

# EFFECTS OF ACID AND ALKALINE TREATMENTS ON EFFICIENCY OF DIATOMACEOUS EARTH IN REMOVAL OF TETRACYCLINE IN AQUEOUS SOLUTION

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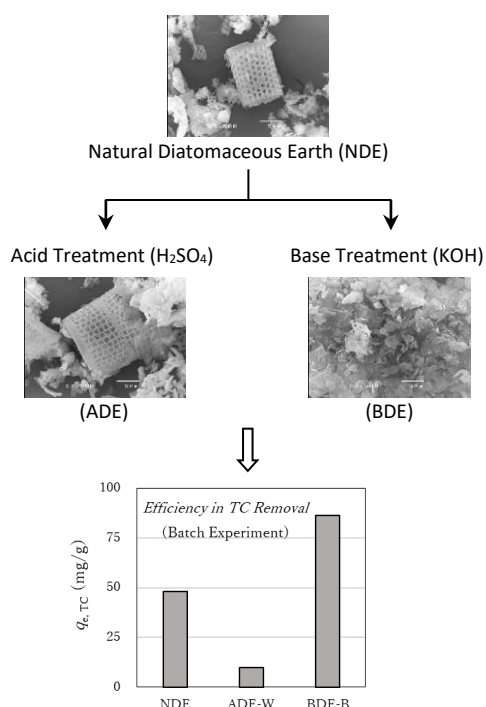
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## Graphical abstract



## Abstract

Contamination of tetracycline (TC) in environment may cause serious problems relating to increase of antibiotic resistance and development of new diseases. This paper focuses on TC removal by simple adsorption treatment and utilization of natural diatomaceous earth (NDE) as a cheap adsorbent. To improve efficiency of NDE, an impregnation method using acid (H<sub>2</sub>SO<sub>4</sub>) or base (KOH) was applied to modify NDE and influences of important activation parameters, concentration of reagent ( $C_{\text{reagent}}$ ), ratio of NDE weight and activating solution volume (*NDE-to-Sol*), temperature ( $T_{\text{act}}$ ) and time ( $t_{\text{act}}$ ), on the efficiencies of the obtained acid and base activated diatomaceous earths (ADE and BDE) were investigated. Batch adsorption experiment was performed at the same condition to evaluate TC adsorption capacities at equilibrium ( $q_{e,TC}$ ) of NDE, ADE and BDE. It was found that acid activation negatively affected  $q_{e,TC}$  and increases of  $C_{\text{H}_2\text{SO}_4}$ ,  $T_{\text{act}}$  and  $t_{\text{act}}$  resulted in poorer ADE. In contrast,  $q_{e,TC}$  was successfully enhanced through activation by KOH;  $T_{\text{act}}$  and  $t_{\text{act}}$  played more significant roles on the enhancement, comparing with  $C_{\text{KOH}}$  and *NDE-to-Sol*; impregnation at higher  $T_{\text{act}}$  and longer  $t_{\text{act}}$  could improve efficiency of BDE and the best BDE (BDE-B) with the highest  $q_{e,TC}$  (86.31 mg/g) was obtained at 3 M, 0.1 g/ml, 80 °C and 9 h.

**Keywords:** diatomaceous earth, sulfuric acid, potassium hydroxide, tetracycline, adsorption

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## 1.0 INTRODUCTION

In the last few decades, the global consumption of antibiotics has dramatically increased [1, 2]. Tetracycline (TC) is one of the most useful antibiotics since it has high activities against various microorganisms such as bacteria, mycoplasma, fungus and parasites. It is generally applied to human and veterinary therapeutics as well as aquaculture farms [1, 2, 3, 4].

