

The application of silicalite-1/fly ash cenosphere (S/FAC) zeolite composite for the adsorption of methyl *tert*-butyl ether (MTBE)

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ABSTRACT

Silicalite-1/fly ash cenosphere (S/FAC) zeolite composite has been applied for batch adsorption of methyl *tert*-butyl ether (MTBE) from water systems. Here the key experimental conditions, including the ratio of initial MTBE concentration to the amount weight of S/FAC, adsorption time and temperature, have been discussed in detail. The results show that approximately 93–95% MTBE could be adsorbed with initial concentration of MTBE solution $1000 \mu\text{g l}^{-1}$. The column flow-through experiments also prove the high capacity of S/FAC composite for MTBE removal. The distinct advantages of S/FAC zeolite composite as adsorbent lie in (1) enhanced adsorption rate and capacity based on hierarchical micro and meso/macroporosity of S/FAC; (2) more easily operation and recycling process by assembly of nano-sized silicalite-1 zeolite on FAC support.

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1. Introduction

Methyl *tert*-butyl ether (MTBE), a widely used gasoline additive, has been identified as potential human carcinogen [1]. The release of MTBE could cause contamination in both ground water and surface water, mainly due to leakage and spillage from underground fuel tanks and pipelines [2]. Recently the United States Environmental Protection Agency (USEPA) has issued a Drinking Water Advisory on MTBE levels not exceeding $20\text{--}40 \mu\text{g l}^{-1}$ [3]. Consequently there is an urgent demand for feasible and efficient methods to remove MTBE from water systems.

Nano-sized zeolites, the inorganic porous materials, with good mechanical and hydrothermal stability, have received much attention as adsorbents for the removal of MTBE [4–8]. Senataral et al. [7] ever studied four high-silica zeolites of silicalite-1, mordenite, zeolite beta and Y for the adsorption of MTBE in water solution. It showed silicalite-1 could be the most effective adsorbent due to its higher hydrophobicity.

However, there remain some bottle-neck problems for nano-sized zeolites in practical environment application, as a result of (1) inconvenient operation of nano-sized crystals; (2) relatively slow mass transportation rate of microporous structure ($<1 \text{ nm}$).

Nowadays the considerable development of nanotechnology may resolve the problems above. It has been reported that nano-

sized zeolite as seeds could be fabricated on various supports for the preparation of hierarchical micro/meso/macroporous zeolite composite [9–11]. Fly ash cenosphere (FAC), an aluminosilicate-rich waste produced in coal-firing power plants, could be a kind of feasible support for zeolite composite, based on its economical low cost; excellent chemical/physical stability; and non-toxic release of its component [10,11]. Recently, the nanozeolite composite zeolite/FAC with a hierarchical porous structure has been successfully prepared by us through a seed-induced hydrothermal treatment method [10,11].

In this study, the optimized nanozeolite silicalite-1, in comparison with nano-sized zeolite β , Y, and ZSM-5, was assembled on fly ash cenosphere to obtain silicalite-1/FAC (S/FAC) zeolite composite, for the higher performance of adsorptive removal of MTBE in water solutions. The self-synthesized S/FAC has been attempted on MTBE removal in the batch adsorption systems. The key experimental conditions, including the ratio of initial MTBE concentration to the amount weight of S/FAC, adsorption time and temperature, have been discussed in detail. Column flow-through adsorption tests were also conducted. All the results given here would contribute S/FAC to large-scale practice for adsorptive removal of MTBE in aqueous phase system in the coming future.

2. Experimental

2.1. Reagents and materials

Tetraethylammonium hydroxide (TEAOH, 25 wt.%) and tetrapropylammonium hydroxide (TPAOH, 1 M) solutions were

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Table 1
Properties of nano-sized zeolite seeds.

Zeolite	Pore size (Å)	SiO ₂ /Al ₂ O ₃	BET (m ² g ⁻¹)
Silicalite-1	5.5 × 5.6	∞	368
ZSM-5	5.5 × 5.6	60	404
β	6.7 × 5.6	26	401
Y	7.4	4	342

obtained from Lancaster Synthesis Co. Ltd. Tetraethylorthosilicate (TEOS, 98 wt.%), poly-(diallyldimethylammonium chloride) (PDDA, 20 wt.%), and poly-(sodium 4-styrenesulfonate) (PSS, 25 wt.%) were obtained from Aldrich. MTBE (purity over 99%, Shanghai Experiment Reagent Co. Ltd.) was diluted to appropriate concentrations for the adsorption process. MTBE (>99.5%) used as a standard for gas chromatography was obtained from Fluka.

