Detecting and Evaluating Detrimental Factors of Clay's Longevity, Selecting, and Optimizing an Appropriate Adsorbent for Operating Time Elevation in the Separation Process of Trace Olefins from Aromatics

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ABSTRACT: Industrial-scale production of aromatic materials is confronted by the problem of removal of impurities such as olefins. Their removal is an essential requirement in marketability. Catalytic adsorbent clay is the most common material used for the removal of olefins from aromatic streams. The current study is focused on increasing the lifetime of a commercial type of clay by identifying the effective parameters in reducing the adsorbent lifetime. An analysis of 3 years of data from a petrochemical complex showed that water, morpholine, and N-formyl morpholine (NFM) contents in the feed stream are the factors reducing the clay lifetime. Various experiments have been performed to determine the individual impacts of these parameters on the clay lifetime. Reducing the water content from 150 to 70 ppm led to a 20% increase in lifetime, while increasing morpholine content from 55 to 160 ppm and NFM content from 0.55 to 91 ppm resulted in 40 and 75% reduction in lifetime, respectively. Also, six types of conventional commercial adsorbents have been tested to minimize the contents of the above-mentioned components before olefin removal by clay. Among them, silica gel showed the best performance. The optimum weight percentage of silica gel relative to the total loaded clay mass was determined to be 10%, which led to a 2.1-fold increase of clay lifetime if silica gel was loaded into the reactor prior to clay loading.
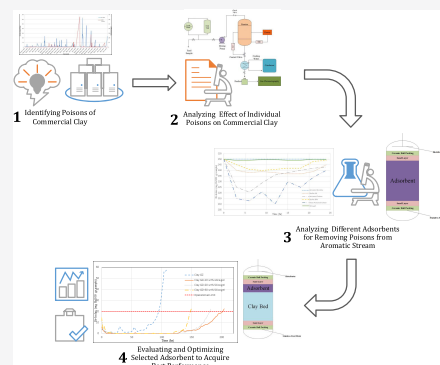
1. INTRODUCTION

In the oil industry, aromatic materials such as benzene, toluene, and xylene (BTX) are obtained from distillation, reformation, and cracking processes. Their production is often accompanied by undesired olefinic impurities, which, despite their low amount, are a huge hinderance in their aromatic applications in downstream units.[1−3]

Two processes have been proposed for removing olefins from aromatic streams:

1. Clay treatment
2. Catalytic hydrogenation treatment

Clay treatment is the most commonly used process of removing olefins from aromatic streams in the chemical industries. In the clay treatment process, the acidic properties of clay make it possible to remove olefins from the main stream by following the Friedel−Crafts reaction. In catalytic hydro-treatment, olefins are saturated by reacting with hydrogen in the presence of catalysts.[4,5] Catalytic hydrogenation, in addition to being costly due to requirement of special conditions, may also be used to remove olefins.[6] Clay is highly diverse, and in addition to its widely known applications in various industries including construction and

ceramic, paper and fillers, drilling mud, casting, and pharmaceutical molds, it is also used as an adsorbent,[7−10] catalyst[11,12] and catalyst support,[13−15] ion exchanger,[16,17] and chattonella marina[18] based on its unique properties.[19,20]

Removing olefins from aromatic streams is essential since the olefin-containing flow results in the deactivation of the catalyst in the downstream petrochemical process units. The amount of olefin content in aromatic streams is assessed by the bromine index (BI). The input flow to the clay treatment unit has typically a BI of about 300−700, which needs to be reduced to below 20.[21]

Several studies have focused on producing different catalysts from clay for olefin removal from aromatic streams. Pu et al.[22] attempted to improve clay by the zeolite MCM-22 and La_2O_3 and were able to raise the lifetime by four times. In another work,[23] they significantly increased the operating time by

modifying clay with a special type of zeolite and reported the increased amount of Lewis acid in the synthesized sample as the reason. There are numerous other similar studies in this field, all with substantial costs for catalyst production. On the other hand, all of the existing studies focus on catalyst production and none have improved the clay lifetime by identifying the detrimental factors and eliminating them. Therefore, in the current study, first pilot tests were performed to analyze the annual data of the units using clay for olefin removal and find the parameters affecting the clay lifetime. Then, various adsorbents were tested to study the detrimental factors affecting the clay lifetime. With an appropriate adsorbent, the corresponding pilot test with clay was conducted at various weight percentages. The optimum adsorbent percentage for eliminating detrimental factors and increasing the clay lifetime for olefin removal from aromatic streams have been reported.

2. METHOD

2.1. Materials. GZ commercial clay was purchased from Sud-Chemie (India). Commercial absorbents like activated alumina, zeolite 4A, activated carbon, zeolite SPX, and silica gel were purchased from Sigma-Aldrich. Nanoactivated carbon was synthesized for tests similar to the other adsorbents according to the procedure by Abdulkareem-Alsultan.[24]

Aromatic hydrocarbons were provided by the Avicenna petrochemical complex for the pilot tests (feed), with the corresponding feed analysis presented in Table 1.

