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# **Adsorption kinetics in removal of basic nitrogen-containing compounds from practical heavy oils by amorphous silica-alumina**

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## **Keywords**

Adsorption; vacuum gas oil; basic nitrogen-containing compounds; amorphous silica-alumina; kinetics; reusability

## **Abstract**

The adsorption behavior of basic compounds in practical vacuum gas oil is quantitatively analyzed on amorphous silica-alumina with acid sites, mesopores and thermal stability. Time course of adsorption capacity was found to be controlled by kinetics but not by equilibrium. The rate of adsorption was found to have pseudo second-order but not pseudo first-order kinetics, indicating that the adsorption rate was mainly controlled by the diffusion of large molecules. The particle size did not influence the adsorption quantity at equilibrium, whereas the smaller particle size increased the adsorption rate. The adsorption quantity at equilibrium was influenced by the molecular structure of basic compound due to steric hinderance around the basic site, whereas the adsorption rate strongly depended on the

molecular size, supporting that the adsorption rate was mainly controlled by the diffusion of compounds in the pores of amorphous silica-alumina. Comparison of solvents showed that the adsorption quantity at equilibrium was influenced by the polarity but not by the molecular size, while the adsorption rate strongly depended on both the polarity and molecular size. The reusability of adsorbent silica-alumina was demonstrated by the stable adsorption capacity and rate after calcination for the regeneration.

## 1. Introduction

The consumption of energy and chemical resources is exponentially increasing over the future, and the demand for fossil fuels inescapably rises to correspond population growth and preservation of living standards, although it is clear that the conventional crude oil is destined to run out. To meet the demands, more unconventional crude oil must be utilized, but it has the hydrocarbon molecules with extremely large number of carbon atoms and sometimes large number of aromatic rings as main components, as well as concentrated sulfur and nitrogen-containing compounds.<sup>1</sup> We developed a novel method of the dealkylation of alkyl polycyclic aromatic hydrocarbons over a solid acid<sup>2,3</sup> to separate the aromatic and aliphatic hydrocarbons at the initial stage of petroleum refinery. It will maximize the yield of mono-cyclic aromatics and minimize the yield of gas components, and is suitable for establishing a new platform of petroleum refinery based on crude-to-chemical strategy as an alternative to fluid catalytic cracking and hydrocracking/hydroprocessing.

However, this novel process needs removal of basic compounds from the feed oil before the treatment to avoid deactivation of the solid acid catalyst employed for the dealkylation.<sup>3</sup> The main purpose of this study is the

analysis of adsorption capacities and rates of adsorption of the basic nitrogen-containing compounds on adsorbent to establish the principles governing the adsorption. In addition to this purpose, the removal of basic compounds must be applied to improve the conventional deep hydrodesulfurization (HDS). The sulfur-containing compounds in the crude oil have been removed by deep HDS with Ni, Co, W and/or Mo catalysts under high temperature and pressure.<sup>4</sup> However, the concomitant basic nitrogen-containing compounds restrict the catalytic activity for HDS, and need to be thus eliminated from the oil by denitrogenation beforehand.<sup>5</sup> Also, hydrocracking and catalytic cracking should be affected by remained basic nitrogen-containing compounds due to poisoning acid sites on the cracking components of catalysts, which are concerned with zeolites and amorphous silica-alumina. Basic nitrogen-containing hydrocarbons have been removed by hydrodenitrogenation (HDN), which requires kinetically multiple steps, consumption of more H<sub>2</sub> gas, and higher temperature and pressure than HDS.<sup>6</sup> For example, the removal of sulfur from a dibenzothiophene molecule needs to add 4 hydrogen atoms, whereas the removal of nitrogen from a quinoline molecule needs to add 8 hydrogen atoms under severe reaction conditions.<sup>7</sup> In addition, it has been difficult to suppress the nitrogen content less than ppm order by HDN. Alternative denitrogenation to HDN, such as oxidative,<sup>8-10</sup> extractive,<sup>11 - 17</sup> and adsorptive<sup>18 - 27</sup> denitrogenation, has been studied recently. Among them, adsorption for denitrogenation does not need heated and pressurized reaction and expensive solvent, and thus should be superior operability and cost to the other methods and can be considered as a prime alternative technique.<sup>28</sup> The purpose of this study is fundamental investigation of the adsorption of basic compounds for the possible wide applications.

Basic nitrogen-containing compounds are adsorbed on solid surface by chemical or physical interactions. Chemisorption forms chemical bonds between the compounds and adsorbent and thus changes the electronic configuration of the compounds such as acid-base interaction, whereas physical adsorption retains the configuration due to interaction through van der Waals or electrostatic forces. Chemisorption is generally more strength and selectivity than physical adsorption, and depends on characteristics of nitrogen-containing compounds. However, it is difficult to regenerate the adsorbent at a low temperature after chemisorption, and thus the adsorbates need to be eliminated from the adsorbent by combustion.

Various adsorbents have been studied for adsorptive denitrogenation of real industrial feedstocks, including alumina,<sup>18</sup> silica gel,<sup>19</sup> activated carbon,<sup>20</sup> ion-exchanged resins,<sup>21</sup> polymers,<sup>23-24</sup> and zeolites.<sup>25-27</sup> A physical interaction is mainly workable on alumina, silica gel, activated carbon, and polymers. A small amount of acid sites on alumina, silica gel and, activated carbon can adsorb basic nitrogen-containing compounds, but the adsorption efficiencies were quite low.<sup>18-20</sup> Cation-exchange resins and zeolites can efficiently remove the basic compounds in the oil with acid-base interaction. However, it is difficult for ion-exchange resins to regenerate due to their low thermal and physical stability. Zeolites could be more appropriate than the others due to much acid sites and superior tolerance to heating and collisions with particles and vessels in the adsorption process. Nevertheless, microporous structure of zeolites should keep huge nitrogen-containing molecules off.

Amorphous silica-alumina possesses relatively much amount of acid sites in large pores (about 2 to 30 nm) and are composed of thermostable and firm structures. Therefore, it is expected to have higher adsorption capacities for the basic compounds and regenerable by burning. We have shown the applicability of amorphous silica-alumina

to the removal of basic compounds as a pretreatment for the dealkylation of alkyl polycyclic aromatic hydrocarbons.

