

Simultaneous adsorption of a mixture of paraquat and dye by NaY zeolite covered with alkylsilane

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Abstract

The surfaces of NaY zeolite particles were modified by the alkylsilylation of *n*-octadecyltrichlorosilane (OTS). Two kinds of modified NaY zeolites were prepared; one with its external surface partially and the other fully covered with alkylsilyl groups. Since the size of OTS is bigger than the pore diameter of NaY, it is attached on the external surface, leaving the internal pore accessible to adsorbate molecules. As a result of alkylsilylation, the adsorption properties of these sorbents were improved. The adsorption properties of these materials were tested by their reaction in a mixture of paraquat and blue dye. The results demonstrate that the alkylsilylated NaY materials are capable of simultaneous adsorption of paraquat and blue dye. Paraquat was selectively adsorbed into the internal pore of the zeolite whereas the dye on the externally attached alkylsilyl groups of the sorbent; displaying the unique bimodal amphiphilic character of the alkylsilylated NaY zeolites.

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1. Introduction

The removal of hazardous organic materials from wastewater is one of the most important environmental issues to be solved today [1]. In real life situation, these materials are usually present as a mixture of hydrophilic and hydrophobic organic compounds. The objective of this study is to design an adsorbent for adsorption of organic materials, specifically the removal of both hydrophilic and hydrophobic organic compounds from water. For this purpose, a mixture of hydrophilic herbicide and hydrophobic dye are used as the model adsorbates. The application of herbicide and dye in agriculture and industries have been detrimental to the environment. Therefore, it is necessary to remove these hazardous materials from water as much as possible [2–4]. The commonly used herbicide and dye are paraquat and blue dye, respectively. Paraquat (1,1'-dimethyl-4,4-bipyridinium dichloride,

PQ), a quaternary nitrogen herbicide, is a highly toxic compound and many cases of acute poisoning and death have been reported over the past few decades [1]. In order to prevent accidental deaths due to confusion with cola, black coffee or other beverages, a blue dye, as a colouring agent, was added to commercial PQ [5]. The use of dyes may also pose some level of human risk. Unfortunately, the ingredients in blue dye are considered proprietary. In general, the dye used is hydrophobic and its chemical structure is bigger than that of PQ [5]. In order to rationalize the adsorption of blue dye, the reactive dye Cibacron Blue 3GA (CB3GA); having the well-known structure shown in Fig. 1 was used.

Alkylsilylation of mesoporous materials has been reported in an attempt to prepare materials for extraction of metal ions [6,7]. The surface properties of zeolites have also been modified by alkylsilylation [8–10]. Recently a new approach in modifying the surface of zeolite by the alkylsilylation of *n*-octadecyltrichlorosilane (OTS) onto the NaY zeolite particles, resulting in hydrophobic zeolites; having

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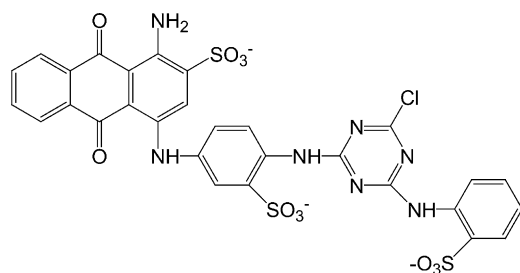


Fig. 1. Chemical structure of Cibacron Blue 3GA.

their surface partially and fully covered with alkylsilyl groups was reported [11,12]. Proposed models of the modified NaY zeolites are depicted in Fig. 2. In the present study, it is demonstrated that the modified NaY zeolite particles can adsorb both PQ and blue dye simultaneously. PQ is preferentially adsorbed on the hydrophilic internal pore whereas blue dye, being hydrophobic is adsorbed on the external surface area of the modified zeolite particle. The effect of partial alkylsilylation on the surface of NaY zeolite on the adsorption of PQ and blue dye is also discussed.