Table 1. Composition of the Hydrocarbon Feed Stream

component	content wt %
nonaromatics	7.65
benzene	29.52
toluene	60.1
ethylbenzene	0.11
p-xylene	0.18
m-xylene	0.34
o-xylene	0.13
C9 and C9+	1.95

2.2. Characterization. Compositions of feed and products were determined by the gas chromatography (GC) analysis (CP-3800, Varian) based on the ASTM D-5134 standard with the Cpsil CB column (height and diameter of 50 m and 0.5 μm, respectively). Morpholine and N-formyl morpholine (NFM) contents of the feed and products were obtained by the GC-Cp-wax52 column (height and diameter of 25 m and 1 μm, respectively). The water content in the feed and products was determined by potentiometer titration by Metrohm devices (Switzerland) according to ASTM E203 and ASTM 1064 standards. The olefin contents of feed and products stream were similarly determined according to the ASTM D 2710-92 standard.

2.3. Pilot Test. Reactor tests of different adsorbents and commercial clay were performed in the pilot (Figure 1a). A total of 7.7 g of each adsorbent and clay were poured into a reactor (height = 50 cm and diameter = 2 cm) equipped with a flow controller and heating system. The sample was placed between two layers of ceramic and sand to be properly packed. The internal arrangement of beds within the reactor during various tests with commercial clay are shown in Figure 1b,c. All of the tests took place at 185 °C and 16 bar pressure with a
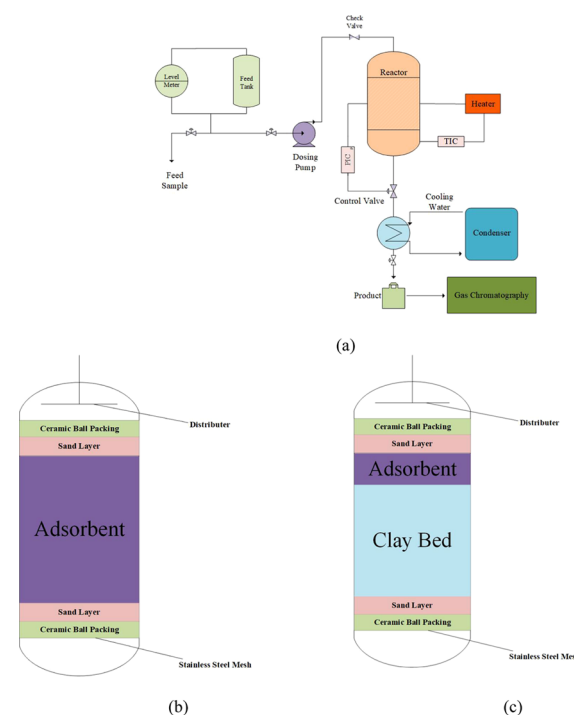

Figure 1. General schematic of the pilot (a), internal structure of the adsorbent-containing reactor (b), and internal structure of the reactor containing the selected adsorbent and commercial clay for evaluating the increase of clay lifetime by adsorbent (c).

weight hourly space velocity (WHSV) of 6.56 h^{-1}, which are the desired operating conditions used in the industrial olefin removal unit.

3. RESULTS AND DISCUSSION

3.1. Parameters Affecting Clay Lifetime. After reviewing the current procedure of the petrochemical complex, annual laboratory data, and literature review,[25−27] three factors influencing the clay lifetime were selected and studied: NFM, morpholine, and water contents of the input feed to the clay reactor.

NFM is used for the extraction of aromatic from nonaromatic hydrocarbons in the upstream of the olefin removal unit. This compound is recovered in the same unit, but its recovery is not complete and therefore some traces remain in the feed stream input to the clay reactor.

The analysis of annual petrochemical data proved the presence of morpholine not previously reported as a new compound of the NFM family with a similar structure. The literature indicates that the temperature and pressure conditions for better progress of the reaction of NFM transformation to morpholine are based on the mechanism shown in Figure 2.[28]

The compounds present in the feed of the olefin removal unit are likely to make bonds with the acidic sites of clay
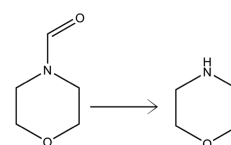