<sup>3</sup> To provide adsorptive denitrogenation with amorphous silica-alumina as a practical process, it is essential to study adsorption kinetics and regenerative ability of adsorbent in chemisorption. In order to construct the process of removal by the adsorption, the quantitative analysis of control factor is required. Therefore, the adsorption kinetics of nitrogen-containing compounds on amorphous silica-alumina was analyzed with pseudo first-order and pseudo second-order kinetic models.<sup>29-31</sup> Pellet of adsorbent is manageable in industrial utilization, but the large particle size probably decreases the adsorption rate. Therefore, the primary concern is the influence of the particle size on the adsorptive kinetics. Practical oil contains wide variety of basic nitrogen-containing compounds (adsorptives) and other components (solvent), which should affect the adsorption rate. To investigate the influences, the model solutions of the practical oil were prepared from nitrogen-containing compounds with various basicity and molecular size and solvents with various polarity and molecular size, and the adsorptive kinetics were compared. The amorphous silica-alumina was examined to regenerate with heating in oxygen flow, and the repeatability of adsorption ability was verified.

## 2. Experimental

### 2.1 Materials

Amorphous silica-alumina (N631-L) was purchased from JGC Catalysts and Chemicals Ltd.. The characteristics were shown in **Table 1** and **Figure S1**. The particle shape had been cylinder (diameter 4.9 mm, height 4.9 mm) as supplied form. The particle was crushed and sieved into three types of samples; 0.5-0.8 mm, 1.0-1.7 mm and

1.7-2.8 mm. Quinoline, phenanthridine, hexane, and benzene were obtained from FUJIFILM Wako Chemicals. Acridine was acquired from Tokyo Chemical Industry. Hexadecyl-naphthalene (isomer mixture) was purchased from ExxonMobil Chemical, and description of the product was Synesstic 5. Vacuum gas oil (VGO) was obtained from vacuum distillation of a middle-east origin crude (final boiling point at 1008 K analyzed by distillation gas chromatography system; specific gravity 0.915 g mL<sup>-1</sup>; C 85.11 wt%, H 12.35 wt%, S 2.35 wt%, N 0.06 wt%).

## 2.2 Preparation of solution

The following solutions were prepared for this study (**Table 2Table 1**). VGO was mixed with benzene and hexadecyl-naphthalene for increasing the fluidity (VGO : benzene : hexadecyl-naphthalene = 1 : 1 : 0.11) and named as solution #1. To examine the influence of nature of basic compounds, 20 μmol g<sup>-1</sup> of quinoline, phenanthridine or acridine was mixed in hexadecyl-naphthalene as a model alkyl polycyclic aromatic hydrocarbon (solution #2-4). As model solutions to study the influences of solvent, 20 μmol g<sup>-1</sup> of quinoline was mixed in benzene or hexane (solution #5-6). To compare the influences by the matrix compounds contained in VGO as a solvent, the solution #1 was once treated with cation exchange resin to remove basic compounds completely, and then, 20 μmol g<sup>-1</sup> of quinoline was added (solution #7).

## 2.3 Adsorption experiments

Amorphous silica-alumina as an adsorbent was dried at 353 K overnight for removal of adsorbed water, and then added to the solution. The amount of added adsorbent was 5.0 wt% to solution #1 or 2.5 wt% to the other

solution. After stirring for determined time, the solutions were filtered off. The amount of base in the solutions was measured by neutralization titration with the perchloric acid method using an automatic neutralization titrator (916Ti-Touch, Metrohm AG). Perchloric acid (0.1 mol L<sup>-1</sup>, acetic acid solution) was dropped into a mixed solution of 80 mL of chlorobenzene, 40 mL of acetic acid, and 20 g of the removed solution. The control experiment without the removed solution was also performed.

The base concentration in the removed solution  $C$  ( $\mu\text{mol g}^{-1}$ ) was calculated from the value after the subtraction of the amount of dropped acid in a control experiment from the amount of the dropped acid until the neutralization point. The adsorption quantity  $q_t$  ( $\mu\text{mol g}^{-1}$ ) at different adsorption time  $t$  (hr) was determined using the following equation:

$$q_t = \frac{(C_0 - C_t)m}{W} \quad (1)$$

where  $C_t$  ( $\mu\text{mol g}^{-1}$ ) is the base concentration at time  $t$  (hr) in the solution.  $W$  and  $m$  are the weight of the adsorbent (g) and the weight of the solution (g), respectively.

The adsorption kinetics was calculated using pseudo first-order and pseudo second-order kinetic models.<sup>29</sup>

The pseudo first-order equation is as follows:

$$\frac{dq_t}{dt} = k_{1ad}(q_e - q_t) \quad (2)$$

where  $q_e$  ( $\mu\text{mol g}^{-1}$ ) is the adsorption capacity at equilibrium, and  $k_{1ad}$  ( $\text{hr}^{-1}$ ) is the rate constant of pseudo first-order adsorption. Equation (2) was integrated with the boundary conditions  $t = 0$  to  $t = t$  and  $q_0 = 0$  to  $q_t = q_t$  to obtain equation (3):

$$\ln(q_e - q_t) = \ln q_e - k_{1ad}t \quad (3)$$

The values of  $\ln (q_e - q_t)$  were plotted against  $t$ .

The pseudo second-order equation is as follows:

$$\frac{dq_t}{dt} = k_{2ad}(q_e - q_t)^2 \quad (4)$$

where  $k_{2ad}$  ( $\text{g mmol}^{-1} \text{hr}^{-1}$ ) is the rate constant of pseudo second-order adsorption. Equation (4) was integrated with

the boundary conditions  $t = 0$  to  $t = t$  and  $q_0 = 0$  to  $q_t = q_t$  to obtain equation (5):

$$\frac{t}{q_t} = \frac{1}{k_{2ad}q_{e,2ad}^2} + \frac{t}{q_{e,2ad}} \quad (5)$$

and

$$h = k_{2ad}q_{e,2ad}^2 \quad (6)$$

$h$  ( $\mu\text{mol g}^{-1} \text{hr}^{-1}$ ) is the initial adsorption rate at time approaching  $t = 0$ . The values of  $t/q_t$  were plotted against  $t$ . If the

plots give a linear relationship,  $q_{e,2ad}$  and  $k_{2ad}$  were determined from slope and intercept

## 2.4 Regeneration of adsorbent

After removal of the basic compounds, amorphous silica-alumina was regenerated by calcination. The sample was packed in a glass tube (i.d. 18 mm) and calcined in a flow of oxygen ( $0.022 \text{ mmol s}^{-1}$ ) at 773 K for 2 hr. After drying at 353 K, the adsorbent was utilized for next removal.