2. Experimental

2.1. Surface modifications

NaY zeolite (CBV100) supplied by Zeolyst International with a surface area of $900 \text{ m}^2 \text{ g}^{-1}$ was used as received. Modified NaY in which the external surface was partially covered with alkylsilane was prepared by attachment of *n*-octadecyltrichlorosilane (OTS), prepared according to the method reported previously [11,12]. Typically, the NaY powder containing water (0.25, 0.50, 0.75 and 1.0 g per gram of NaY) was immersed in 5 ml toluene containing $500 \mu\text{mol}$ of OTS (Aldrich) and the suspension was shaken for 5 min at room temperature. Then, the solid was collected by centrifugation and dried at 110°C for 5 h. Addition of a small amount of water to the hydrophilic NaY surface led to aggregation due to the capillary force of water between particles. Under these conditions, it is expected that only the outer surface of aggregates, which is in contact with the organic phase can be modified with OTS. The partially modified sample was

labeled w/o-NaY. Fully modified NaY labeled as o-NaY was prepared without the addition of water.

In order to establish their surface structures, each w/o-NaY and o-NaY sample (0.06 g) was added into an immiscible mixture of *n*-hexane (2 ml) and water (2 ml). Then, the mixture was stirred vigorously at 1000 rpm for 2 h and kept under static condition for 12 h. The capability of the particles to stabilize the liquid–liquid system to form an emulsion was attributed to their hydrophobic–hydrophilic character and hence their surface structure [13,14].

Photographs of emulsion formed in the presence of modified NaY zeolites were taken under an optical microscope. In order to specify whether the type of emulsion was oil-in-water (o/w) or water-in-oil (w/o), hydrophilic methylene blue was used as the indicator.

Study on the adsorption kinetic of adsorbed water was carried out in order to determine its role in the determination of the adsorption capacity and alkylsilyl coverage of the modified NaY samples. About 1 g of modified NaY sample was dehydrated under vacuum at 100°C overnight. After dehydration, the sample was exposed to water vapour at room temperature, followed by the determination of the percentage of adsorbed water as a function of time.

2.2. Adsorption of dyes and paraquat

The dye used was Cibacron Blue 3GA (CB3GA) from Sigma. Adsorption was carried out by stirring 20 ml of 500 ppm CB3GA solutions in the presence of 0.4 g of modified NaY samples at room temperature. The adsorption kinetics experiments were carried out in a 50 ml Pyrex glass bottle. Modified NaY adsorbents were used after degassing at 100°C overnight in the vacuum oven. The CB3GA solutions were contacted for 2 h and analyzed spectrophotometrically at λ_{max} of 601 nm.

A commercial PQ (18.3%) by Bayer in the presence of blue dye as the coloring agent was used in the adsorption experiments. The intensity of the blue colour of the dye is used as a measure of concentration. Adsorption was carried out by stirring 25 ml of 300 ppm PQ solutions at room temperature. The PQ solutions were contacted for 5, 10, 15, 30 and 60 min with 0.4 g modified NaY zeolite, after degassing at 100°C overnight in the vacuum oven. The PQ and blue

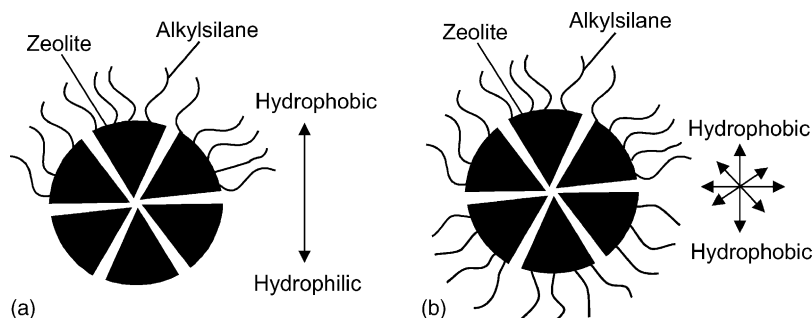


Fig. 2. Proposed model of modified zeolite particles in which their surface are (a) partially and (b) fully covered with alkylsilyl groups.

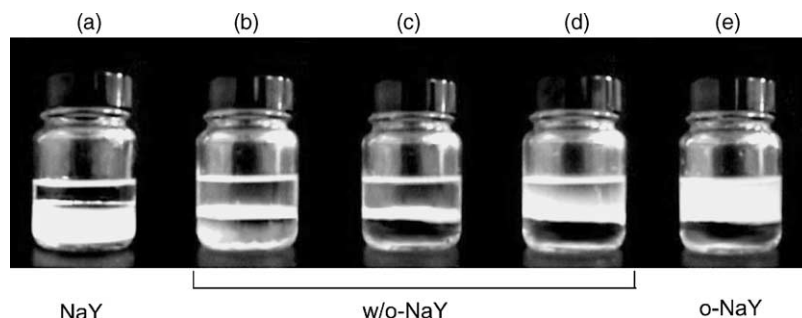


Fig. 3. The photographs show the distribution of (a) NaY, (b)–(d) w/o-NaY and (e) o-NaY solid particles when added to hexane–water mixture. The w/o-NaY was prepared with the amount of added water to form NaY aggregates before attachment of OTS was (b) 1.00 g, (c) 0.50 g and (d) 0.25 g water per gram NaY.