Fly ash cenosphere ($\leq 75 \mu\text{m}$) was provided by Shanghai Zhengmei Sub-nanoscale Material Manufacture Co. Ltd. with listed components of SiO₂ 55–65%, Al₂O₃ 26–35%, Fe₂O₃ 1–5%, CaO 0.2–0.6%, MgO 1–2%, Na₂O 0.5–4.0%, K₂O 0.01–2%, TiO₂ 0.5–2%. The FAC used was selected carefully to avoid the secondary contamination to environment. The analysis of concerned heavy metals such as Mercury, Arsenic, Chromium, Lead and Selenium was performed by inductively coupled argon plasma–atomic emission spectrometry (ICP–AES) or atomic absorption spectrometry (AAS), with reference to EPA Method 3050B/3051/3052/3060. No such metals were detected in the FAC.

2.2. Preparation and characterization of sorbents

Zeolite silicalite-1, ZSM-5, β and Y, of which the size lies in the range of 90–180 nm, were prepared according to methods reported in literatures [12–15]. The four different zeolite seeds varied in their pore size and SiO₂/Al₂O₃ ratio, as listed in Table 1. The first step of the assembly procedure for zeolite composite is the seeding process. A homogeneous layer of nanosilicalite-1 was seeded onto the support FAC in accordance with the layer-by-layer (LbL) technique described in the literature [11]. Secondly, a clear hydrogel with composition of (TPA)₂O: 32.5, SiO₂: 130, EtOH: 1564 H₂O was stirred for 24 h for aging under ambient temperature to obtain the precursor. Then, 0.4 g silicalite-1 seeded FAC with 5 ml precursor was subjected to hydrothermal treatment at 140 °C. The final products were calcined at 550 °C in air to remove the organic template. The BET surface area of FAC and S/FAC are 0.217 and 73 m² g⁻¹, respectively. The average percent of silicalite-1 assembled on the FAC was 20 wt.% according to the calculation previously [16].

The nano-sized zeolite crystal seeds and S/FAC composite were characterized by powder X-ray diffraction (XRD, BRUKER-AXIS D8 ADVANCE), scanning electron microscopy (SEM, Philips Sirion 200 microscope), Fourier transform infrared (FT-IR, Shimadzu IR Prestige-21) and N₂ adsorption–desorption measurements (Micromeritics ASAP 2010 apparatus).

2.3. Seeds optimization and adsorptive properties study of S/FAC

The optimization of nano-sized zeolite crystal seeds including silicalite-1, ZSM-5, β and Y was performed in the initial MTBE batch adsorption experiments. Each type of zeolite crystal seeds (weight amount 5 mg) was added to a solution of 25 ml with an initial MTBE concentration of 1000 μg l⁻¹, and the contact time lasted 24 h to reach adsorption equilibrium.

The adsorptive properties of the final S/FAC composite as well as silicalite-1 were studied in the subsequent adsorption experiments. To obtain the adsorption isotherms, samples (5 mg) of S/FAC and silicalite-1 were added to solutions of 100–1000 μg l⁻¹ MTBE and

equilibrated. Meanwhile, the adsorption rate of S/FAC and silicalite-1 was acquired by measuring the MTBE concentration after a certain contact time (0.25–24 h). In addition, the effect of ambient temperature on the MTBE adsorption by S/FAC and silicalite-1 was also studied.

After separation by centrifugation (for zeolites) or filtration (for the S/FAC composite), the MTBE concentration in the liquid phase was analyzed by headspace/GC–MS method using a Shimadzu GC/MS–QP 2010 instrument. The detection limit is 10 μg l⁻¹.

2.4. Column flow-through adsorption experiments

The breakthrough test using S/FAC as sorbent was carried out in a quartz column, having an inside diameter of 4 mm and an outside diameter of 6 mm, with a column length of 150 mm. About 100 mg of the nanozeolite composite S/FAC was packed in the vertical column having a bed length of 20 mm. Upflow conditions were used in the experiment. At room temperature, solutions with certain MTBE concentration were pumped into the fixed-bed flow reactor at a flow rate of 3 ml h⁻¹. MTBE content of the effluent was sampled at different operating times and analyzed by a Shimadzu GC/MS–QP 2010 instrument.