### 3. Results

Firstly, adsorption behavior of basic compounds in Solution #1 on amorphous silica-alumina (5.0 wt% for Solution #1) was observed. **Figure 1** shows time courses of amount of adsorbed basic compounds ( $q_t$ ) on amorphous silica-alumina with various particle sizes. There were no significant differences of the adsorption quantity ( $q_e$ ) after at most 150 h, most probably at the saturation due to equilibrium, between the silica-alumina samples, indicating that the equilibrium adsorption capacity  $q_e \approx 85 \mu\text{mol g}^{-1}$ . This value was obviously smaller than the cation exchange capacity of this silica-alumina,  $0.15 \text{ mol kg}^{-1} = 150 \mu\text{mol g}^{-1}$ . These indicates that the adsorption of bases on the silica-alumina in the present conditions was classified to be the chemisorption due to acid-base interaction between the base molecules and a part of cation exchange sites (Brønsted acid sites); the equilibrium adsorption capacity was probably determined by the amount of accessible acid sites on the adsorbent in the given conditions, and the time course of adsorption capacity was thus found to be controlled by kinetics. The adsorption time to realize the equilibrium was observed to be several tens to hundreds of hours, telling us the necessarily for analysis of kinetics and kinetic parameters of adsorption for design of practical process.

The adsorption rate increased as the particle size decreased. At 2 h of adsorption time, the  $q_t$  on the samples with 0.5-0.8 mm and 1.0-1.7 mm of particle size were 2.3 and 1.5 times larger than that on the sample with 1.7-2.8 mm, respectively (**Figure S2**). Pseudo first-order kinetic plots of  $\ln(q_e - q_t)$  versus  $t$  were presented in **Figure 2**, where  $\ln(q_e - q_t)$  was calculated as  $q_e = 85 \mu\text{mol g}^{-1}$ . The plots do not indicate linear relation, but downwardly convex curvilinear relationships. Therefore, it is identified that order of the rate equation was larger than first-order. **Figure 3** shows pseudo second-order kinetic plots of  $t/q_t$  against  $t$ . All the plots increase linearly. Simonin clarified that

diffusion-limited adsorption in liquid phase provided second-order kinetics.<sup>31</sup> Therefore, the thus found availability of pseudo second-order kinetics suggests that the diffusion of basic compounds or solvents in the particle was rate-limiting, because faster adsorption in larger pores is followed by slower adsorption in smaller pores close to molecular size of basic compounds or solvents.

The saturated adsorption quantities ( $q_{e,2ad}$ ) and the initial adsorption rates at  $t \rightarrow 0$  ( $h$ ) were obtained from the slopes and the intercepts of the plots (**Figure S3** and **Table 3**). The rate constants  $k_{2ad}$  were calculated from the values of  $q_{e,2ad}$  and  $h$ . All the  $q_{e,2ad}$  values calculated from (6) were consistent with the experimentally observed values ( $q_e$ ), approximately  $85 \mu\text{mol g}^{-1}$ . The particle size of amorphous silica-alumina did not influence the  $q_{e,2ad}$ . However,  $h$  and  $k_{2ad}$  on the samples with 0.5-0.8 mm and 1.0-1.7 mm of particle size were 14 and 3 times larger than that on the sample with 1.7-2.8 mm, respectively.

In the following, some basic compounds and solvents for model solutions were used, and influences of their compounds on kinetic parameters were studied. In the cases, adsorption quantity in the model reaction was larger than that in Solution #1, and thus the added silica-alumina with 0.5-0.8 mm of particle size was 2.5 wt% to various model solutions.

Quinoline, acridine, and phenanthridine as basic compounds were dissolved in hexadecyl-naphthalene as a solvent (Solution #2-4, **Figure 4**). Quinoline is bicyclic aromatic molecule, while acridine and phenanthridine are tricyclic aromatics. The order of  $pK_a$  is phenanthridine < quinoline < acridine, and therefore basic strength of acridine is stronger than those of the others. **Figure 5** indicates time courses of  $q_t$  on the amorphous silica-alumina. The order of adsorption rate was acridine < phenanthridine < quinoline. At 2 h of adsorption time, the  $q_t$  of quinoline was 1.5

times larger than those of acridine and phenanthridine (**Figure S4**). **Figure 6** shows pseudo first-order kinetic plots. The plots indicate downwardly convex curvilinear relationships, and thus order of the rate equations should be larger than first-order. Pseudo second-order kinetic plots increases linearly (**Figure 7**), indicating again that the adsorption rate was controlled by diffusion. The  $q_{e,2ad}$ , the  $h$ , and the  $k_{2ad}$  were presented in **Figure S5** and **Table 4**. The order of  $q_{e,2ad}$  was acridine < phenanthridine < quinoline. On the other hand,  $h$  and  $k_{2ad}$  of quinoline were far larger than those of acridine and phenanthridine, whereas acridine and phenanthridine showed similar kinetic parameters.

Quinoline was dissolved in hexane, benzene, and hexadecylphthalene (Solution #2, 5-6) to investigate influence of the solvents on adsorption rate. In addition, Solution #1, from which basic compounds was completely removed, as a solvent was also mixed with quinoline. The prepared mixture was described as Solution #7. **Figure 8** displays time courses of the  $q_t$  on amorphous silica-alumina from the above solutions (time course in hexadecylphthalene was shown in **Figure 5**), demonstrating significant differences of the  $q_e$  and adsorption rate. The order of  $q_e$  was benzene  $\approx$  Solution #1(as a solvent) < hexadecylphthalene < hexane. Adsorption rate in hexadecylphthalene solution was extremely slower than those in the other solutions. Pseudo first-order kinetic plots in **Figure 9** revealed that orders of the rate equations were larger than first-order. Pseudo second-order kinetic plots in **Figure 10** show linearity, indicating the diffusion control. **Table 5** showed  $q_{e,2ad}$ ,  $h$ , and  $k_{2ad}$ . In hexadecylphthalene (shown in **Table 4**),  $q_{e,2ad}$  of quinoline was larger than that in benzene. There were slight differences in  $q_{e,2ad}$  in benzene, hexane and VGO diluted by benzene (Solution #1). The order of  $h$  in the solutions was hexadecylphthalene < benzene < hexane, while the order of  $k_{2ad}$  in the solutions was hexadecylphthalene < hexane < benzene.  $h$  and  $k_{2ad}$  in Solution #1(as a solvent) indicated the intermediate value between those in benzene and hexadecylphthalene.