Detection of TC residues, existing as parental drugs and their derivatives in the effluents of wastewater treatment plants, in aquaculture water and in the ecosystem including surface, river and ground water, in various countries around the world has been reported [1, 2, 3, 4]. The spread of TC residues in environment may seriously cause adaptation of microorganisms, increase of antibiotic resistance and finally development of new diseases [4]. Unfortunately, conventional wastewater treatment plants cannot completely remove TC

from wastewater [2, 3, 4, 5]. It is, therefore, necessary to develop an effective method for TC removal in wastewater treatment.

Several techniques such as adsorption, photolysis, ozonation, Fenton, photo-Fenton, membrane filtration, reverse osmosis, electrochemical process and flocculation and coagulation have been investigated for TC removal in aqueous solution [3, 4, 6]. Amongst these techniques, adsorption seems to be the most promising technology for TC removal due to its simplicity and low cost of operation. Several types of adsorbents with large surface area including activated carbons, carbon nanotubes, graphene oxide, biochar, natural clay, metal oxides, metal-organic framework mesoporous material, polymeric resins as well as the derivatives of these materials have been extensively investigated for TC removal from aqueous solution [7, 8, 9, 10, 11, 12]. However, available of cheap and abundant adsorbent that can be used without complicated treatment should be important for the success of adsorption treatment.

Diatomaceous earth (DE) or diatomite is a siliceous material which is naturally and abundantly available at low cost all around the world. Due to its excellent properties in uniformity of pore structure, high porosity, large surface area, low density and high stability, it has been widely used in various industrial applications such as filtration media, adsorbents, catalyst carriers, insulators, concrete fillers, biosensors [13, 14, 15, 16, 17, 18]. In literature, various techniques such as thermal treatment, chemical treatment, thermo-chemical treatment, hydrothermal treatment, precipitation and sol-gel were examined to modify physico-chemical properties and enhancing efficiencies of NDE as well as spent DE in removal of dyes, heavy metals and herbicides from wastewater numerously reported [19, 20, 21, 22]. Chao et. al. reported the potential of application of commercial DE for TC removal, without clarification of preparation method and DE properties [23].

Chemical activation using strong acids or bases as activating reagents has been widely used as a common procedure for preparation of natural clays which mainly contain oxides of Si and Al. During the treatment, acid or alkali attack leads to not only removal of residues but also dissolution of ions from the clay structure. Consequently, rearrangement of the structure, change of crystallinity, composition, type and amounts of surface functional groups, surface area and porous properties of the treated clays could be expected [24]. However, these complex changes strongly depend on composition of the clay itself as well as the condition of the treatment.

Impregnation with acid or base solution is considered as a simple method that could modify DE properties resulting in improving adsorption efficiency of DE [23, 25, 26]. Using 1-3 M of  $H_2SO_4$ , HCl,  $H_3PO_4$ , NaOH or KOH solutions increased methylene blue adsorption capacities about 1.69-fold to 2.52-fold, depending on type and concentration of the chemical [27]. However, effect of activating parameter on performance and properties of DE were not clearly reported for all the selected activating reagents.

The aim of this study was to investigate the feasibility of utilization of low-cost local diatomaceous earth (DE) as a highly effective adsorbent for removal of tetracycline from wastewater. Natural diatomaceous earth (NDE), sulfuric acid treated diatomaceous earth (ADE) and potassium hydroxide treated diatomaceous earth (BDE) were prepared and their efficiencies in tetracycline adsorption were comparatively

evaluated in isothermal batch experiment at the identical adsorption condition. Effects of important activation parameters, including concentration of activating solution ( $C_{reagent}$ ), ratio of NDE weight and activating solution volume ( $NDE-to-Sol$ ), activation temperature ( $T_{act}$ ) and activation time ( $t_{act}$ ), on the adsorption efficiencies of the prepared ADE and BDE were determined. In addition, the feasible activation approach was proposed based on these findings.

## 2.0 METHODOLOGY

### 2.1 Materials and Chemicals

Natural diatomaceous earth (NDE) was obtained from a local clay factory in Lampang, Thailand. It was fine powder and brown yellow in color.

