

Feasibility of Biological Elimination of COD, Ammonia-Nitrogen and Total Nitrogen from HTS Molecular Sieves Wastewater Using SBR Processes

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Abstract

The wastewater from hollow titanium silicate (HTS) zeolite consists essentially of high concentrations of COD and salt, and low ammonia-nitrogen concentrations (or high, sometimes). These chemical pollutants are produced in very large quantities during oil refining and are very difficult to manage on site. In addition, they can be very harmful to the environment when released without any treatment. The aim of this study is to evaluate, on the one hand, the feasibility of removing the COD from HTS wastewater using a sequencing batch reactor (SBR) and, on the other hand, to test the combined effect of nitrification and denitrification under different conditions of treatment on the elimination of Total Nitrogen (TN) from HTS wastewater containing a high concentration of ammonia-nitrogen. SBR intermittent domestication tests of sludge have been successfully carried out with wastewater from a municipal treatment plant with a COD removal rate of 87%. Subsequently, HTS wastewater containing high concentrations of COD was treated by this SBR system. After three months of operation, the efficiency of COD elimination fluctuated between 47% and 67%. Therefore this result could serve as a precursor to a possible second COD bioprocessing. The results obtained during nitrification of the same HTS molecular sieves wastewater with low C/N ratio gave, under an operating temperature below 10°C (winter conditions), less than 16% of total nitrogen (TN) removal. When the temperature was increased to 40°C, the TN removal efficiency remained worse. These observations make it possi-

ble to affirm that the change in temperature solely had no effect on oxidation of TN. Thereafter, two SBR devices were used for the denitrification process: one containing HTS wastewater, activated sludge and glucose as carbon source, and the other only HTS wastewater and activated sludge. In both cases, the elimination of TN still low even with an increase in the amount of glucose. These situations show that the TN removal was not only depended on type of carbon source. Based on the results of nitrification and denitrification tests, it may turn out that the activated sludge microorganisms' activities were affected by the HTS molecular sieves wastewater high concentration as well as the salinity (about 3%) of this kind of wastewater.

Keywords

HTS Zeolite Wastewater, COD Removal, SBR Process, Nitrification, Denitrification

1. Introduction

Nowadays, the special development of catalysts used in oil refining processes results in a great economic benefit. Among these catalysts, Hollow Titanium Silicate (HTS) zeolite is a new catalyst (Xia et al., 2016), which is widely used in various oil refining operations. However, the production and the use of these catalysts generate a large amount (thousands tons/year) of toxic and harmful wastewaters (Cao et al., 2019; Boethling & Lynch, 1992; Xiang et al., 2016). These wastewaters generally consist of high salt, low (or sometimes high) ammonia-nitrogen and high COD concentrations. Their structures contain tetrapropylammonium hydroxide (referred to as TPAOH) which are similar to that of quaternary ammonium salt compounds (QACs) (Tezel et al., 2006; Xia et al., 2017). Moreover, they are also full of organic pollutants which are not easy to biodegrade (Cao et al., 2019; Boethling & Lynch, 1992). In fact, the persistence of high organic pollutant concentrations may be due to HTS zeolite's physicochemical structure and properties which for example do not favor the accessibility of bulk organic molecules to inner tetrahedral framework Ti sites (Boethling & Lynch, 1992; Xia et al., 2017). Thus, the external drainage from HTS molecular sieves production device wastewaters should contain a large number of TPAOH and a very high COD concentration in the effluent which are not environmental-friendly (Friedel, 1994; Shon et al., 2011).

Since wastewaters coming from the production of catalysts have been subjected to strict regulations, several technologies for organic matter removal have been proven to be relatively effective (Herney-Ramirez et al., 2010). Among them are the following methods: physical (adsorption), chemical (micro-electrolysis, photoelectric Catalytic oxidation), photocatalytic degradation, Fenton reagent (Fongsatitkul et al., 2004; Pan et al., 2001), potassium tetraoxo ferrate (II) reagent, and cationic surfactant method, biochemical (aerobic, anaerobic, and aro-

bic-anaerobic combination process) (Scott & Ollis, 1995; Zheng et al., 2013). However, because of their high energy consumption, their affinity for certain dangerous reagents and therefore their high pollution and complex functioning, most of these methods are sometimes considered as pre-treatment methods. It is also estimated that these methods have high overall costs as much as the quality of their effluents does not always meet discharge standards. In comparison, and as they provide less costly and environmental-friendly solutions, biological treatment methods seem to be more appropriate (Kargi & Dinçer, 1997; Morsyleide et al., 1998; Ren & Zhang, 2010). Moreover, such HTS-sieve wastewaters have low and sometimes high concentrations of ammonia species, and therefore special attention should be paid on them. In fact, SBR nitrification and denitrification, biofilms and other biological treatment processes used to treat this type of ammonia species has shown the difficulty of their effective removal (Morsyleide et al., 1998; Ren & Zhang, 2010). Despite a number of studies on wastewater containing QACs materials (Xiang et al., 2016; Li, 2011; Zhu & Xiao, 2000), it should be noted that very little attention has so far been paid to the biological disposal of HTS type catalysts used by petroleum refineries.