Influence of the regeneration of amorphous silica-alumina on amount of adsorbed basic compounds was then studied. The added silica-alumina with 0.5-0.8 mm was here 10.0 wt% to Solution #1, and the used silica-alumina was heated at 773 K to regenerate. **Figure 11** showed amount of adsorbed basic compounds ( $q_t$ ) from Solution #1 on the silica-alumina.  $q_t$  was approximately maintained during the twice regeneration cycles. It was revealed that adsorption property of the silica-alumina was stable during regeneration.

#### 4. Discussion

Adsorption rate of basic compounds in Solution #1 by the amorphous silica-alumina with various particle sizes was calculated. All the silica-alumina showed the same saturated adsorption quantity ( $q_{e,2ad}$ ), whereas the time until reaching saturated adsorption increased with the particle size (**Table 3**). The order of all the adsorption rate equations was represented as 2. Therefore, it was inferred that the rate-determining step was diffusion but not elementary adsorption process.<sup>31</sup> The rate constant ( $k_{2ad}$ ) and initial adsorption rate ( $h$ ) increased as particle size decreased. Therefore, the whole rate was presumed to be determined by diffusion rate of basic compounds and heavy hydrocarbons in particles of the silica-alumina. It was supposed that hydrophobic adsorbates and heavy hydrocarbons diffused on hydrophilic internal surface in the particles, and the particle size increased with increasing averaged length of diffusion path to adsorption sites in the particles, and therefore larger particle size prominently gained time until reaching adsorption equilibrium, corresponding to the smaller rate constant.

Influence of difference of basic compounds as adsorbents on adsorption rate was then investigated. The

solution was prepared by addition of basic compounds to hexadecyl-naphthalene as a model solvent of heavy hydrocarbon. The order of the basicity is phenanthridine < quinoline < acridine (**Figure 4**). As in Solution #1, the order of all the adsorption rate equations was represented as 2. There was the slight difference in the saturated adsorption quantities ( $q_{e,2ad}$ ), acridine < phenanthridine < quinoline. These basic compounds possess a lone pair on the N atom, which is bonded to acidic -OH group of the silica-alumina in parallel with aromatic rings. Therefore, steric hindrance around the N atom should concern tendency of adsorption. It was speculated to be responsible that adsorption of acridine on acid sites of the silica-alumina was inhibited by a large steric hindrance due to two benzene rings next to the pyridine ring, whereas adsorption of bicyclic aromatic quinoline had smaller steric hindrance than those of tricyclic aromatics. Therefore  $q_{e,2ad}$  of phenanthridine was more than that of acridine. Dicyclic aromatic quinoline has the molecular size smaller than the others, and thus the larger  $q_{e,2ad}$ . The steric hindrance was supposed to influence equilibrium adsorption. The orders of the rate constant ( $k_{2ad}$ ) and initial adsorption rate ( $h$ ) were acridine  $\approx$  phenanthridine < quinoline. It was speculated that the diffusion rate of bicyclic aromatic quinoline was larger than that of tricyclic aromatic acridine and phenanthridine. In summary, the base strength difference did not influence the adsorption rate, while the steric factors mainly affected. It is suggested that  $q_{e,2ad}$  depended on steric hindrance around basic sites and the molecular size to some extent, whereas  $k_{2ad}$  and  $h$  depended on the molecular size. Also, the orders were relatively similar to order of the diffusion coefficients for the basic compounds in water (**Table S1**). In summary, equilibrium adsorption predominates over the saturated adsorption quantities ( $q_{e,2ad}$ ), whereas diffusion kinetics predominates over the initial adsorption rate ( $h$ ) and the rate constant ( $k_{2ad}$ ).

Influence of the solvents on adsorption rate was also investigated. The solution was prepared by addition

of quinoline to various solvents. The order of all the adsorption rate equations can be also represented as 2. The order of the  $q_{e,2ad}$  in the solutions was benzene < hexadecyl-naphthalene < hexane. The  $q_{e,2ad}$  in Solution #1 (as a solvent) was nearly equal to that of benzene. Quinoline as an adsorbate has a lone-pair electron on a nitrogen atom and thus high polarity (dielectric constant:  $\epsilon = 9.16$ ). Compared between C6 solvents, the polarity of benzene ( $\epsilon = 2.28$ ) is higher than that of hexane ( $\epsilon = 1.89$ ), and thus interaction of benzene with quinoline was stronger than that of hexane. It was speculated that adsorption quantity of a basic compound increased as an interaction between an adsorbate and a solvent was weak, therefore  $q_{e,2ad}$  in hexane was more than that in benzene. C28 hydrocarbon of hexadecyl-naphthalene is a huge molecule, but the  $q_{e,2ad}$  in hexadecyl-naphthalene was larger than that in benzene. Hexadecyl-naphthalene is presumed to have polarity between benzene and hexane. Solution #1 (as a solvent) contained larger molecules and large quantity of benzene, therefore the  $q_{e,2ad}$  in Solution #1 (as a solvent) was comparable to that in benzene. Thus,  $q_{e,2ad}$  was mainly influenced by polarity of the solvent, but not by the molecular size. The order of  $h$  in the solutions was hexadecyl-naphthalene < benzene < hexane. Comparison of benzene with hexane (both C6 hydrocarbons) indicates that higher polarity of benzene increased the interaction force with quinoline, and thus  $h$  decreased. Huge molecules of hexadecyl-naphthalene decreased  $h$ . Solution #1 (as a solvent) indicated the intermediate value between hexadecyl-naphthalene and benzene, due to inclusion of benzene and huge hydrocarbons.  $k_{2ad}$  in hexadecyl-naphthalene was also lower than those in the C6 hydrocarbons, whereas  $k_{2ad}$  in hexane was lower than that in benzene.  $k_{2ad}$  was calculated from an equation ( $k_{2ad} = h / q_{e,2ad}$ ), and thus increased as  $q_{e,2ad}$  decreased. Consequently,  $k_{2ad}$  in benzene showed higher than those in the others.  $k_{2ad}$  in Solution #1 (as a solvent) was low on the same reason of  $h$ . It was suggested that  $q_{e,2ad}$  as amount of the equilibrium adsorption depended on polarity of the solvent, whereas

$h$  as the initial adsorption rate depended on both of the polarity and the molecular size of the solvent. Therefore, the compatibility of the adsorbate and the solvent considerably influences the adsorption of the basic compounds.<sup>32</sup>

Quinoline is less compatible with hexane than benzene.