3. Results and discussion

3.1. Optimization of nanozeolite seeds for the assembly of zeolite composites for MTBE removal

Fig. 1 shows the behaviour of different zeolites after 24 h contact with MTBE solution. The initial concentration of MTBE was 1000 μg l⁻¹. It was found that silicalite-1 had the highest affinity for MTBE at this relatively low concentration level, reducing the solution concentration from 1000 to 120 μg l⁻¹. It could also be observed that ZSM-5 was efficient at removing MTBE from solution, with a removal efficiency of 78%. In comparison, zeolite Y removed only ~15% of the MTBE in solution, while zeolite β was intermediate in the order (~36%) as the percent removal of MTBE from solution ranking silicalite-1 > ZSM-5 > β > Y.

It is well-established that the sorption characteristics of zeolite-type materials are defined by pore size and charge properties [17]. Zeolites with high SiO₂/Al₂O₃ ratios (limited Al substitution for Si within the framework resulting in low charge in the structure) have a low capacity for retaining cations, but are more hydrophobic and can therefore adsorb organic molecules. The selectivity for

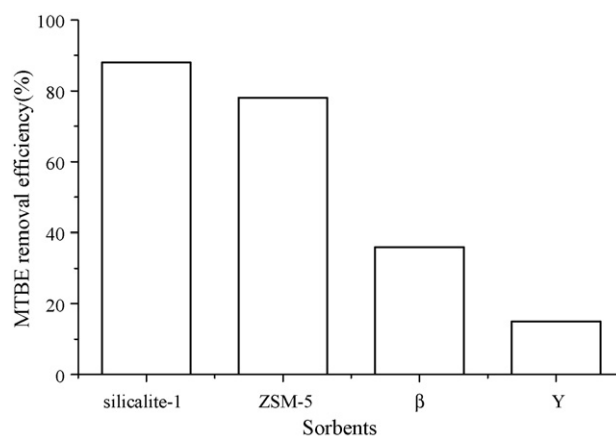


Fig. 1. Comparison of the behaviour of different sorbents for the removal of MTBE from water solutions (initial concentration of MTBE 1000 μg l⁻¹, contact time 24 h, 20 °C).

molecules depends on constraints imposed by the pore size and shape. Therefore, only molecules having similar dimension to the pore diameter can be effectively adsorbed.

Silicalite-1, the most hydrophobic among the four zeolites, is the aluminium free form of ZSM-5 and also has a 10-membered ring MFI structure. These MFI pores are elliptical with diameters of 0.55 and 0.56 nm, making them slightly smaller than the effective diameter of MTBE (0.62 nm) [6]. Thus, it may be difficult for MTBE to be adsorbed into the MFI pores. However, according to our experimental results, both silicalite-1 and ZSM-5 proved to be effective for the removal of MTBE from solution. The results were consistent with another study [7], which reported a new concept in realizing the adsorption of MTBE onto MFI zeolites by using a multi-step potential model, from which the researchers estimated the dimensions of MTBE to be 0.575 nm × 0.593 nm × 0.72 nm and

suggested that MTBE must deform slightly to fit within the pores of MFI zeolites. The combination of a sufficient number of defects in the crystalline structure and the natural vibrations in the crystal lattice may facilitate the penetration of MTBE molecules into the pores.

It was hypothesized that the MTBE adsorption capacity of ZSM-5 zeolites would increase with increasing SiO₂/Al₂O₃ ratio [4,8]. As shown in Fig. 1, zeolite silicalite-1 (SiO₂/Al₂O₃ ratio of ∞, the Al-free form of ZSM-5) showed a removal efficiency of MTBE obviously higher than ZSM-5 (SiO₂/Al₂O₃ ratio of 60). The results suggest that the improvement of the hydrophobic character of the pore walls of the zeolite would favour the adsorption of MTBE molecules. Zeolite β and Y used in this experiment were selected mainly due to their synthesis process simpler and faster. However, the high Al contents lead to their lower hydrophobicity. Therefore, these zeolites did not