The main objectives of this study are to investigate: 1) whether the HTS molecular sieves wastewater COD can be biodegraded; 2) whether the ammonia-nitrogen ($\text{NH}_3\text{-N}$) and the total nitrogen (TN) removals are efficient; and 3) whether the HTS molecular sieves wastewater COD can be used as a carbon source for denitrification.

2. Materials and Methods

2.1. Materials

2.1.1. Quality of HTS Molecular Sieve Wastewaters

Quality and biochemical properties of HTS molecular sieve wastewaters have been measured using China National Environmental Protection Agency's methods from factory as given by **Table 1**.

Effects of sample softness and biodegradation are particularly pronounced for the No. 2 wastewater such as BOD/COD ratio is less significant (0.06) in No. 1 wastewater than the No. 2 (BOD/COD ratio = 0.30).

2.1.2. Chemical Parameters and Analytical Methods

During the whole process, the wastewaters' chemical parameters characterized and determined were COD (Chemical oxygen demand), $\text{NH}_3\text{-N}$ (Ammonia-nitrogen), TN (Total nitrogen), Cl^- (Chlorine ions), and SO_4^{2-} (Sulfate ions). Technical details of analyzed parameters and analytical methods are presented in **Table 2**.

2.1.3. SBR Reactor

1) Experimental apparatus

The main parts of SBR bioreactor (**Figure 1**) are made with transparent plexiglass. During this study, the SBR processes involved 3 L and 9 L total volumes reactors both made with transparent plexiglass.

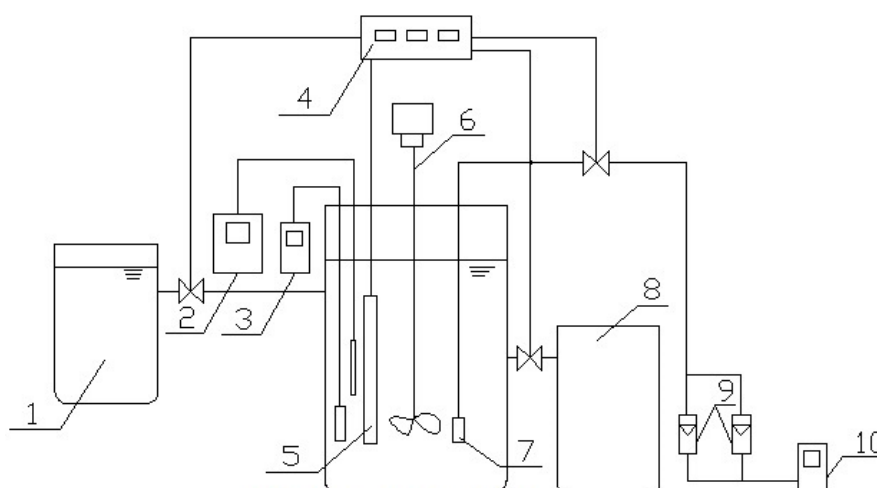
Table 1. Quality of HTS molecular sieve wastewaters.

Items	No. 1 water	No. 2 water
COD (mg/L)	10,400	3333
Ammonia-Nitrogen (mg/L)	101	79
pH	8.26	8.96
BOD ₅	670	1000
BOD/COD	0.06	0.30

Table 2. Analytical projects and methods.

Analyzed parameters	Analytical methods
COD	Potassium dichromate method (GB/T 11914-1989)
NH ₃ -N	Distillation and titration method (GB/T 7478-1987)
Total Nitrogen (TN)	Alkaline potassium sulfate nodule method (GB 11894-89)
Cl ⁻	Color rendering titration method (GB/T 13025.5-2012)
SO ₄ ²⁻	Barium capacity method (GB/T 13025.8-2012)

All these parameters are measured at the beginning and the end of each SBR cycle.

**Figure 1.** Schematic diagram of SBR. 1—Water inlet tank; 2—pH-meter; 3—DO-meter; 4—Automatic control device; 5—Heater; 6—Stirrer; 7—Air stone diffuser; 8—Water outlet tank; 9—Air rotameter; 10—Air pump.

Air stone diffuser is installed in the reactor, and the aeration amount (dissolved oxygen DO) is controlled by adjusting the intensity of the aerator (DO-meter). The bioreactor is also equipped with related temperature and pH control equipment, and continuous online dissolved oxygen analyzer. An automatic control device, allows the regular schedule of water outlet, water inlet, aeration and idle processes.