Sulfuric acid ( $H_2SO_4$ , 98%), potassium hydroxide (KOH, AR grade, 85%, Univar) and inhouse distilled water were used to prepare aqueous solutions of activating reagents.

As a model solution of wastewater containing tetracycline (TC) group antibiotics, aqueous solution was prepared using tetracycline hydrochloride (AR grade, 99%, Vesco Pharmaceutical Co., Ltd.) and inhouse distilled water.

### 2.2 Characterization

Composition of the obtained natural diatomaceous earth was analyzed using a X-ray Fluorescence Spectrometer (JEOL; JSX3400R).

Porous properties including BET specific surface area ( $SSA_{BET}$ ), total pore volume ( $V_T$ ) and mean pore diameter ( $d_p$ ) were observed by measurement of adsorption-desorption isotherm of nitrogen at 77 K using a TriStar II Plus 3.02 (Micromeritics).

Morphological structures of the obtained powders were observed using a scanning electron microscope (LSM-5410LV; JEOL).

Crystalline structure was observed using an X-ray diffractometer (Empyrean Series 3; Malvern PANalytical®) under  $Cu K\alpha$  radiation at a speed of 5 °/min from 5 to 80°.

### 2.3 Treatments of Diatomaceous Earth

NDE was crushed and sieved to the particle size in the range of 180 to 850  $\mu m$  and used without further purification.

Acid activated diatomaceous earth (ADE) was prepared by impregnation method under reflux conditions. Typically, 3 g of NDE was mixed with 50 ml of sulfuric acid solution ( $NDE-to-Sol = 0.06 g/ml$ ,  $C_{reagent} = 4 M$ ) in a round bottom flask immersed in a silicone oil bath. The mixture was continuously stirred using a magnetic stirrer and heated to the activation temperature ( $T_{act}$ ) of 90 °C. After activation at constant temperature for 4 h ( $t_{act} = 4 h$ ), the mixture was naturally cooled to room temperature, the solution was taken out. To wash the obtained ADE, 100 ml of distilled water was added, the mixture was slightly shaken and ADE was separated from the washed water by centrifugation. This washing was performed several times until pH of the washed water was around 7. ADE was finally separated from the washed water by vacuum filtration through a filter paper (Whatman, pore diameter = 2.5  $\mu m$ ). The

obtained ADE was dried in an oven at 110 °C for 3 h before being stored in a desiccator.

Activation by KOH was also performed using impregnation method. Typically, 2 g of NDE was mixed with 20 ml of KOH solution ( $NDE\text{-to-Sol} = 0.1$  g/ml,  $C_{\text{reagent}} = 3$  M) in a glass bottle. The mixture was shaken at the activation temperature ( $T_{\text{act}}$ ) in an orbital shaker at 190 rpm. After the activation time was reached, the sample was then naturally cooled to the room temperature and washed with the distilled water with same procedure as washing of ADE. Then, the obtained BDE was dried and stored in the desiccator.

To investigate effects of activating reagent ( $H_2SO_4$  and KOH) and activation parameters on the modification of NDE,  $C_{\text{reagent}}$ ,  $NDE\text{-to-Sol}$ ,  $T_{\text{act}}$  and  $t_{\text{act}}$  were varied as summarized in Table 1.

**Table 1** Conditions for activation of NDE by  $H_2SO_4$  and KOH

Name	Reagent	$C_{\text{reagent}}$ (M)	$NDE\text{-to-Sol}$ (g/ml)	$T_{\text{act}}$ (°C)	$t_{\text{act}}$ (h)
ADE-1	$H_2SO_4$	2	0.06	90	4
ADE-2		4	0.06	90	4
ADE-3		6	0.06	90	4
ADE-4		4	0.02	90	4
ADE-5		4	0.10	90	4
ADE-6		4	0.06	80	4
ADE-7		4	0.06	100	4
ADE-8		4	0.06	90	2
ADE-9		4	0.06	90	6
BDE-1	KOH	1	0.10	60	1
BDE-2		3	0.10	60	1
BDE-3		5	0.10	60	1
BDE-4		3	0.05	60	1
BDE-5		3	0.15	60	1
BDE-6		3	0.10	50	1
BDE-7		3	0.10	70	1
BDE-8		3	0.10	60	2
BDE-9		3	0.10	60	3