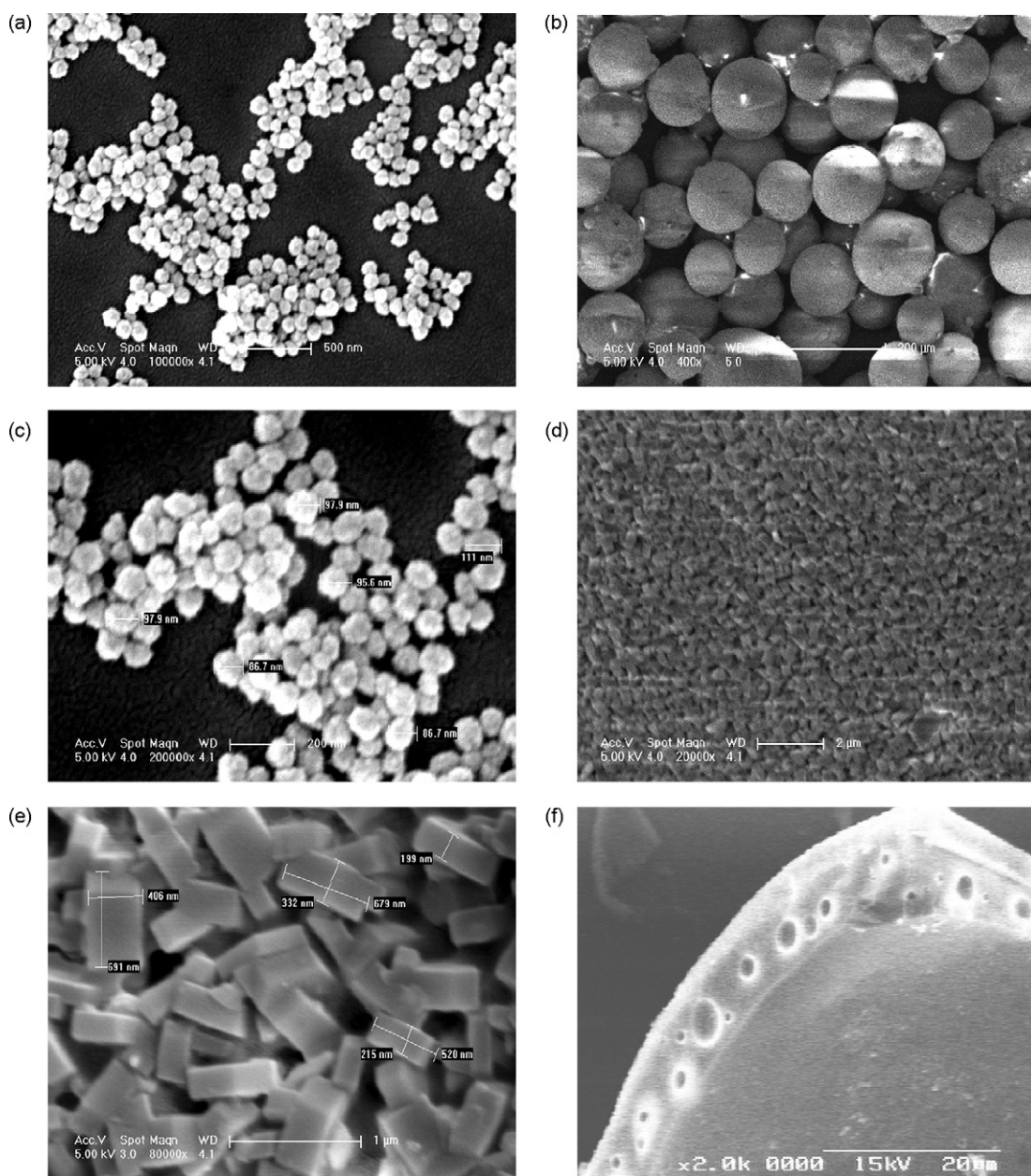


Fig. 2. SEM images of silicalite-1 crystals at low (a) and high (c) magnifications, the surface of zeolite silicalite-1-seeded FAC (d), the resulting S/FAC spheres at low (b) and high (e) magnification, and the bilayered shells from the cross-section view (f).

perform so well as expected in spite of their larger pore diameters (0.67 nm \times 0.56 nm of β and 0.74 nm of γ) being more appropriate to accommodate the MTBE molecules.

The results of the experiments showed that the hydrophobicity of the zeolite with suitable size and structure was the dominating factor in the adsorption of MTBE. Therefore, the silicalite-1 crystal was selected to be the seed for the subsequent assembly of the nanozeolite composite.