The reusability of silica-alumina was stable to calcination at 773 K. Therefore, removal of basic compounds from VGO with silica-alumina expects to be a promising process in oil refinery.

## 5. Conclusions

In this study, basic nitrogen-containing compounds in VGO as a practical oil was removed by adsorption with amorphous silica-alumina through acid-base interaction. The kinetics was analyzed with pseudo first-order and pseudo second-order kinetic models. Consequently, the order of all the adsorption rate equations was represented as 2, and thus it was deduced that the rate-determining step was the diffusion of the nitrogen-containing compounds and solvents in the adsorbent. The analysis of kinetic study revealed that particle size of the adsorbent, nitrogen-containing compounds, and solvents influenced on adsorption of basic nitrogen-containing compounds. Small particle size of the adsorbent increased the rate constant ( $k_{2ad}$ ) and initial adsorption rate ( $h$ ) in removal from Solution #1, but saturated adsorption quantities ( $q_{e,2ad}$ ) was not influenced. It was speculated that hydrophobic adsorbates and heavy hydrocarbons was difficult to diffuse in hydrophilic interior adsorbent, therefore time until reaching adsorption equilibrium become longer. Among various nitrogen-containing compounds, there were difference in  $k_{2ad}$  and  $h$ , and slight difference in  $q_{e,2ad}$ . It was speculated that the diffusion rate of bicyclic aromatic quinoline was larger than that of tricyclic aromatic acridine and phenanthridine. It can be stated that the parameters were not influenced by the basicity of adsorbates. The influence of the solvents expected as coexisting substances in VGO on adsorption rate was evaluated.  $q_{e,2ad}$  was influenced by polarity of a solvent, not by molecular size. It was speculated that  $q_{e,2ad}$  increased as an interaction between an adsorbate and a solvent weaken. It was deduced that the observed difference in  $h$  was seriously influenced by molecular size, and moderately by the polarity. The regeneration of the used adsorbent was carried out through the calcination at 773 K. The reusability of the amorphous silica-alumina was verified. In a sum-

mary, adsorption kinetics and repeatability in removal of basic nitrogen-containing compounds with amorphous silica-alumina were revealed, therefore this method is promising in prospective oil refinery.

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**Table 1**

The characteristics of N631-L

		Parameter
Composition/ wt%	as SiO <sub>2</sub>	81
	as Al <sub>2</sub> O <sub>3</sub>	13
Cation exchange capacity* <sup>1</sup> / mol kg <sup>-1</sup>		0.15
Specific surface area, S <sub>BET</sub> / m <sup>2</sup> g <sup>-1</sup>		525
Most frequent pore size* <sup>2</sup> / nm		4

\*<sup>1</sup> amount of Brønsted acid sites, \*<sup>2</sup> consideration from pore size distribution

**Table 2** Solutions employed for adsorption experiments

	Matrix	Basic compound	Concentration / $\mu\text{mol g}^{-1}$
#1	VGO : benzene : hexadecyl-naphthalene = 1 : 1 : 0.11	not added but originally contained by VGO	5.9
#2	Hexadecyl-naphthalene	Quinoline	20
#3	Hexadecyl-naphthalene	Phenanthridine	20
#4	Hexadecyl-naphthalene	Acridine	20
#5	Benzene	Quinoline	20
#6	Hexane	Quinoline	20
#7	Solution #1 (VGO : benzene : hexa- decyl-naphthalene = 1 : 1 : 0.11) treated with cation exchange resin to remove basic compounds	Quinoline	20

**Table 3** Calculated parameters from pseudo second-order kinetic plot for the removal of basic compounds

by amorphous silica-alumina with various particle size

Particle size / mm	Adsorption capacity at equilibrium ( $q_{e,2ad}$ ) / $\mu\text{mol g}^{-1}$	Initial adsorption rate ( $h$ ) / $\mu\text{mol g}^{-1} \text{hr}^{-1}$	Rate constant ( $k_{2ad}$ ) / $\text{g mmol}^{-1} \text{hr}^{-1}$
0.5 – 0.8	86	286	38.38
1.0 – 1.7	85	69	9.59
1.7 – 2.8	85	21	2.87

**Table 4** Calculated parameters from pseudo second-order kinetic plot for the removal of various basic compounds by amorphous silica-alumina with 0.5-0.8 mm of particle size

	Adsorbate	Adsorption capacity at equilibrium ( $q_{e,2ad}$ ) / $\mu\text{mol g}^{-1}$	Initial adsorption rate ( $h$ ) / $\mu\text{mol g}^{-1} \text{hr}^{-1}$	Rate constant ( $k_{2ad}$ ) / $\text{g mmol}^{-1} \text{hr}^{-1}$
#2	Quinoline	701	358	0.73
#3	Phenanthridine	670	129	0.29
#4	Acridine	621	124	0.32

**Table 5** Calculated parameters from pseudo second-order kinetic plot for the removal of quinoline dissolved with various solvents by amorphous silica-alumina with 0.5-0.8 mm of particle size

	Solvent	Adsorption capacity at equilibrium ( $q_{e,2ad}$ ) / $\mu\text{mol g}^{-1}$	Initial adsorption rate ( $h$ ) / $\mu\text{mol g}^{-1} \text{hr}^{-1}$	Rate constant ( $k_{2ad}$ ) / $\text{g mmol}^{-1} \text{hr}^{-1}$
#5	Benzene	498	16081	64.91
#6	Hexane	756	26604	46.55
#7	Solution #1 (as a solvent)	486	7441	31.47