dye concentration analysis of filtrate was carried out at λ_{\max} of 256 and 634 nm, respectively. Adsorption kinetic experiments were immediately conducted with 1.0 cm light path quartz cells using Perkin-Elmer Lambda 900.

3. Results and discussion

3.1. Physical properties

In this part, the physical properties of alkylsilane-modified NaY zeolites are discussed in order to clarify the effects of alkylsilylation to their surface properties. The follow-on part, the surface properties of the adsorbents are correlated to the character of dye and paraquat which are adsorbed on them.

The dispersion behaviour of partially silylated NaY sample (w/o-NaY) and totally silylated NaY sample (o-NaY) are shown in Fig. 3. The dispersibility indicates that as more water is added to NaY, the more hydrophilic is the resulting w/o-NaY particles. It was found that the addition of more than 90 wt.% water per gram NaY could totally wet the pow-

der to form the ‘wet cake’. After attachment of alkylsilyl groups, the resulting particles seemed heterogeneous; some particles were located at the phase-boundary while others were dispersed in water (see Fig. 3(b)). The addition of ca. 50 wt.% water per gram NaY gave the highest stability; locating the w/o-NaY particles at the phase-boundary as observed in Fig. 3(c). Results in Fig. 3 suggest that there is a correlation between alkylsilyl coverage on the surface of NaY with the distribution of modified NaY in the hexane–water mixture. This argument is clarified with the water adsorption experiments.

As shown in Fig. 4, it was clearly observed that the amount of adsorbed water on o-NaY was significantly lower than those of w/o-NaY and NaY. Apparently, the amount of water added before alkylsilylation led to changes in alkylsilyl coverage on the surface of modified NaY. The higher the amount of water added, the lower was the alkylsilyl coverage. It is obvious that alkylsilyl groups should be attached to the external surface of NaY zeolite since the estimated molecular size of alkylsilane (ca. 0.50 nm \times 2.60 nm), the source of alkylsilyl, is larger than the size of the entrance pore of NaY zeolite

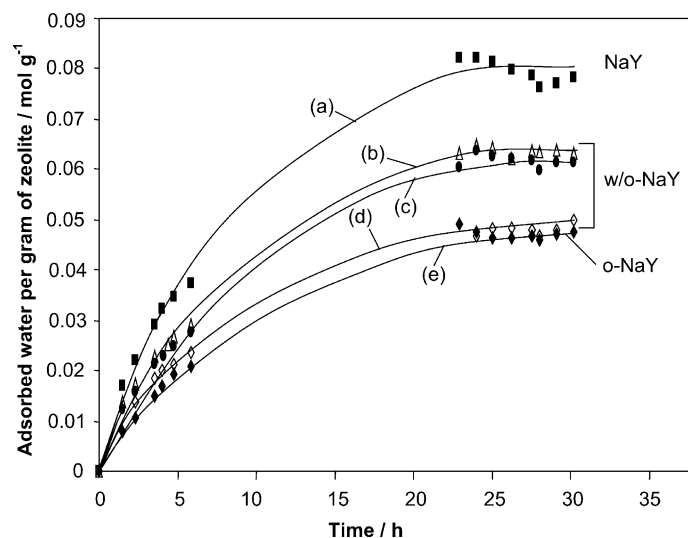


Fig. 4. Percentage of adsorbed water on the surface of (a) NaY, (b)–(d) w/o-NaY and (e) o-NaY. The modified NaY used are the same as in Fig. 3.