Figure 2. Mechanism of NFM transformation to morpholine.
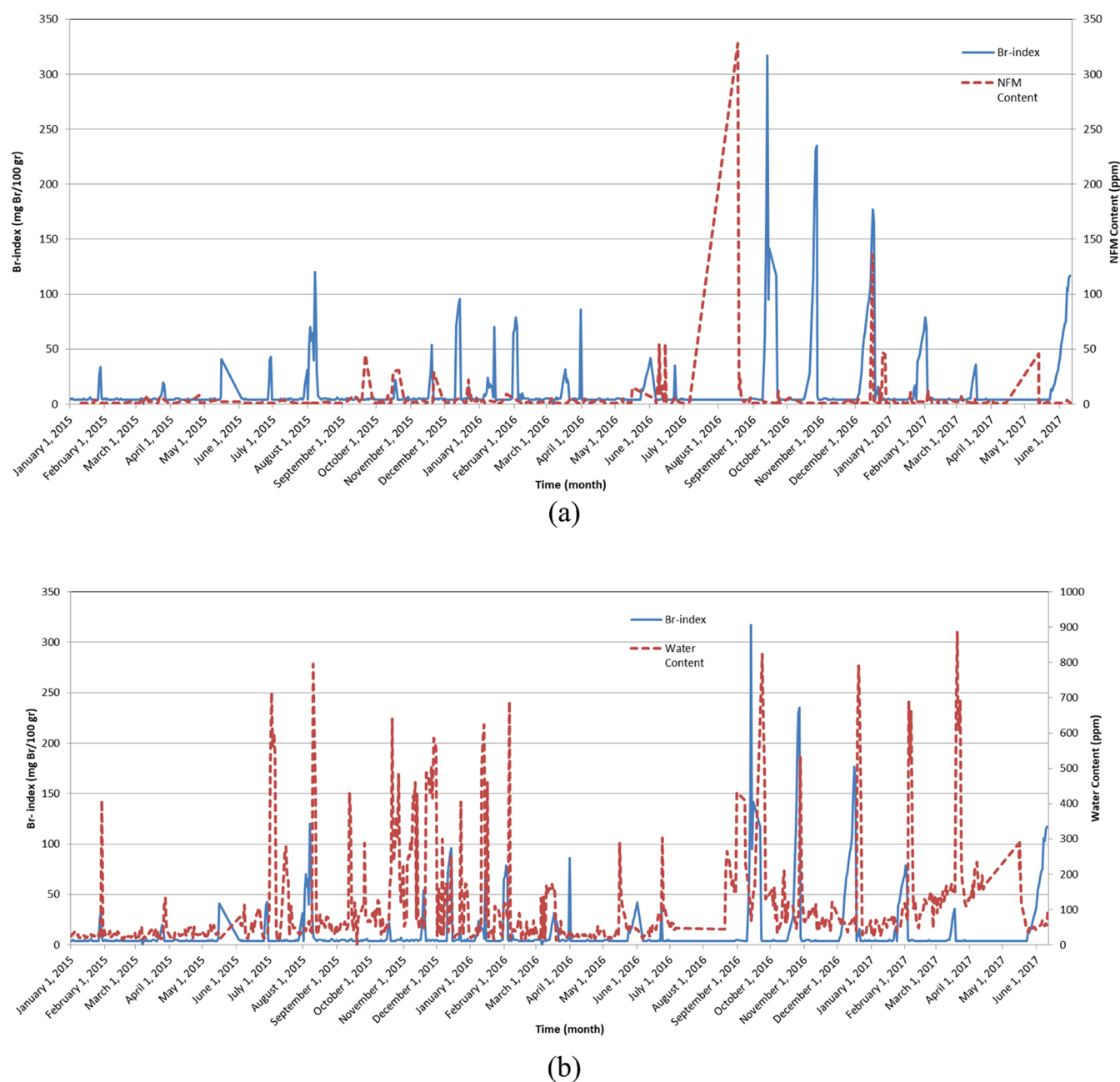
(a)

(b)

Figure 3. Effect of NFM content (a) and water content (b) on clay running time in 3 years.

because of the nitrogen in their structure and can, therefore, reduce the running time.[27] The effect of NFM content on the BI of the product stream of the olefin removal unit during 3 years of operation is shown in Figure 3a. Between October and November 2015, when the NFM content of the input feed stream was high, the deactivation of clay occurred faster than in other months. Since the existence of morpholine in the stream was not expected, no data was collected and thus its effect was not studied.

The water content was also determined as a possible factor influencing the reduction of the clay lifetime. The increase in the water content of the feed can be attributed to various parameters such as water leakage within the heat exchanger before the reactor due to corrosion. Figure 3b shows the effect of water content on the BI of the product stream of the olefin removal unit in the three-year period. It can be seen that in

certain months, e.g., between July and August 2015, when the water content of the feed was high, deactivation of adsorbent occurred relatively sooner. To analyze the individual effect of each of these factors on the reduction of clay lifetime, experiments were designed, as presented in the following section. Experimental errors were measured and found to be within acceptable ranges.

3.2. Effect of Individual Parameters Affecting the Reduction of Clay Lifetime. To analyze the effect of each parameter, a constant feed containing water (150 ppm), morpholine (55 ppm), and NFM (0.55 ppm) was received online from the plant. The following experiments were then carried out to obtain the effect of each of the parameters on the reduction of clay lifetime.