- Figure 1** Time courses of amount of adsorbed basic compounds ( $q_t$ ) on amorphous silica-alumina with various particle size
- Figure 2** Pseudo first-order kinetic plot for the removal of basic compounds by amorphous silica-alumina with various particle size
- Figure 3** Pseudo second-order kinetic plot for the removal of basic compounds by amorphous silica-alumina with various particle size
- Figure 4** Chemical structure and  $pK_a$  at 25 °C of basic nitrogen-containing compounds
- Figure 5** Time courses of various adsorbed basic compounds ( $q_t$ ) on amorphous silica-alumina with 0.5-0.8 mm of particle size
- Figure 6** Pseudo first-order kinetic plot for the removal of various basic compounds by amorphous silica-alumina with 0.5-0.8 mm of particle size
- Figure 7** Pseudo second-order kinetic plot for the removal of various basic compounds by amorphous silica-alumina with 0.5-0.8 mm of particle size
- Figure 8** Time courses of adsorbed quinoline ( $q_t$ ) dissolved with various solvents on amorphous silica-alumina with 0.5-0.8 mm of particle size
- Figure 9** Pseudo first-order kinetic plot for the removal of quinoline dissolved with various solvents by amorphous silica-alumina with 0.5-0.8 mm of particle size
- Figure 10** Pseudo second-order kinetic plot for the removal of quinoline dissolved with various solvents by amorphous silica-alumina with 0.5-0.8 mm of particle size

**Figure 11**

Amount of adsorbed basic compounds ( $q_t$ ) from Solution #1 on amorphous silica-alumina. (a) First removal, (b) second removal after regeneration and (c) third removal after regeneration.

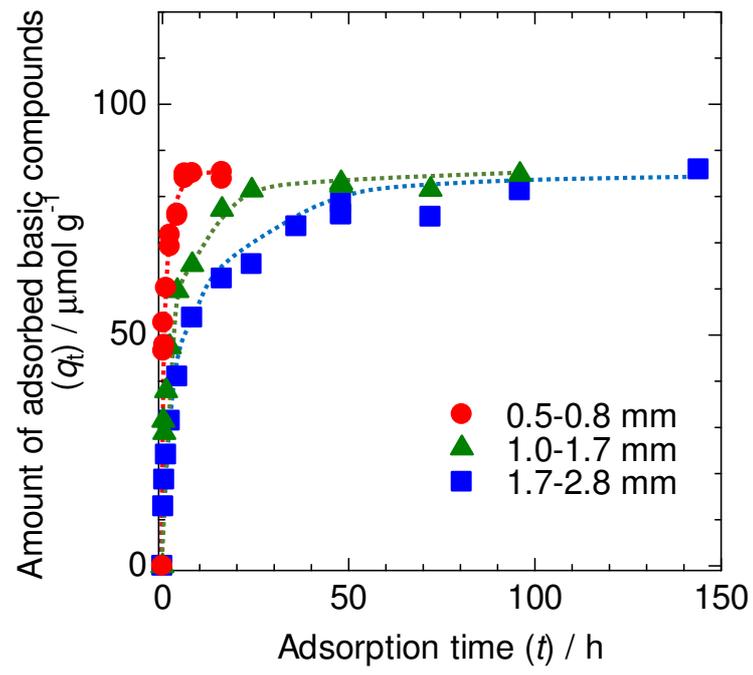


Figure 1

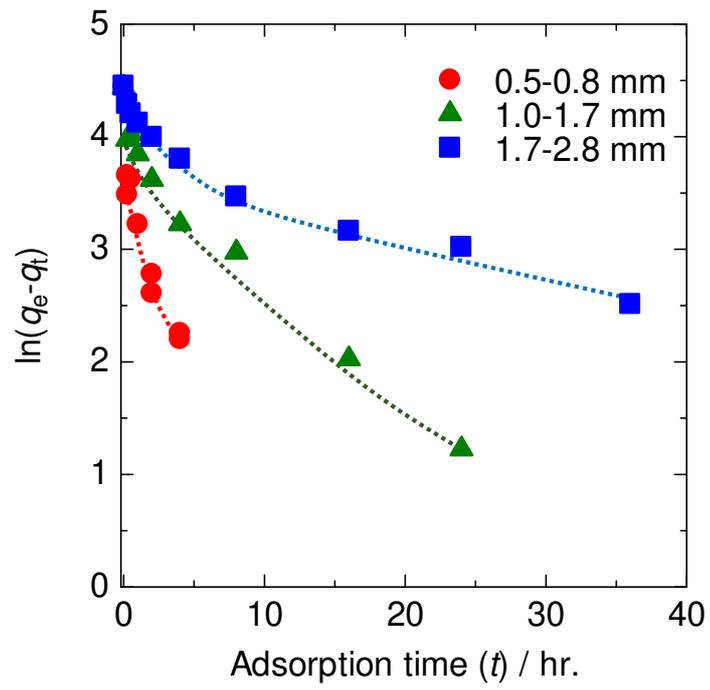


Figure 2

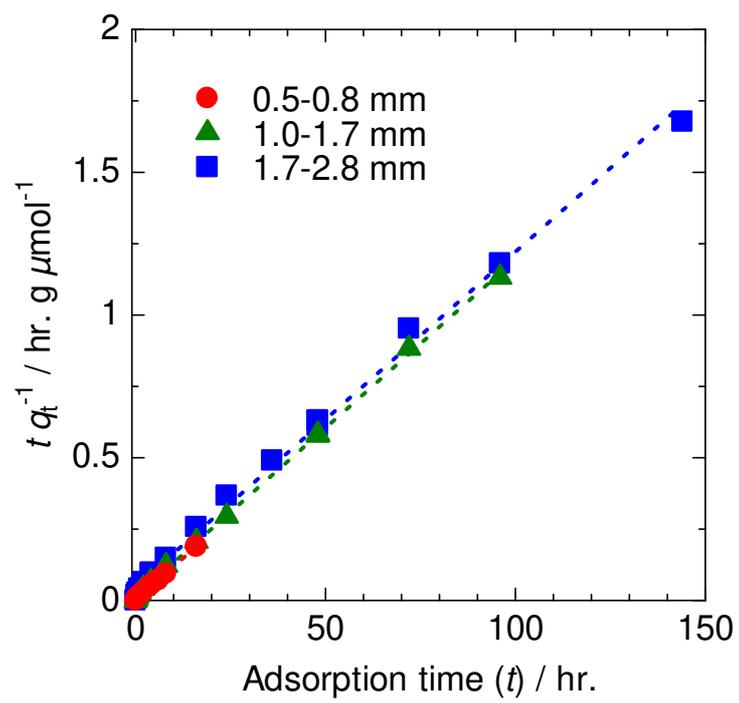
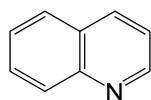
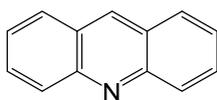


