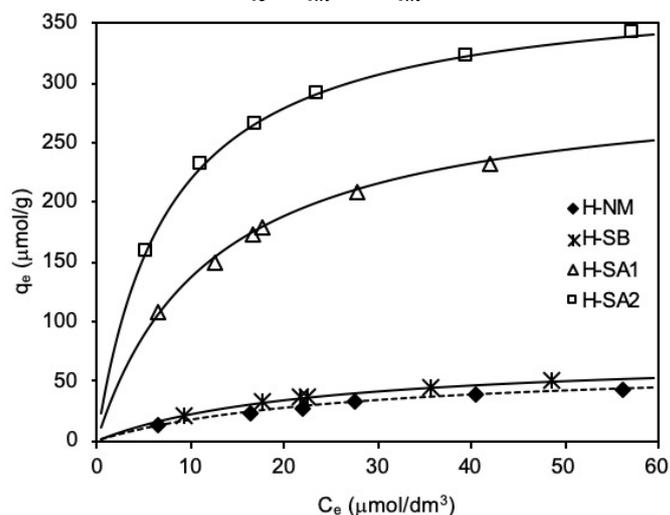
Fig. 3. Adsorption isotherms of Direct Orange 26 from aqueous solution on the halloysites

where: K_F ((µmol/g)(dm³/µmol)$^{1/n}$) and n are the Freundlich equation constants, q_m is the Langmuir maximum adsorption capacity (µmol/g), and b is the Langmuir constant (dm³/µmol).

The Freundlich and Langmuir isotherm parameters were calculated from the intercept and slope of $\ln q_e$ vs. $\ln C_e$ and C_e/q_e vs. C_e, respectively, and are given in Table 5.

Table 5. The Freundlich and Langmuir isotherm parameters of DO26 adsorption on the halloysites

Adsorption isotherm	Adsorbent			
	H-NM	H-SB	H-SA1	H-SA2
Freundlich				
K_F ((µmol/g)(dm³/µmol)$^{1/n}$)	4.901	7.315	51.13	89.21
n	1.792	1.956	2.381	3.184
R^2	0.982	0.971	0.962	0.943
RMSE	5.12	7.87	6.51	10.95
Langmuir				
q_m (µmol/g)	64.93	74.07	303.0	384.4
b (dm³/µmol)	0.037	0.044	0.082	0.133
R^2	0.994	0.997	0.999	0.999
RMSE	4.02	2.98	2.02	2.75

As seen from the isotherm parameters, the Langmuir equation showing higher values of R^2 as well as lower values of RMSE than those obtained for Freundlich model. The Langmuir model provides the better correlation for the experimental data which suggests that the DO26 adsorption on the halloysites occurs with monolayer and uniformity of identical active sites on the adsorbent surfaces.

The Freundlich (K_F) as well as the Langmuir (q_m) parameters followed the sequence H-NM < H-SB < H-SA1 < H-SA2. The adsorption capacities of the halloysites were closely correlated with their specific surface areas – they increased, in the same order, as the S_{BET} increased. The modification of halloysite by sodium benzoate led to a slight increase in its specific surface area, which resulted in a slight increase in its adsorption capacity. Much better results were obtained for acid-activated halloysites. The adsorption capacity of H-SA1 as well as H-SA2 exceeds several times the adsorption capacity of H-NM.

Table 6 compares the adsorption capacity of different types of adsorbents used for removal of DO26 dye. All this shows that halloysites are very effective adsorbents for removing dyes from water and that acid-activation allows to increase their adsorption capacity several times, thus making them very interesting and promising materials that can be an alternative to other expensive adsorbents, e.g. activated carbons.

Table 6. Comparison of DO26 dye adsorption on various adsorbents

Adsorbent	Adsorption capacity (mg/g)	Reference
halloysite H-NM	49.13	This study
halloysite H-SB	56.04	This study
halloysite H-SA1	229.3	This study
halloysite H-SA2	290.6	This study
beech wood sawdust	2.78	Izadyar and Rahimi, 2007
cherry wood sawdust	3.48	Kuśmierek et al., 2020
pine wood sawdust	3.49	Kuśmierek et al., 2020
oak wood sawdust	3.73	Kuśmierek et al., 2020
PVA–alginate immobilised rice husk	16.78	Safa et al., 2011
rice husk	19.96	Safa and Bhatti, 2011
magnetic Fe@graphite core-shell nanocomposite	28.30	Konicki et al., 2017
rye straw	30.84	Tomczak and Tosik, 2014
carboxymethyl cellulose immobilised rice husk	34.25	Safa et al., 2011
HCl treated rice husk	46.98	Safa et al., 2011