## 2.4 Adsorption Experiment

Adsorption experiment was performed to investigate influence of activating agent and effects of the activation parameters on efficiency of the obtained adsorbent in TC removal. The dried adsorbent (0.02 g) was mixed with TC solution (10 ml) in a glass bottle. The mixture was then continuously shaken at 190 rpm in an orbital shaker at room temperature ( $T_{\text{ads}} = 26.5$  °C). After 6 h of adsorption, where the equilibrium of adsorption previously was confirmed, liquid sample (1 ml) was taken for quantification of TC. All adsorption experiments were performed at the same condition: initial concentration ( $C_0$ ) of 400 mg/l and adsorbent loading of 2 g/l. All the results reported here were the average of three replications.

Concentration of TC in aqueous solution was measured at wavelength of 355 nm using a UV-visible spectrophotometer (Evolution 210, Thermo Fischer Scientific). Calibration curves were constructed in range of 1 – 30 mg/l and  $R^2$  were not less than 0.9996.

To compare the efficiencies of all adsorbents, TC removal efficiency,  $R_{\text{TC}}$  (%), and adsorption capacity at equilibrium,  $q_e$  (mg/g), were calculated using Eqs. (1) and (2), respectively.

$$R_{\text{TC}} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{V(C_0 - C_e)}{m_{\text{DE}}} \times 100 \quad (2)$$

$C_0$  and  $C_e$  are concentrations of TC at initial time and at equilibrium (mg/l), respectively,  $V$  is volume of TC solution (l) and  $m_{\text{DE}}$  is mass of adsorbent (g).

## 3.0 RESULTS AND DISCUSSION

### 3.1 Properties of Adsorbents

Composition and porous properties of NDE are summarized in Table 2. XRF analysis revealed that NDE mainly consisted of  $SiO_2$ ,  $Al_2O_3$  and  $Fe_2O_3$  with the amounts of 71.90, 11.70 and 6.28 wt%, respectively. It also contained trace amount of  $K_2O$  (1.61 wt%). Nitrogen adsorption-desorption of NDE was categorized to Type IV of IUPAC system and  $SSA_{\text{BET}}$ ,  $V_T$  and  $d_p$  were 25.39  $m^2/g$ , 0.0298  $cm^3/g$  and 4.69 nm, respectively.

As will be clarified later, in the discussion on effects of activations on the obtained ADEs and BDEs, efficiency of all obtained ADEs were poorer than NDE whereas activation by KOH may improve adsorption efficiency of BDE. Only ADE with the worst performance (ADE-W; prepared at  $C_{H_2SO_4} = 4$  M,  $NDE\text{-to-Sol} = 0.06$  g/ml,  $T_{\text{act}} = 100$  °C and  $t_{\text{act}} = 4$  h) and BDE with the best performance (BDE-B) prepared in this work at  $C_{\text{KOH}} = 3$  M,  $NDE\text{-to-Sol} = 0.1$  g/ml,  $T_{\text{act}} = 80$  °C and  $t_{\text{act}} = 9$  h were selected as representatives to observe the modifications of composition (XRF), porous properties ( $SSA_{\text{BET}}$ ,  $V_T$  and  $d_p$ ), morphology (SEM) and crystallinity (XRD) due to the acid and base treatments.

As seen in Table 2, the composition of NDE was differently altered by the treatments; the acid treatment resulted in decrease of all compositions excepted  $SiO_2$  and hence Si/Al increased. On the contrary, only  $SiO_2$  content was reduced and the reduction of Si/Al ratio was found after KOH activation. As for porous properties, acid treatment resulted in slight increase in  $SSA_{\text{BET}}$  and significant increase in  $V_T$  and  $d_p$ . On the contrary, KOH activation resulted in decrease of  $SSA_{\text{BET}}$  and significant increase in  $V_T$  and  $d_p$ .