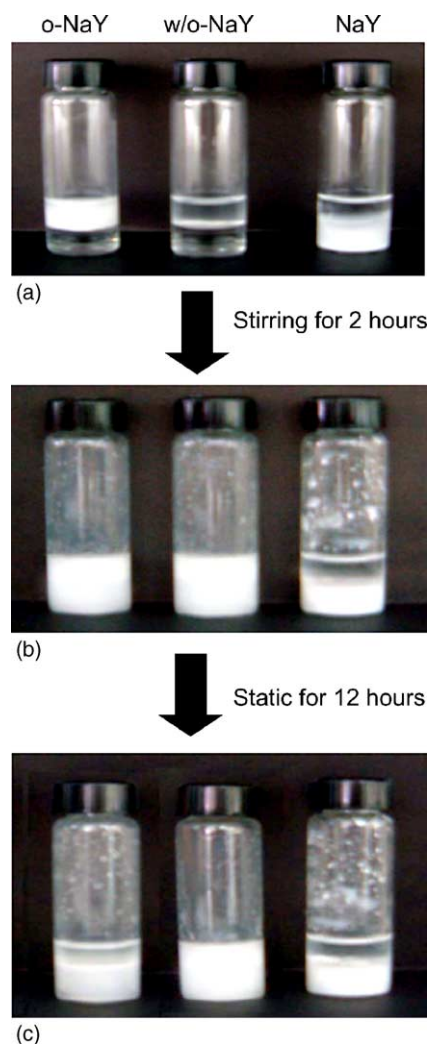


Fig. 5. The photographs showing the distribution of NaY, w/o-NaY and o-NaY solid particles (a) when added to hexane-water mixture, (b) after stirring for 2 h and (b) after keeping under static conditions for 12 h. The w/o-NaY used is the same solid particles used in Fig. 3(c).

(ca. 0.70 nm). Hence, the high surface coverage of alkylsilyl groups on the surface prevented water from entering the pore of NaY zeolite.

Fig. 5 shows the distributions of the NaY, w/o-NaY and o-NaY samples in a mixture of *n*-hexane and water, after stirring for 2 h and keeping under static condition for 12 h. It confirms that sample w/o-NaY (solid particles in Fig. 3(c)) is located at the liquid–liquid boundary mixture of *n*-hexane and water, whereas NaY and o-NaY are dispersed in aqueous water and organic *n*-hexane phase respectively. One expects that if the solid particles were able to be located at the phase-boundary, these particles may act as an effective emulsifying agent. To confirm this consideration, the mixture was then stirred. It was observed that emulsion was formed in the system containing w/o-NaY and o-NaY (Fig. 5(b)). In the emulsion form, the specific interfacial interactions between the particles surface and the two immiscible liquid phases increased the surface contact (wettability) of the particles with

the organic and aqueous phases. For maximum efficiency, the particles should be wetted preferentially by the two liquid phases. If the solid particles were too strongly wetted by either of the two liquid phases, the required stabilizing action would not result [15]. To confirm this, the stability of the emulsion in the presence of the solid particles was examined. Interestingly, the emulsion was stabilized by w/o-NaY for upto 12 h, whereas stability of emulsion of the system containing o-NaY was only 1 h. As shown in Fig. 5, it is clearly demonstrated that an emulsion has been formed, resulting in an abrupt visual homogenization. In contrast, no emulsion was formed in the system containing NaY; which suggests that w/o-NaY possesses a good bimodal amphiphilic character that stabilizes the immiscible mixture of organic and aqueous phases to form a more stable emulsion.

Fig. 6 shows the optical microscope photographs of the type of emulsion formed; the o-NaY and w/o-NaY act as emulsifiers to stabilize the *n*-hexane and water mixture forming the water-in-oil type emulsion. In order to correlate the amphiphilic character with the surface structure, a fluorescence microscopic study was carried out [16]. It has been established that each w/o-NaY particle has both hydrophobic and hydrophilic surfaces. Therefore, the results described above are experimental evidence to the proposed models shown in Fig. 1.

3.2. Adsorption of dye and paraquat

Fig. 7 shows the adsorption of CB3GA by various modified NaY. The amount of adsorbed CB3GA decreased with decreasing hydrophilicity of adsorbent. NaY did not adsorb CB3GA. This result confirms that CB3GA is adsorbed by the alkylsilyl groups. The trend in adsorption implies that there is a correlation between the surface coverage of alkylsilyl groups and the adsorption capacity of the modified NaY as supported by the adsorption experiments of water shown in Fig. 4. The higher is the alkylsilyl coverage, the lower is the adsorption capacity of water and hence the higher is the adsorption of CB3GA. If the w/o-NaY has a bimodal amphiphilic surface structure; where one side of the external surface is hydrophilic and the other is hydrophobic, then a mixture of hydrophilic and hydrophobic compounds could be adsorbed simultaneously by this system. To confirm this expectation, a mixture containing hydrophilic PQ and hydrophobic blue dye was used as adsorbates.