3.2.3. Effect of solution chemistry

Solution chemistry, including pH and ionic strength, are very important factors that can control the adsorption process as they can influence the charge of the adsorbent surface and adsorbate molecules, therefore inducing the electrostatic adsorbent-adsorbate interactions. The effect of solution pH and solution ionic strength on adsorption efficiency of the halloysites towards the removal of DO26 were investigated and results are shown in Figs. 4a and 4b, respectively.
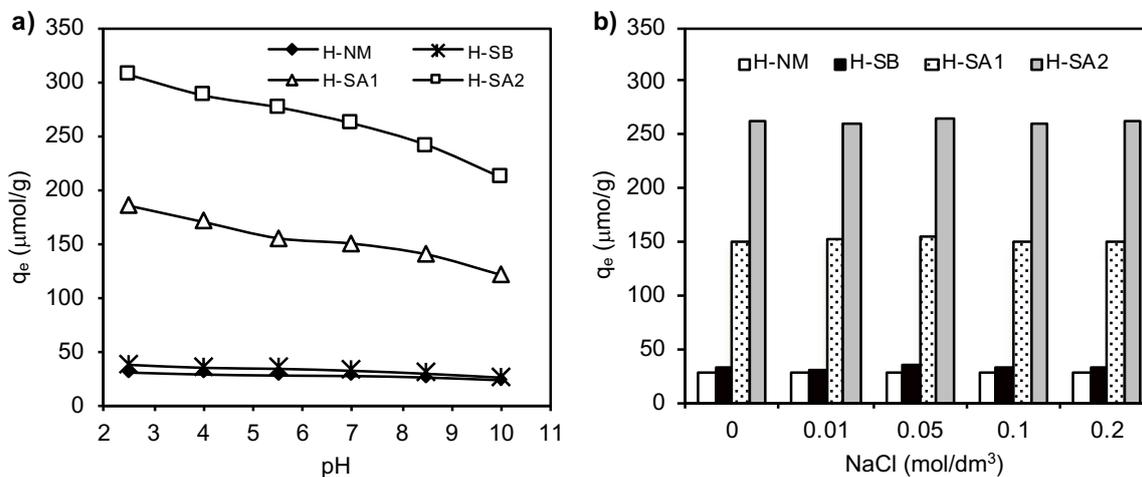
Fig. 4. Effects of initial solution pH (a) and solution ionic strength (b) on adsorption of Direct Orange 26 on the halloysite samples

The results from Fig. 4a show a decrease in removal efficiency with increasing pH to a minimum value on all of the halloysites. This behavior is due to the anionic nature of the dye, since it interacts with positively (pH < pH_{PZC}) or negatively (pH > pH_{PZC}) charged groups on the adsorbent surface. Under acidic (at a pH below pH_{PZC}) or alkaline (at a pH above pH_{PZC}) conditions the Al–OH and/or silanol Si–OH halloysite surface groups causing that the surface of the adsorbent is positively or negatively charged, respectively (Matusik, 2016). The points of zero charge of the halloysites were determined as described elsewhere (Kuśmierek et al., 2016) and were found to be 6.5, 6.1, 5.0 and 4.5 for H-NM, H-SB, H-SA1, and H-SA2, respectively. The DO26 is an anionic azo dye with sulfonic acid groups ($R-SO_3Na$) that occur in the dissociated form (as a sulfonate anions, $R-SO_3^-$) in the aquatic solution. The highest adsorption capacity values at pH of 2.5 is due to attractive electrostatic force between the positively charged adsorbent surface and negatively charged DO26 molecules. As the pH of the solution increases, the number of positively charged sites on the adsorbent surface decreases (and thus the number of negatively charged sites increases) which generates an electrostatic repulsive force with the dye anion. Similar phenomenon was reported for the adsorption of DO26 onto rice husk (Safa and Bhatti, 2011), magnetic Fe@graphite core-shell nanocomposite (Konicki et al., 2017) and on various sawdust (Kuśmierek et al., 2020).

The effect of sodium chloride concentration on the adsorption of DO26 on the halloysite samples is presented in Fig. 4b. According to these results, the inorganic salt presence (solution ionic strength) plays a secondary role in the DO26 adsorption on the halloysites.

4. Conclusions

In this study, raw halloysite (H-NM) as well as halloysites modified by sodium benzoate (H-SB) and sulfuric acid (H-SA1 and H-SA2) were applied as an attractive low-cost adsorbent for the removal of Direct Orange 26 azo dye from aqueous solution. The kinetic data were studied in terms of the pseudo-first and pseudo-second order kinetic models. The best fitting results were obtained with the pseudo-second order equation. The k_2 adsorption rate constants followed the sequence: H-NM < H-SB < H-SA1 < H-SA2. The equilibrium adsorption data were fitted to the Freundlich and Langmuir isotherms and the best results were achieved with the Langmuir model. The adsorption capacities of halloysites toward DO26 increased in the order: H-NM < H-SB < H-SA1 < H-SA2. The effects of solution pH and

ionic strength on the adsorption of DO26 were also investigated. The adsorption of the dye was pH dependent, while the ionic strength had negligible effect on the adsorption process. This study shows that halloysites, especially acid-activated halloysites, are an effective low-cost adsorbent for the removal of typical dyes form water.

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