Figure 3



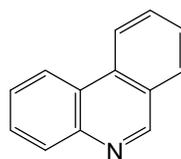
Quinoline

4.97



Acridine

5.56



Phenanthridine

4.52

**Figure 4**

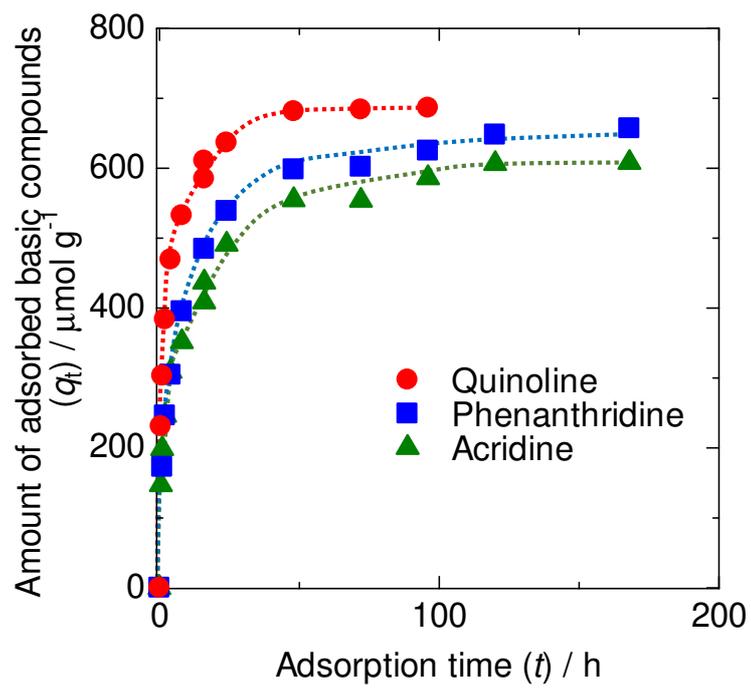


Figure 5

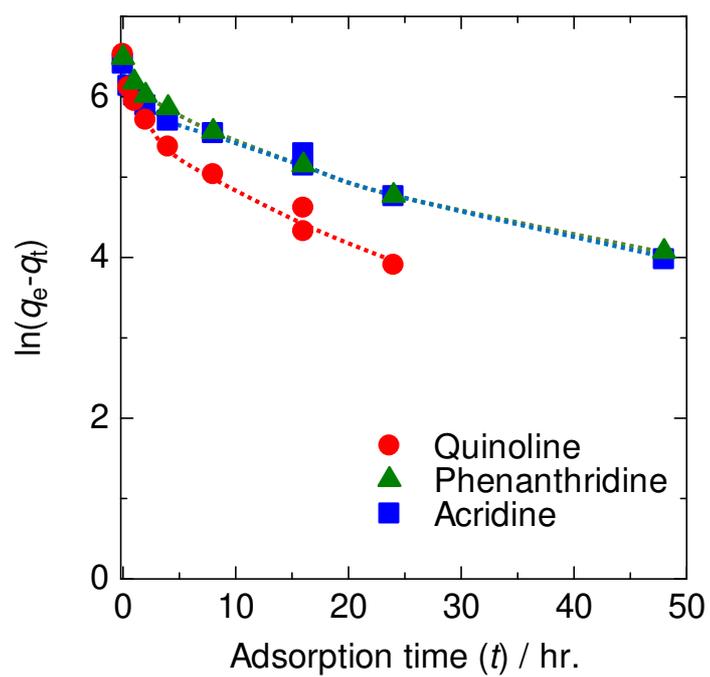


Figure 6