3.2. The assembly of S/FAC zeolite composite using optimized silicalite-1 as seeds

Colloidal silicalite-1 was prepared according to the literature [14]. The obtained nano-sized silicalite-1 crystals with an average size of 90 nm are shown in Fig. 2a and c. Fig. 2b, d and e shows that after the LbL technique and hydrothermal treatment, the FAC spheres are coated with homogeneous nano-sized zeolites. Almost all of the products were retained on the initial spherical morphology of FAC (Fig. 2b), while the silicalite-1 seeds deposited earlier on the outer surface of FAC had grown into cubic crystals of several hundred nanometres (Fig. 2e), covering the shells completely (Fig. 2b and d). The SEM image (Fig. 2f) indicates that the final hollow spheres possess bilayered shells: an outer layer of compact zeolite and an inner layer of FAC shell.

The XRD analysis results of silicalite-1, FAC and S/FAC are shown in Fig. 3. Having differences from original FAC (Fig. 3d), new peaks at $2\theta = 7.8^\circ, 8.7^\circ, 23^\circ, 24.5^\circ$ were found in the XRD pattern of S/FAC (Fig. 3b). These peaks are well comparable to the pattern of the MFI zeolite (Fig. 3a), confirming the formation of silicalite-1 crystals on the surface of FAC. The infrared (IR) spectra of the samples were measured as illustrated in Fig. 4. In contrast to the silicalite-1 seeds (Fig. 4a), the IR spectrum of S/FAC (Fig. 4b) shows typical Si–O–Si framework bands, including the characteristic double ring vibration at ca. 550 cm^{-1} as found in the MFI-structured zeolites, thereby confirming the presence of zeolite silicalite-1 in the S/FAC composite. Overall, these results prove the successful assembly of the S/FAC zeolite composite.

3.3. Adsorption of MTBE by S/FAC composite

The adsorption isotherms of S/FAC and silicalite-1 were developed with different MTBE initial concentrations (from 100 to

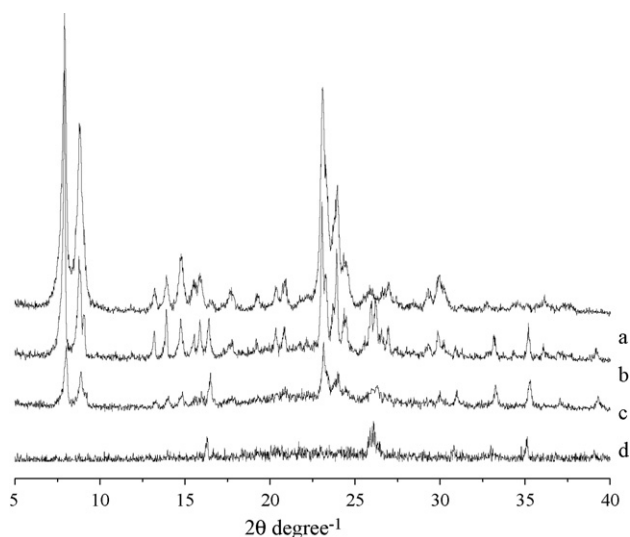


Fig. 3. XRD patterns of the silicalite-1 (a), S/FAC (b), regenerated S/FAC (c) and original FAC (d).

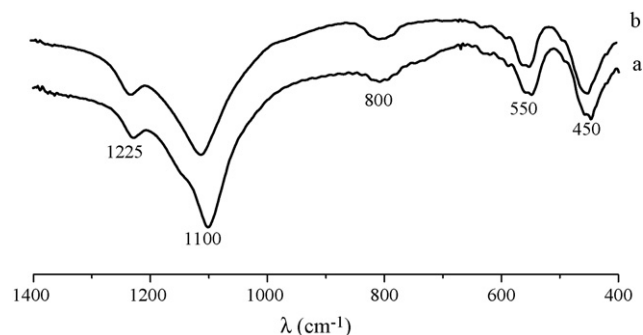


Fig. 4. FT-IR patterns of the silicalite-1 (a) and S/FAC (b).

$1000\text{ }\mu\text{g l}^{-1}$, the level of concern for drinking water). Fig. 5 shows that the MTBE adsorption capacity of S/FAC and silicalite-1 increased linearly (R^2 of 0.988 and 0.997, respectively) with the MTBE equilibrium concentration, yielding distribution coefficients (slope of MTBE adsorption capacity versus MTBE equilibrium concentration) of 64.6 and 35.6 l g^{-1} . From these data, the S/FAC composite clearly showed a greater removal capacity than silicalite-1. This indicates that the adsorption capacity of silicalite-1 for MTBE significantly increased after being assembled on the FAC.