**Table 2** Composition of NDE, ADE-W and BDE-B

Property	Unit	NDE	ADE-W	BDE-B
$SiO_2$	wt%	71.90	81.60	51.20
$Al_2O_3$	wt%	11.70	7.86	19.20
$Fe_2O_3$	wt%	6.28	0.56	10.90
$K_2O$	wt%	1.61	1.54	5.69
MgO	wt%	0.412	0.236	0.843
CaO	wt%	0.215	0	0.692
Si/Al	-	5.44	9.18	2.35
$SSA_{\text{BET}}$	$m^2/g$	25.39	27.92	18.48
$V_T$	$cm^3/g$	0.0298	0.1101	0.1071
$d_p$	nm	4.69	15.78	23.19

As seen in SEM micrograph of NDE, Figure 1(a), it contains both good frustules as well as small debris. Most parts of NDE

still had uniform and ordered arrangement of the pores in their structures, Figure 1(b). Diameters of the pores roughly measured were around 1  $\mu\text{m}$ . After acid treatment by  $\text{H}_2\text{SO}_4$  at the most severe treatment condition, ADE-W shown in Figures. 1(c) and (d), these pores slightly enlarged and no significant change in morphology was observed. However, dramatical change in morphology of the prepared sample was observed

after treatment by KOH. Figures. 1(e) and (f) obviously show that no frustule in good shape and no well-arrange pore, as existing in NDE and ADE-W, were observed in BDE-B. Moreover, BDE-B appeared as agglomeration of fine flake-like units with the sizes of agglomerates widely varied from less than 1 to as large as 50  $\mu\text{m}$ . Etching reaction by KOH during the activation should be considered as the cause of this dramatical change.