3.2.1. Effect of Water Content. To analyze the effect of reduction of water content on clay lifetime, a feed with 70 ppm
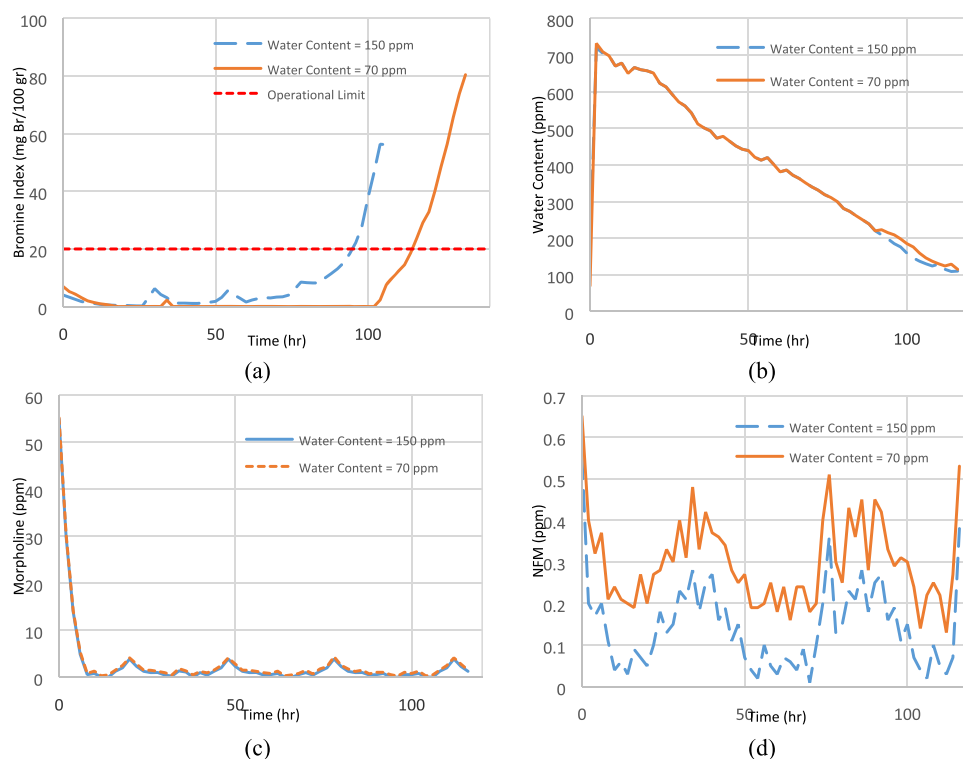
Figure 4. Effect of water content on the BI of the output product and deactivation of clay (a). Variations of the effect of water content of the output product on clay deactivation by water (b). Variations of the effect of morpholine content of the output product on clay deactivation by water (c). Variations of the effect of NFM content of the output product on clay deactivation by water (d).
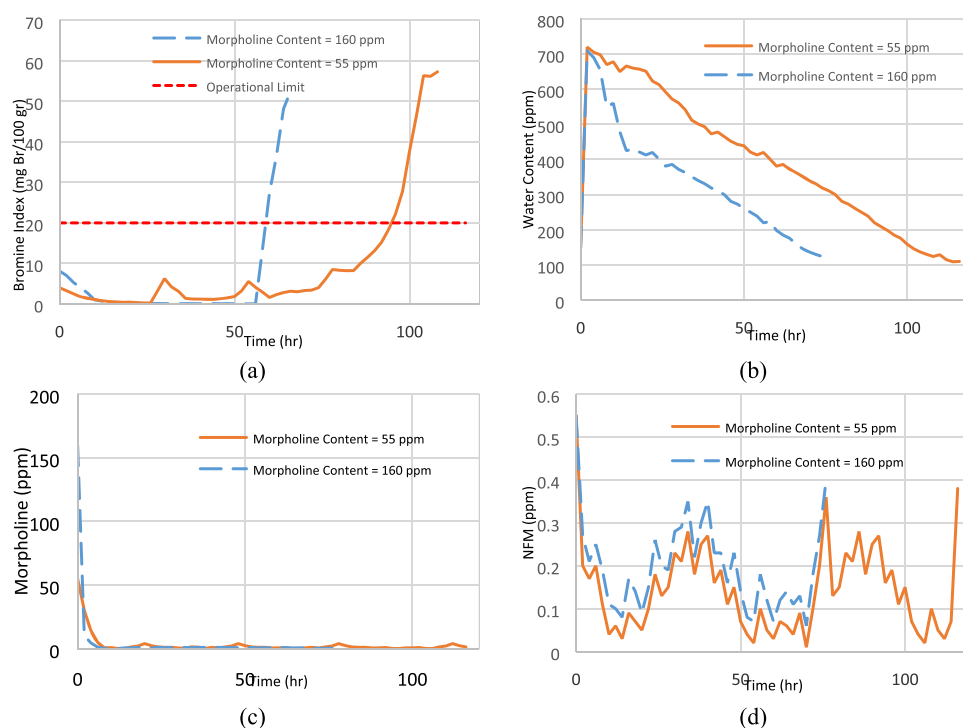

Figure 5. Effect of morpholine content on the output product BI and deactivation of clay (a). Variations of the effect of water content of the output product on clay deactivation by morpholine (b). Variations of the effect of morpholine content of the output product on clay deactivation by morpholine (c). Variations of the effect of NFM content of the output product on clay deactivation by morpholine (d).

water was used, while morpholine and NFM contents were held constant in each test to evaluate the effect of water content separately. Figure 4 presents the BI of the product during the lifetime of the adsorbent, variations of water content in the product output with time, and variations of morpholine and NFM with time.