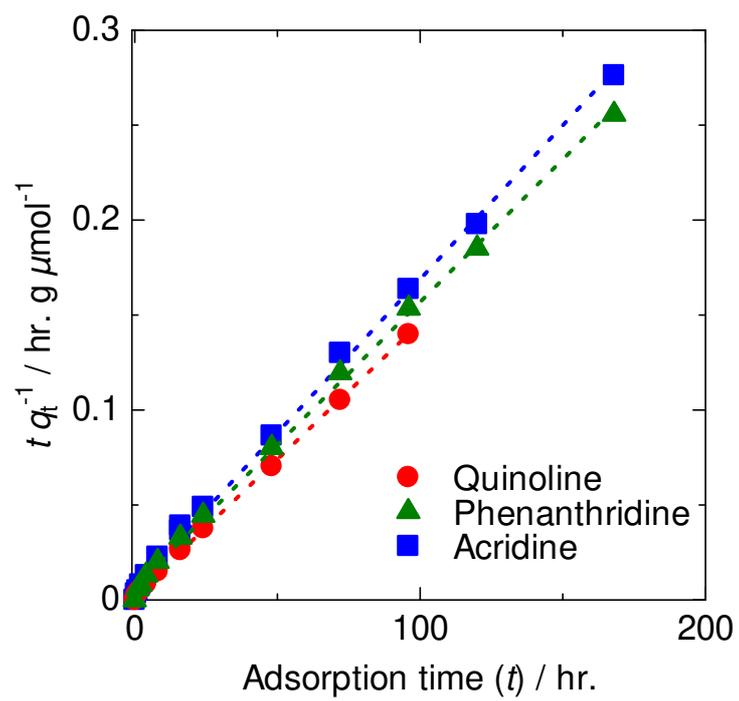


Figure 7

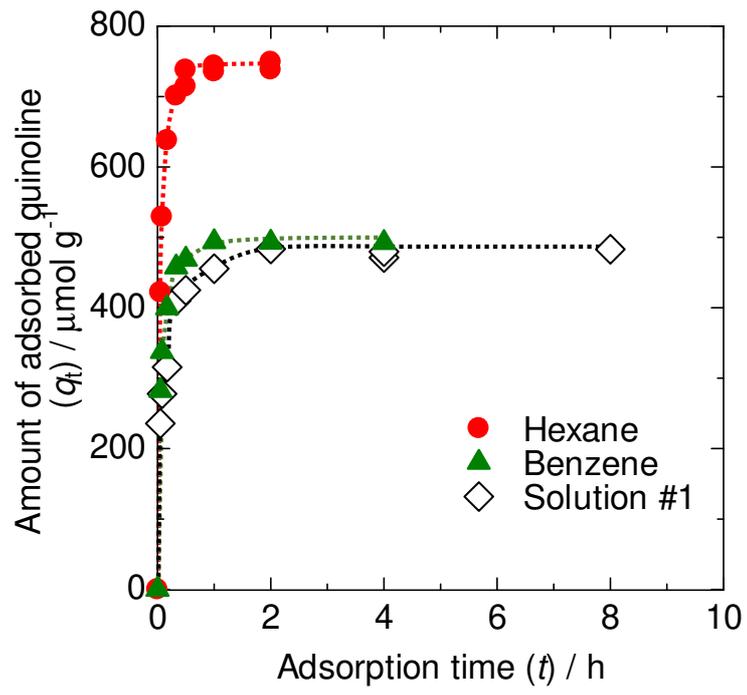


Figure 8

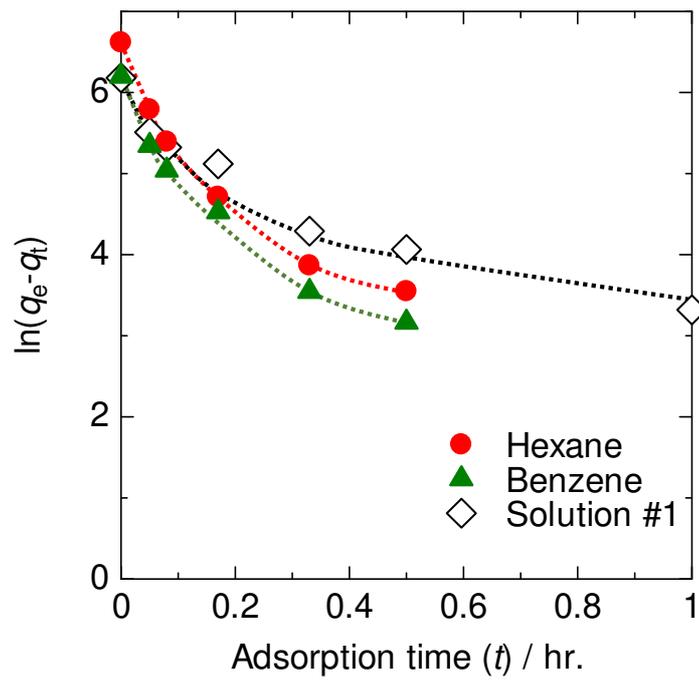


Figure 9

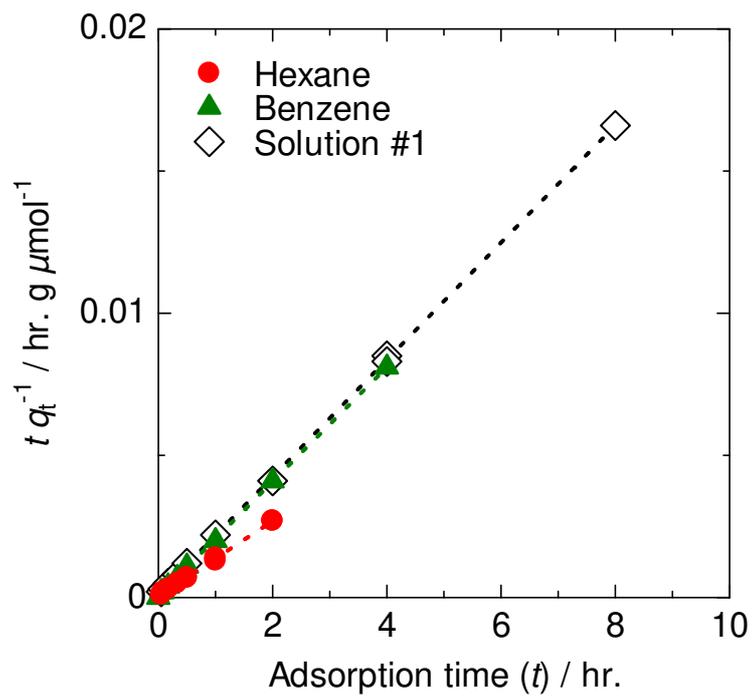
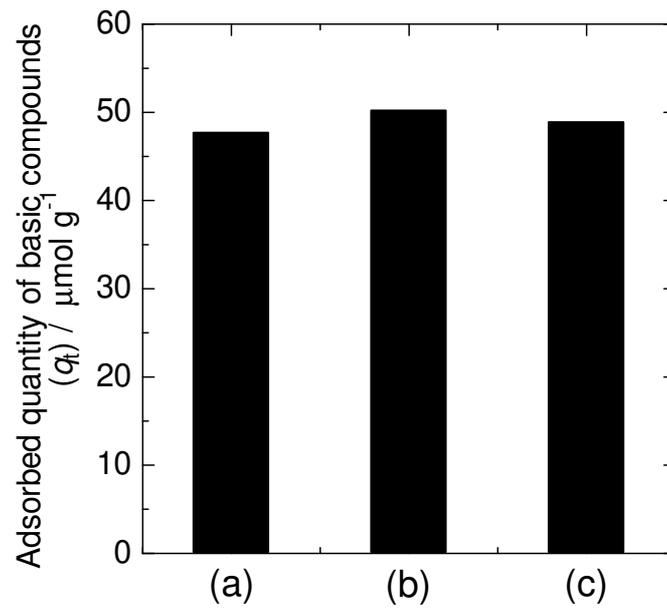


Figure 10



**Figure 11**