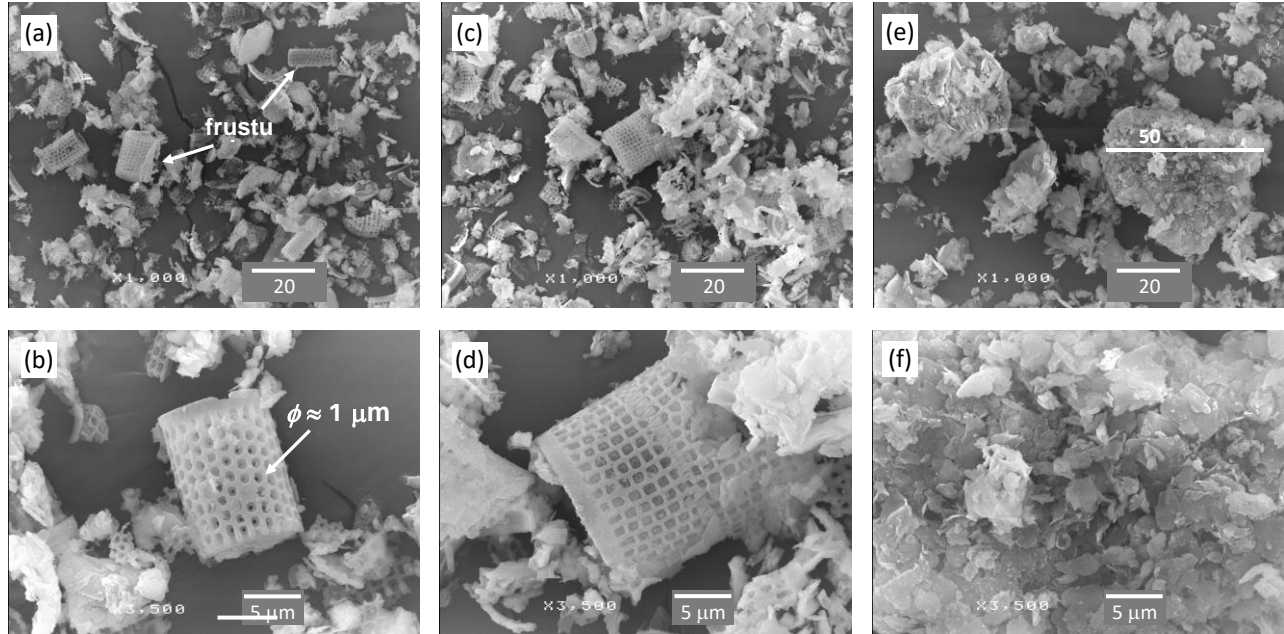


Figure 1 SEM images of (a, b) NDE, (c, d) ADE-W and (e, f) BDE-B

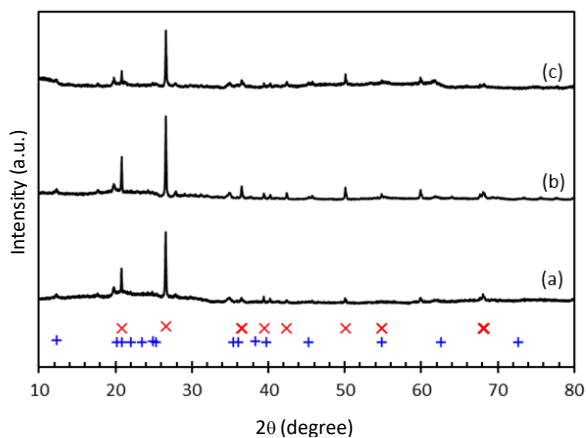


Figure 2 XRD patterns of (a) NDE, (b) ADE-W, and (c) BDE-B, (x) silica, (+) Kaolinite

XRD patterns of NDE, ADE-W and BDE-B are presented in Fig. 2(a), (b) and (c), respectively. Figure 2(a) reveals that NDE has a typical diffraction pattern of quartz with two strong peaks at  $2\theta = 20.8$  and  $26.6^\circ$ . The low intensity of peak appearing at  $12.37^\circ$  was assigned to trace of kaolinite, consisting Al, Si and O. Insignificant change of these peaks in the XRD pattern of ADE was observed, indicating that the crystalline structures in NDE were stable under the acid treating condition. In contrast, after the treatment by KOH, the peak at  $12.37^\circ$  disappeared and the relative intensity of the peaks at  $26.6^\circ$  and  $20.8^\circ$  significantly

changed, indicating that etching by KOH resulted in removal of kaolinite and transformation of quartz to different crystallite silica.