Figure 4a indicates that the feed with a water content of 150 ppm deactivates the clay in 96 h. On the other hand, as the
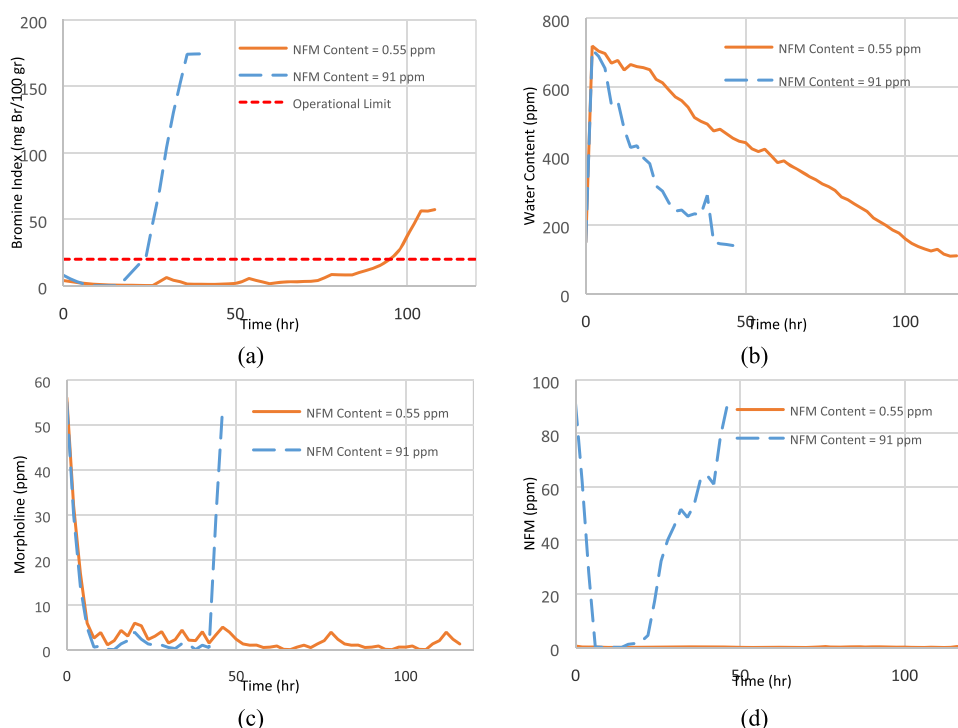
Figure 6. Effect of NFM content on the output product BI and deactivation of clay (a). Variations of the effect of water content of the output product on clay deactivation by NFM (b). Variations of the effect of morpholine content of the output product on clay deactivation by NFM (c). Variations of the effect of NFM content of the output product on clay deactivation by NFM (d).

water content is reduced to 70 ppm, this time increases by about 20% to 116 h, which shows that the clay is hydrophilic, which results in reduced catalytic performance and its deactivation.

According to Figure 4b, the water content drastically increases in the product stream at the beginning of clay lifetime, which can be attributed to the internally adsorbed water molecules in the structure from the surroundings before the experiment. Moreover, the water content diagram shows that at the experiment temperature, clay releases the absorbed water molecules, and the input and output concentrations of water in the stream remain approximately constant.

Figure 4c,d also suggests that morpholine and NFM are adsorbed on the acidic sites of clay and both can reduce the lifetime. However, since equal amounts of morpholine and NFM were used in both tests, only the decrease in water content of the feed stream has been considered as the increasing factor of clay lifetime.

3.2.2. Effect of Morpholine Content. To analyze the effect of increased morpholine content on the clay lifetime, the morpholine content was raised to 160 ppm by manual injection. Water content and NFM were held constant as mentioned in Section 3.2.1 to study the individual effect of morpholine. Figure 5 shows the BI results of the product during the adsorbent lifetime, variations of water content with time in the output product, and variations of morpholine and NFM contents with time.

The information in Figure 5a indicates that the feed with a 55 ppm morpholine content is capable of deactivating clay in 96 h. The deactivation time (intersection with Bl = 20) drops by about 40% to 58 h when the morpholine content is raised to 160 ppm. This proves that the acidic sites of clay absorb morpholine and are, in fact, deactivated. With the gradual adsorption of this molecule, acidic sites of clay are deactivated,

eliminating its catalytic potential in the process; in other words, morpholine poisons the catalysts.

Figure 5b, which shows the variation of the water content of the product stream with time, provides results similar to those given in Section 3.2.1, as does Figure 5c,d for morpholine and NFM, respectively. Since the water content and NFM are similar in this experiment, in this test, only the increased morpholine content of the feed stream reduces the clay lifetime.

3.2.3. Effect of NFM Content. To analyze the effect of NFM content on clay lifetime, the NFM content was increased to 91 ppm by manual injection. Water and morpholine contents were held constant to study the individual effect of NFM. Figure 6 shows the results of the product's BI during the adsorbent lifetime, variation of water content with time in the output product, and variation of morpholine and NFM contents with time.

The information in Figure 6a indicates that the feed with a 0.55 ppm NFM content is capable of deactivating clay in 96 h. The deactivation time (intersection with Bl = 20) drops by about 75% to 24 h when the NFM content is raised to 91 ppm. This shows that the acidic sites of clay absorb NFM and are, in fact, deactivated. With the gradual adsorption of this molecule, acidic sites of clay are deactivated; thus, the clay loses its catalytic characteristic as it becomes poisoned by NFM.

Figure 6b, which shows the variation of the water content of the product stream with time, gives similar results as mentioned in Sections 3.2.1 and 3.2.2, as does Figure 6c,d for morpholine and NFM, respectively. Since water and morpholine contents are similar in this experiment, in this test, only the increased NFM content of the feed stream is a reducing factor of the clay lifetime.