As shown in Fig. 8, all systems containing zeolites: NaY, w/o-NaY and o-NaY can adsorb PQ. The degree of the rate of adsorption of PQ in decreasing order is as follows: NaY > w/o-NaY > o-NaY. In comparison, the degree of the rate of adsorption of blue dye in decreasing order is as follows: o-NaY > w/o-NaY > NaY, although at the beginning (upto 5 min), the adsorption rate of w/o-NaY is faster than that of o-NaY (Fig. 9). It is also shown that NaY does not adsorb either blue dye or CB3GA at all.

Results in Figs. 8 and 9 show that despite blue dye not being adsorbed at all, the adsorption rate of PQ by NaY is

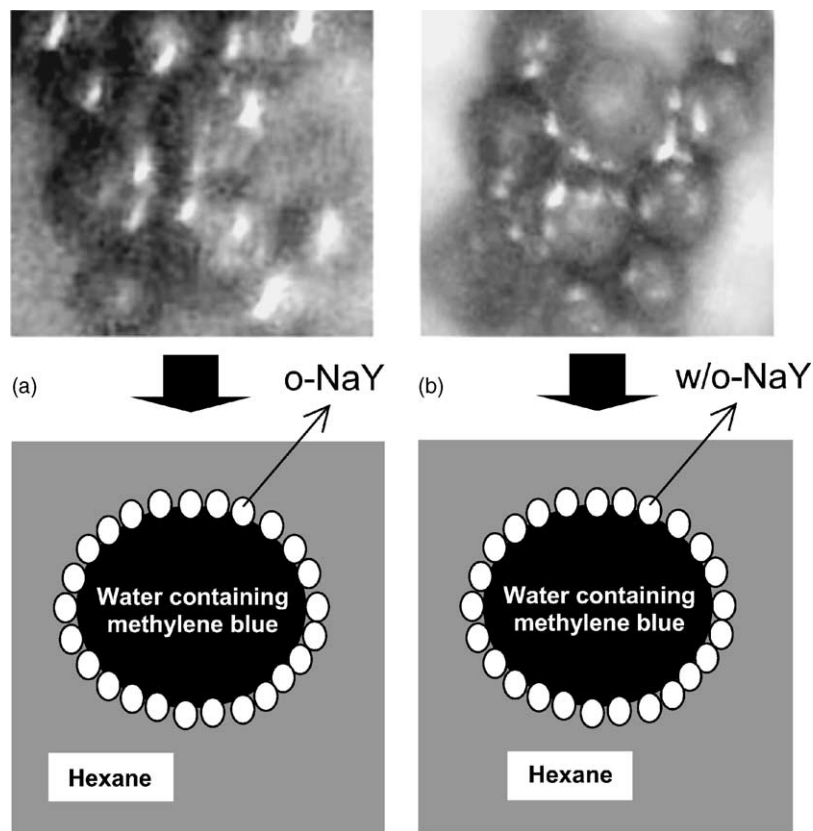


Fig. 6. Photographs of w/o type of emulsion stabilized by (a) o-NaY and (b) w/o-NaY. The w/o-NaY used is the same as in Fig. 5. Photographs were taken from the emulsion after 2 h under stirring conditions.

relatively fast. In contrast, the adsorption rates of PQ and blue dye by o-NaY are slow and fast, respectively. This evidently suggests that although the C₁₈ chains on the o-NaY has high hydrophobicity, the network still has channels which are available to PQ even though at a considerably slow rate. It also confirms that C₁₈ chains on the w/o-NaY and o-NaY play a role in the adsorption of the dye molecules. The w/o-NaY simultaneously adsorbs PQ and blue dye, although at a considerably slower rate than that of NaY and o-NaY.