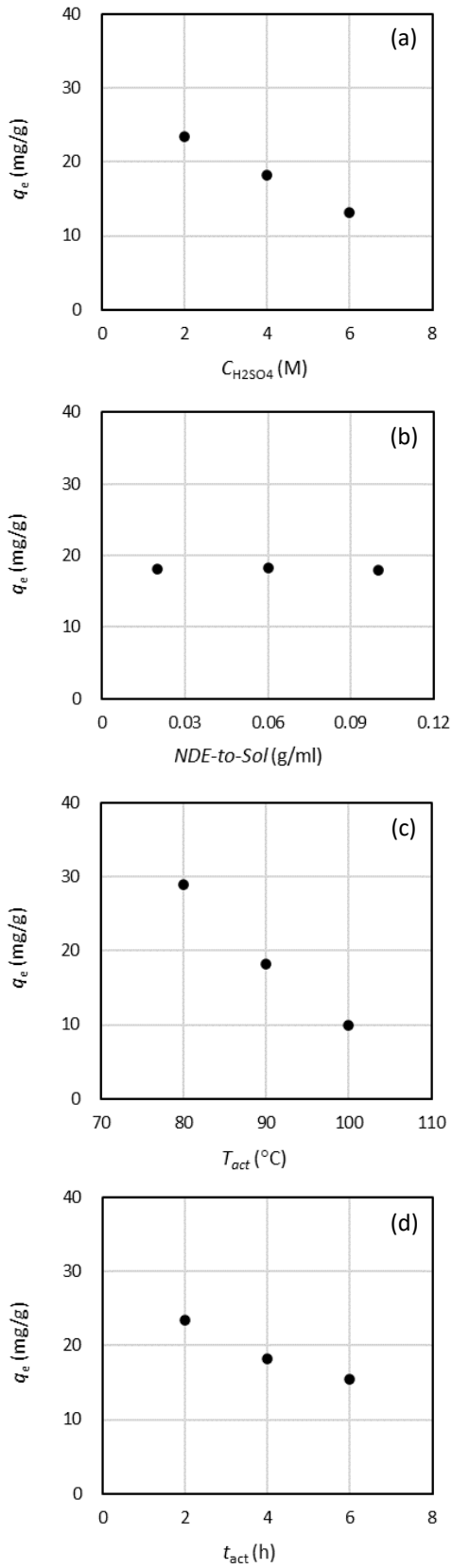
### 3.2 Adsorption Performance of NDE

Batch adsorption experiment at initial concentration of 400 mg/l and adsorbent loading of 2 g/l showed that adsorption of TC on NDE reached its equilibrium within 6 h and at the equilibrium NDE removed 23.41 % of TC with the adsorption capacity of 48.11 mg/g.

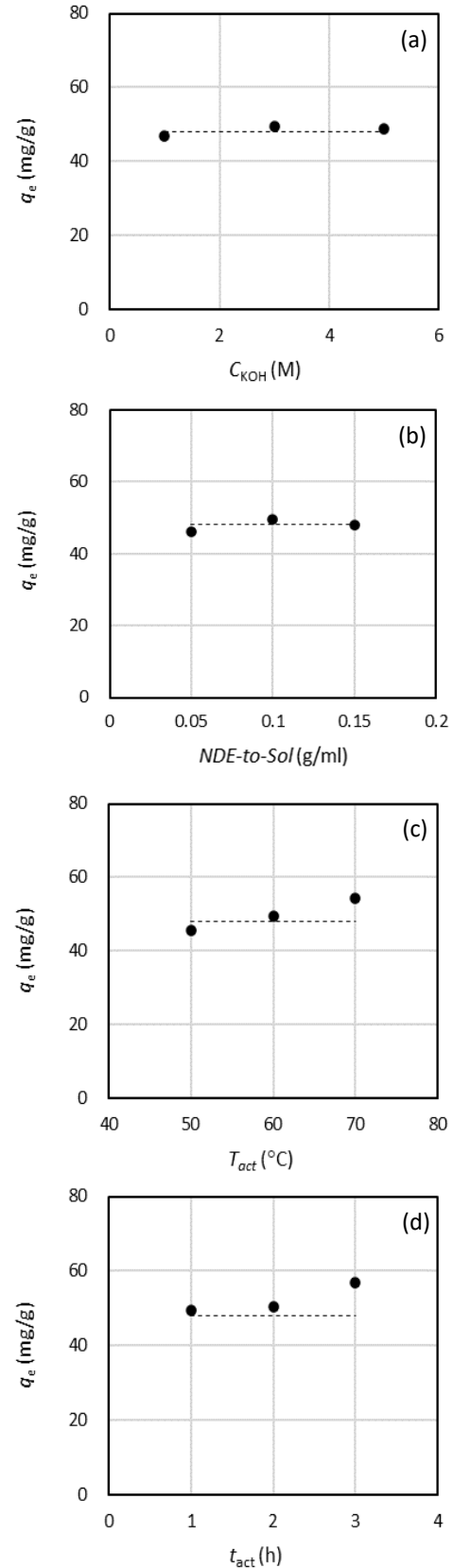
### 3.3 Effects of Activation Parameters on Efficiencies of ADE

$R_{TC}$  of all the obtained ADEs were calculated and were within 4.91 – 14.30 %, indicating that there was no limitation due to saturation of adsorption.