3.3. Tests of Different Adsorbents Affecting Clay Lifetime. Once the factors reducing the clay lifetime are
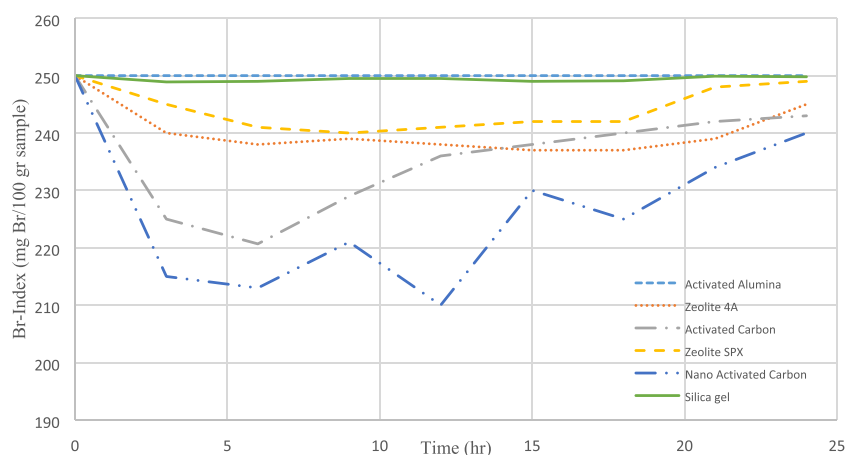
Figure 7. Variations of the product's olefin content with time in different tests.
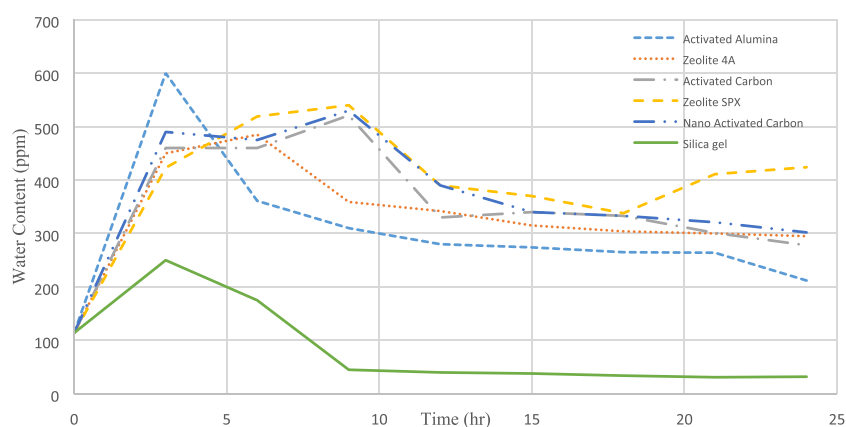

Figure 8. Variations of the product's water content with time in different tests.
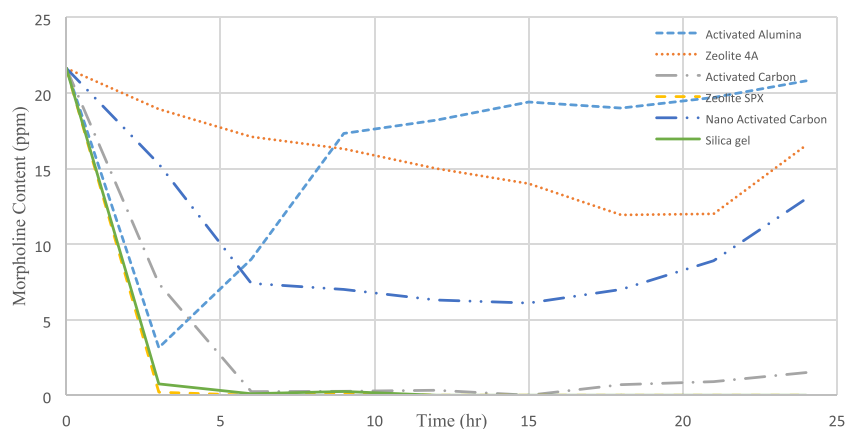

Figure 9. Variations of the product's morpholine content with time in different tests.

known, a strategy is required to minimize these effects. There are numerous methods to achieve this goal, each requiring altered operational conditions or even modifying the initial design, which was not feasible and was, therefore, put aside. One alternative, however, was using an appropriate adsorbent before olefin removal from clay for its longevity. Accordingly, six adsorbents, namely, activated alumina, zeolite 4A, activated carbon, zeolite SPX, and silica gel, which are all frequently used adsorbents in oil and petrochemical industries, were tested. Nanoactivated carbon, which is an effective and relatively new

adsorbent, was synthesized according to the procedure by Abdulkareem-Alsultan et al.[24] and tested accordingly.

In these tests, a constant feed composition with BI = 250 ppm, water content = 114 ppm, morpholine content = 21.63 ppm, and NFM content = 15.44 ppm were received online from the operating plant and adsorbent was loaded into the reactor (Figure 1b). The test was carried out in a setup pilot (Figure 1a). The results are presented in Figures 7−10, which respectively indicate the content variations of olefin, water, morpholine, and NFM with time in different tests. Table 2
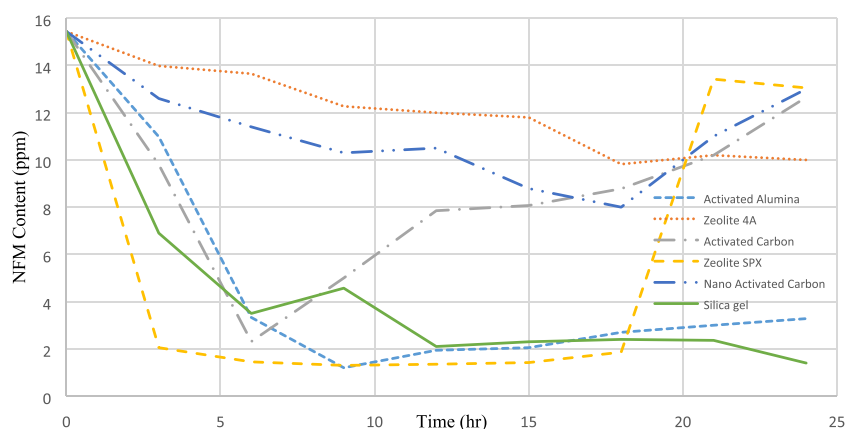
Figure 10. Variations of the product's NFM content with time in different tests.