From the above results, the adsorption behaviour of modified NaY particles could be rationalized by correlating it with their amphiphilic character and hence their surface structure. It is possible that the hydrophilic and hydrophobic regions of w/o-NaY, as shown in Fig. 2(a), play an important role in the eventual adsorption of the PQ and blue dye. PQ is adsorbed easily by entering the pore through the hydrophilic part, whereas the blue dye molecule is adsorbed on the alkylsilyl

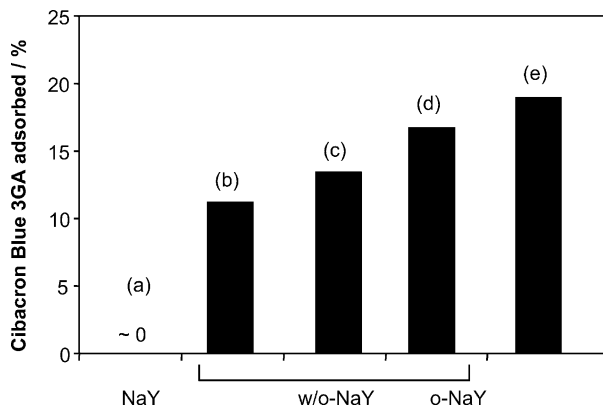


Fig. 7. Adsorption of CB3GA on (a) NaY, (b)–(d) w/o-NaY and (e) o-NaY. The w/o-NaY used is the same as in Fig. 3. All experiments were done with 0.4 g of zeolite, 20 ml of 500 ppm of CB3GA.

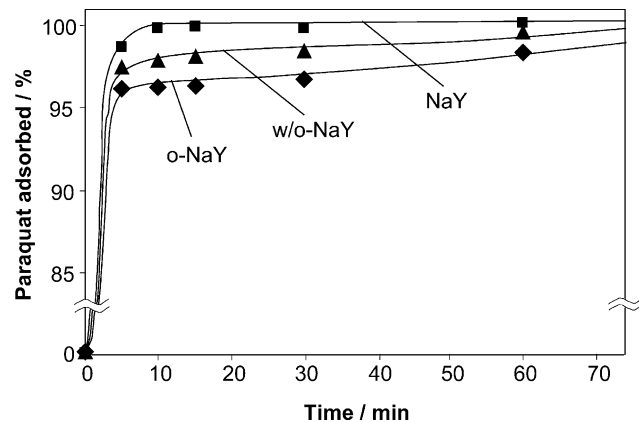


Fig. 8. Adsorption of PQ on NaY, w/o-NaY and o-NaY. The w/o-NaY used is the same as in Fig. 5. All experiments were done with 0.4 g of zeolite, 25 ml of 300 ppm of PQ.

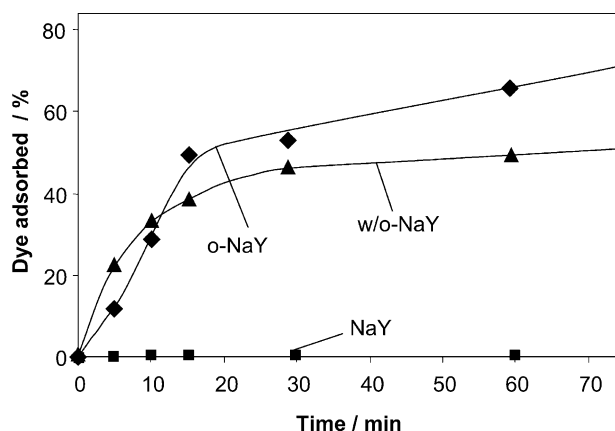


Fig. 9. Adsorption of blue dye on NaY, w/o-NaY and o-NaY. All experiments were done similar to that of the adsorption conditions shown in Fig. 8.

groups. In case of o-NaY, the adsorption of PQ in the pore is retarded by the hydrophobic alkylsilyl groups which are located on the fully covered external surface (see Fig. 2(b)). However, at present, we only demonstrate the application of this adsorbent system in the adsorption of commercial PQ containing blue dye as a model. The adsorption of the other chemical systems is currently being studied in our laboratory.

4. Conclusions

The results described above indicate that NaY zeolite loaded with alkylsilane is particularly capable of simultaneous adsorption of paraquat and blue dye. The adsorption rates of the paraquat and blue dye were affected by the surface coverage of alkylsilyl groups on NaY. Paraquat was adsorbed on the pore, relatively easier, with the presence of hydrophilic part on the external surface of partially alkylsilylated NaY zeolite. On the other hand, the dye molecule was adsorbed on the alkylsilyl groups. If the external surface of the NaY zeolite particles was completely covered with alkylsilyl groups, the adsorption of paraquat was retarded because it must overcome the barrier of the hydrophobic alkylsilyl groups. In

conclusion, a novel integrated chemical system consisting of a modified alkylsilane-modified porous particles capable of simultaneous adsorption of a mixture of hydrophilic and hydrophobic organic compounds has been demonstrated.

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