Having a composite of silicalite-1 and FAC, in which the silicalite-1 is dispersed on the surface of the support FAC, can avoid the aggregation and coagulation of nano-sized crystals, and may enable the use of silicalite-1 itself as an adsorbent confined in an isolated and practically usable medium in aquatic solutions. Besides this, the obtained hierarchical composite was found to have macropores linked to the zeolite micropores, which permit easy access to the zeolite micropores owing to the reduction of the intercrystalline diffusion resistance [18,19]. It is considered that this characteristic of the S/FAC composite could account for the enhancement of the adsorptive features of silicalite-1.

Fig. 6 illustrates the typical behaviours of silicalite-1 and S/FAC obtained at 20°C . After addition of the S/FAC composite, a fast decrease of the concentration of MTBE in solution was observed during the first 2 h. Then, the concentration of MTBE decreased slowly and remained unchanged after 6 h, removing 93.3% of MTBE from solution. In comparison, an obvious decrease of MTBE concentration occurred during the first 6 h in the case of silicalite-1 crystals as the adsorbent, and adsorption reached equilibrium after 10 h, with a removal efficiency of MTBE 87.3%. These results

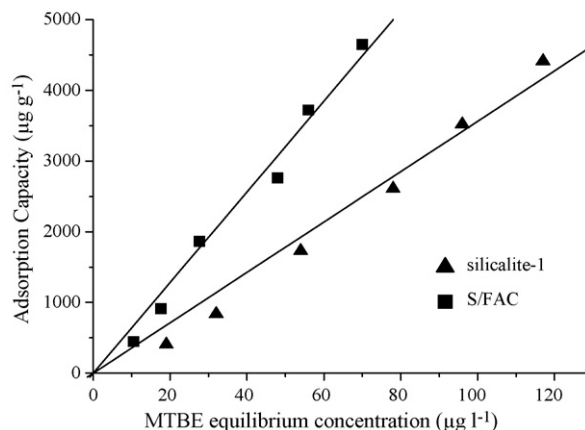


Fig. 5. MTBE sorption isotherms of silicalite-1 and S/FAC (20°C).

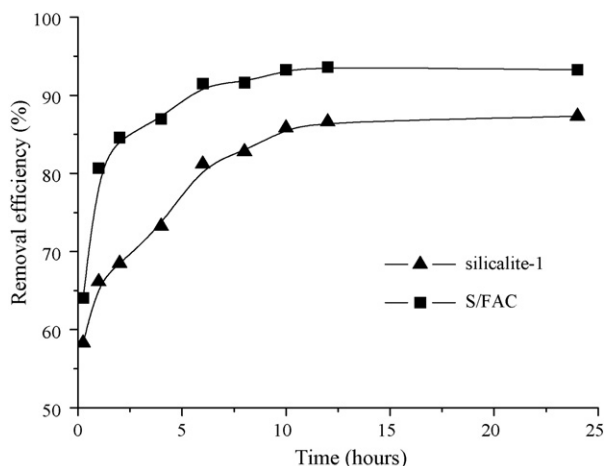


Fig. 6. Adsorption rate of MTBE on S/FAC and silicalite-1 (initial concentration of MTBE $1000 \mu\text{g l}^{-1}$, 20°C).

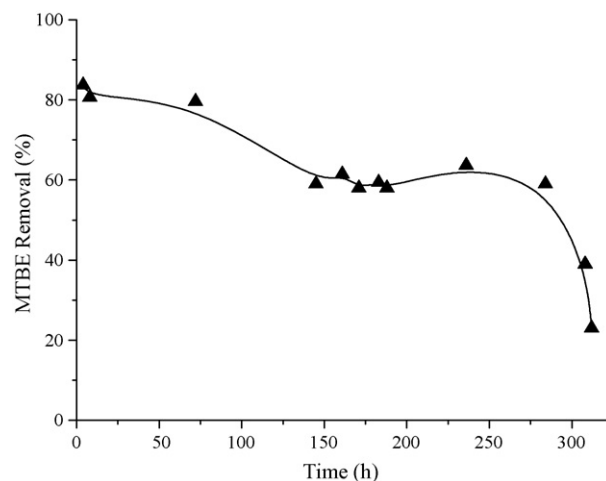


Fig. 7. Variation of MTBE removal with adsorption time on composite S/FAC.

suggest a faster adsorption rate of the S/FAC composite than silicalite-1 crystals for the removal of MTBE, which may be due to the better diffusion of MTBE to the zeolite (external diffusion) on FAC.