Table 2. GC Analysis of Feed and Products of Different Test (Mole %)

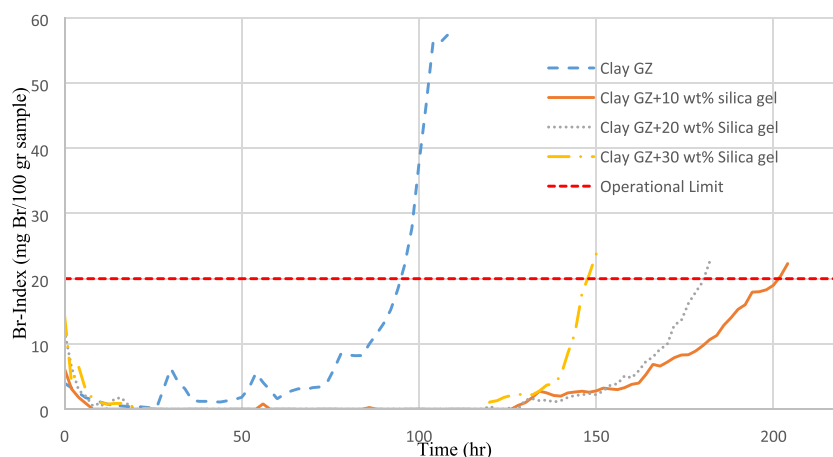| component	feed	product					
		activated alumina	zeolite 4A	activated carbon	zeolite SPX	nano activated carbon	silica gel
C6	31.835	32.4	32.54	32.413	31.847	32.1	31.839
C7	67.6	67.1	66.98	67.029	67.597	67.15	67.57
C8	0.526	0.43	0.411	0.501	0.456	0.681	0.526
C9	0.003	0.003	0.003	0.007	0.05	0.004	0.004
C10+	0.036	0.067	0.066	0.05	0.05	0.065	0.061

Figure 11. Product's olefin content variations with time in the clay lifetime increase test by different amounts of silica gel.

displays the analysis of the feed and products related to different adsorbent tests.

The adequate adsorbent should reduce the water, morpholine, and NFM contents in the feed stream considerably without affecting the olefin content; since olefin removal should exclusively be carried out by clay and if the adsorbent is involved in olefin removal as well, it leads to its quick deactivation. The selected adsorbent should not alter the feed composition and lead to the loss of aromatic and other desired products of the petrochemical complex. Based on the results, the silica gel adsorbent achieves all of the above; since silica gel does not reduce water, morpholine, and NFM contents significantly, it does not have a considerable effect on olefin content and has the lowest impact on the composition of the main compounds entering the reactor (Table 2).

3.4. Effect of Selected Adsorbent on the Increase of Clay Lifetime and Optimization. Since the operational and design conditions of the plant could not be changed in this

study, the proposed solution plan was as follows: The selected adsorbent (silica gel) and clay were loaded into the same reactor, where first water, morpholine, and NFM contents were reduced by silica gel and then the olefin content was reduced by clay to acquire BI <20 (Figure 1c). Therefore, selecting the amount of silica gel and allocating a proper volume of the reactor to the adsorbent were the next important challenges. Less than the required amount of silica gel would be unable to eliminate the harmful compounds that cause the quick deactivation of clay; however, more silica gel would cause a lower clay loading with limited volume of the reactor.