As shown in Figure 3, concentration of  $\text{H}_2\text{SO}_4$ , activation temperature and activation time strongly influenced the efficiencies of the obtained ADEs while effect of *NDE-to-Sol* on the efficiencies was negligible in the tested range. In addition, the performances of all ADEs were poorer than NDE,  $q_{e, ADEs}$  were in the range of 9.95 – 29.00 mg/g. It was difficult to explain this trend by the alteration of porous properties. Hence, the poorer efficiency should be considered as a result of the decrease of Si/Al.



**Figure 3** Effects of activation parameters (a)  $C_{H_2SO_4}$ , (b) NDE-to-Sol, (c)  $T_{act}$  and (d)  $t_{act}$  on efficiency of ADE



**Figure 4** Effects of activation parameters (a)  $C_{KOH}$ , (b) NDE-to-Sol, (c)  $T_{act}$  and (d)  $t_{act}$  on efficiency of BDE, (- - -)  $q_e$  of NDE as reference

### 3.4 Effects of Activation Parameters on Efficiencies of BDE

$R_{TC}$  of all the obtained BDEs were also calculated and it was confirmed that there was no saturation of adsorption occurred in the tested range;  $R_{TC} = 22.18 - 27.64 \%$ .

As shown in Figure 4, efficiency of BDE was improved as the activation temperature and the activation time were increased whereas concentration of KOH and *NDE-to-Sol* slightly influenced efficiency of BDE. Depending on the base treatment parameters, efficiencies of some BDEs were superior to NDE,  $q_{e, BDEs}$  were in the range of 45.75 – 57.04 mg/g.

### 3.5 Preparation of High Efficiency Adsorbent from NDE

The results discussed in the previous sections indicated the potential of activation of NDE by impregnation with KOH for application of TC removal in wastewater treatment. Therefore, to enhance efficiency of BDE, two important parameters ( $T_{act}$  and  $t_{act}$ ) were extended to wider range (80 °C and 12 h, respectively) and the insignificant parameters ( $C_{KOH}$  and *NDE-to-Sol*) were fixed at 3 M and 0.1 g/ml. It was found that the best BDE (BDE-B) was obtained at 80 °C and 9 h. At the adsorption condition of  $C_0 = 400$  mg/l, adsorbent loading = 2 g/l and room temperature, it could remove about 42.58 % of TC in the solution, corresponding to 86.31 mg/g. In comparison with efficiency of NDE,  $q_{e, BDE-W}$  was improved to reach around 1.79-fold of  $q_{e, NDE}$ . Depletion of Si/Al ratio likely affecting the surface silanol group was considered as a reason of enhancement of adsorption efficiency.

Although the complete isotherm data should give better comparison with the previous work [23] where Langmuir maximum adsorption capacity ( $q_m$ ) at 318 K of the commercial diatomite was around 20-303 mg/g, depending on adsorbent loading (1-5 g/l) [23], BDE-B prepared in this study should be considered as one of good adsorbents for TC removal.

## 4.0 CONCLUSION

In this study, natural diatomaceous earth (NDE) and diatomaceous earth modified by impregnation method using sulfuric acid and potassium hydroxide (ADE and BDE) were comparatively investigated. Comparison of SEM images and XRD patterns clearly revealed that etching by KOH significantly modified surface morphology, pore and crystallinity of NDE while  $H_2SO_4$  slightly affected these properties of NDE. As for TC removal efficiency, batch adsorption experiment indicated that the acid treatment resulting in poor adsorbents was not suitable to activate NDE for TC removal application, however, the activation by KOH was effective for this application. The most efficient BDE was obtained when NDE was treated with KOH at 3 M, 0.1 g/ml, 80 °C, 9 h. Its adsorption capacity was about 1.79-fold of  $q_{e, NDE}$ .

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