Table 2 shows the behaviour of the S/FAC composite and silicalite-1 for the removal of MTBE under different temperature conditions. The temperature condition of MTBE adsorption process is specially designed in view of both S/FAC composite large-scale application in environmental field in the future and the inherently characteristics of MTBE. Three typical solution temperatures (10 , 20 , 30°C), which are below the boiling point of MTBE 55.2°C , were selected to perform the study. As the temperature variation is not big, no obvious effect of temperature was found on the adsorption of MTBE by S/FAC and silicalite-1 even the process should be exothermic.

3.4. Column experiments

In groundwater in which MTBE was detected, the concentration of MTBE was ranging from 0.2 to $23,000 \mu\text{g l}^{-1}$ [20]. Therefore, two solutions of different MTBE concentrations within this range were selected to conduct the column experiments.

In one experiment, a solution of 10 mg l^{-1} MTBE was pumped into the column at a flow rate of 3 ml h^{-1} at room temperature. MTBE removal versus adsorption time on composite S/FAC from solution is displayed in Fig. 7. As can be seen, 80% of MTBE was removed in the initial 72 h solution effluent by the composite S/FAC. Then, the MTBE removal decreased gradually to nearly 60% at 145 h, and was continuously reduced to 23% at 312 h. The other column-flow adsorption experiment was carried out by pumping a solution with concentration of MTBE $1000 \mu\text{g l}^{-1}$. The MTBE concentration for the sample collected in the first 72 h was below the detection limit ($10 \mu\text{g l}^{-1}$).

Table 2
Behaviour of S/FAC and silicalite-1 under different temperature conditions (10 , 20 , 30°C).

Initial concentration ($\mu\text{g l}^{-1}$)	Removal efficiency (%)	
	Silicalite-1 10/20/30 °C	S/FAC 10/20/30 °C
1000	86.7/88.3/87.4	91.1/93.3/94.8
600	88.1/87.1/85.4	93.0/91.8/92.3
200	87.2/85.3/84.7	92.1/93.2/94.1

3.5. Regeneration process of the S/FAC composite

S/FAC can be easily recovered by filtration. Conventionally, separation of zeolites from solution is carried out in high-speed centrifugal separator ($>10,000 \text{ rpm}$) rather than by filtration operation, because of the colloidal properties of nano-sized crystals. A relative simple recovery process is therefore beneficial to the practical application of S/FAC composites. The regeneration of the recovered S/FAC can be realized by heating in air at 500°C for approximately 4 h. The XRD pattern of the composite showed no obvious change in structure of S/FAC after regeneration (Fig. 3c).

4. Conclusion

The S/FAC zeolite composite, which obtained through assembling an optimized nanozeolite seed silicalite-1 and support FAC, was applied as a promising adsorbent to the efficient removal of MTBE from water systems. A linear model reasonably fit the S/FAC and silicalite-1 isotherms, with partition coefficients of 64.6 and 35.6 l g^{-1} , indicating a higher adsorption capacity of S/FAC than that of silicalite-1. The preferential conditions for the removal of MTBE by adsorption can be described through the case that 5 mg of the S/FAC composite adsorb 93.3% MTBE from 25 ml aqueous solution with an initial concentration of MTBE $1000 \mu\text{g l}^{-1}$ when equilibrium establishes after 6 h. At two different MTBE concern level, the column flow-through experiments were carried out. The results confirmed high capacity of S/FAC composite for MTBE removal.

The drawbacks of using nanozeolites such as aggregation in solution could be avoided after assembly. The employment of S/FAC zeolite composite may be a solution, technically and economically feasible to remove MTBE from water, because of the more convenient operation and recycling of the micro-sized particles, and the reuse of the low-cost FAC. Further studies, such as shortening the synthesis time, using less organic template in the synthesis, competitive adsorption of natural organic matters, and column parameter optimization etc., are deemed necessary in order to optimize the silicalite-1/fly ash cenosphere (S/FAC) zeolite composite for the adsorption of methyl *tert*-butyl ether.

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