Therefore, to optimize the amount of silica gel, three tests were designed, in which 10, 20, and 30% of total clay mass loaded into the reactor were allocated to silica gel. A constant feed with BI of 220 ppm, water content of 150 ppm, morpholine content of 55 ppm, and NFM content of 0.55 pm was obtained from the plant process online. The schematic
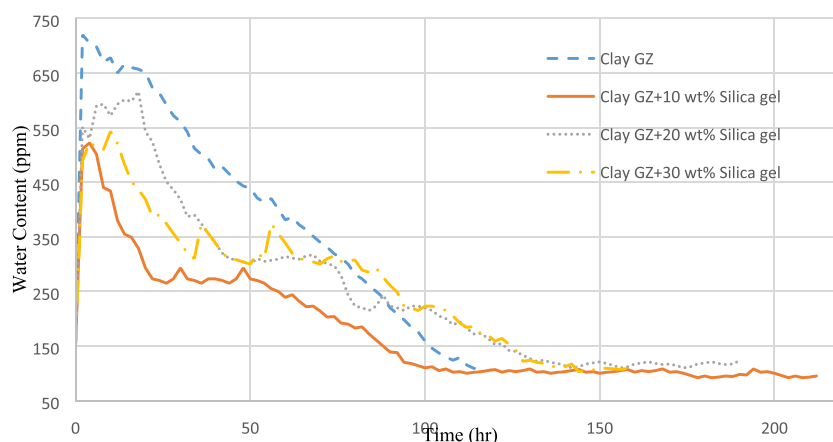
Figure 12. Product's water content variations with time in the clay lifetime increase test by different amounts of silica gel.
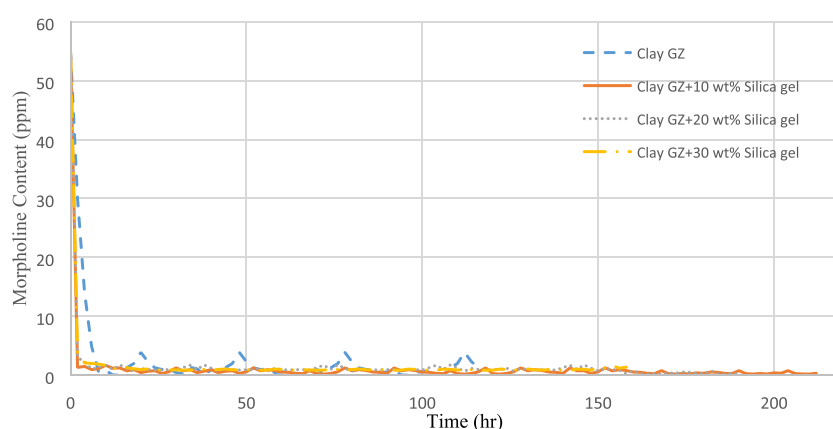

Figure 13. Product's morpholine content variations with time in the clay lifetime increase test by different amounts of silica gel.
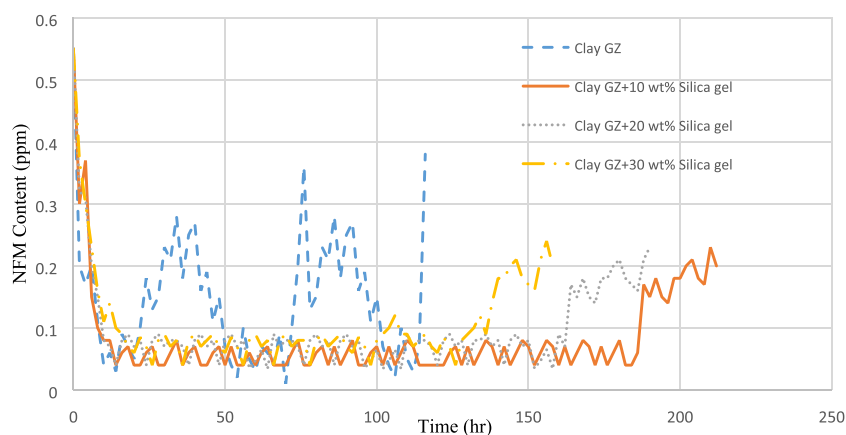

Figure 14. Product's NFM content variations with time in the clay lifetime increase test by different amounts of silica gel.

layout of the pilot and the internal structure of the reactor are depicted in Figure 1a,c, respectively.

The results of the above tests are presented in Figures 11−14, which respectively indicate the content variations of olefin, water, morpholine, and NFM with time. It can be seen that allocating 10% of the total clay mass to silica gel in the olefin removal reactor reduced the lifetime from 96 to 202 h (2.1-fold increase). For 20 and 30% values, this time reached 182 and 148 h (1.9- and 1.5-fold increase), respectively. It can, therefore, be concluded that increasing the silica gel weight percentage from 10 to 30% results in reduced clay lifetime.

Variations of water, morpholine, and NFM contents of the product stream with time indicate the advantage of using 10% silica gel compared to 20 and 30%. In other words, it exhibited better performance in reducing the water, morpholine, and NFM contents of the product stream compared to the other values of this adsorbent. Hence, 10% silica gel was selected as the optimum amount to increase the clay lifetime.

3.5. Annual Economic Analysis of Using the Optimum Amount of Silica Gel. Due to the 2.1-fold increase of clay lifetime after using 10% silica gel, the economics of the plant was affected accordingly. In the

studied unit without any intervention, clay was capable of removing olefin from the input feed for 45 days, thus requiring to be replaced eight times a year. The optimum amount of silica gel increases the lifetime to 96 days, which is a significant cost reduction either in clay purchase or in loading/unloading operations. On the other hand, silica gel cost is similar to clay, and it can be claimed that in each batch, the final price is equivalent to loading the reactor with only clay.

4. CONCLUSIONS

Water, morpholine, and NFM were observed as clay lifetime reducers, and their impact was determined. Silica gel was found to be the most efficient adsorbent in reducing clay lifetime among the six types studied. Allotting 10% of the clay mass to silica gel as the optimum amount of this adsorbent, and loading silica gel into the reactor before clay, resulted in a 2.1-fold increase in clay lifetime, which resulted in a significant reduction of costs related to the adsorbent purchase, operations, and loading into the reactor. The approximately equal cost of clay and silica gel were particularly important to consider this design as practical and making it an economic plan to reduce production costs.

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Notes

The authors declare no competing financial interest.

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