2) SBR flow chart

The SBR cycle (**Figure 2**) consists of five steps, which are carried out in sequence as: 1) fill, 2) react (On/Off aeration), 3) settle, 4) draw, and 5) idle.

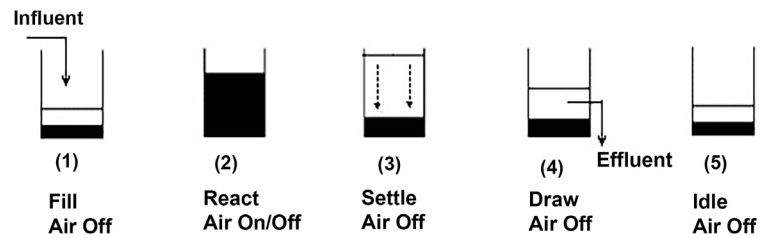


Figure 2. Schematic diagram of a five steps SBR system cycle.

2.2. Methods

2.2.1. Domestication of Municipal Sewage Plant's Sludge

The activated sludge from one municipal sewage plant was selected for SBR experiments. First, the sludge was recovered after precipitation and supernatant removal. Thereafter, water with a small amount of glucose and ammonia-nitrogen was injected into the reactor for stuffy exposure of 2 days. After supernatant removal, the remaining sludge was added to 9 L total volume SBR reactor.

In the early stage of domestication, only glucose water was used in order to facilitate sludge domestication. Then, for each cycle the feed (or intake) water was composed by reducing gradually the glucose concentration while increasing the HTS molecular sieves wastewater concentration. A solution of trace elements nutrient was added, and sodium bicarbonate or phosphoric acid was used to maintain the pH neutral around 7. Each cycle was composed of 4 L feed water and the operation consisted of 8 h aeration phase and 2 hours anoxic phase. The Hydraulic Residence Time (HRT) and the settle steps were both of 2 hours. At the end of each cycle, the supernatant was discharged in respect with a liquid exchange ratio of 44%. For each cycle, feed water and effluent characteristics of COD as well as sludge's SV_{30} , MLSS and SVI were tested.

2.2.2. Treatment of HTS-Sieves Wastewater by SBR Domesticated Sludge

At the end of domestication processes, processes of COD removal from the HTS molecular sieves wastewater were tested during three months. The feed water was entirely composed of HTS molecular sieves wastewater, pH was maintained between 6 and 8. Feed water's COD concentrations were changed by cycle and were between 400 and 2900 mg/L. Operational conditions were those adapted to sludge domestication. For each cycle, feed water and effluent characteristics of COD as well as sludge's SV_{30} , MLSS and SVI were measured.

2.2.3. Nitrification and Denitrification Properties of HTS-Sieves Wastewater by SBR Processes

To perform nitrification and denitrification processes, and contrary to the previous water quality data, another HTS molecular sieves wastewater with high ammonia-nitrogen concentration was studied by SBR system.

1) Nitrification process

The process involved 9 L effective volume SBR reactor. At the beginning, 3 L of activated sludge and 2 L of HTS molecular sieves wastewater were poured into

the SBR reactor. When the sludge's MLSS concentration and the MLVSS/MLSS ratio were 9.9 mg/L and 0.9, respectively. The aeration condition was maintained to provide dissolved oxygen (DO) of around 2 mg/L. Operational temperature of first case was room temperature (winter period with temperature around 10°C), and second case at 40°C. Wastewater's characteristics of COD, NH₃-N, NO₃-N and TN concentrations were analyzed.

2) Denitrification process

It is well established that the microorganisms cannot degrade the HTS molecular sieves wastewater when used as carbon source. Hence, two SBR devices were used in this experiment: HTS molecular sieves wastewater, sludge and glucose as carbon source were added into the first one while into the second only HTS molecular sieves wastewater and sludge were added.

At the beginning of the experiment, 1.5 L of sludge and 1.5 L of HTS molecular sieves raw wastewater were added into the two devices. After adding 500 mg/L of glucose in the second device, sludge's properties test has showed MLSS of 4.1 mg/L and MLVSS/MLSS ratio of 0.9. The operational conditions involved stirring of wastewater, the temperature kept at 24°C and the DO below 0.5 mg/L. Wastewater's characteristics of COD, NO₃-N and TN concentrations were analyzed.

3. Results and Discussion

3.1. Municipal Sludge Domestication by SBR Process

SBR process summary of COD removal rate, sludge properties and the specific parameters are summarized in subsequent **Table 3** while **Figure 3** and **Figure 4** illustrate the results of COD removal efficiency and the sludge performance, respectively.

According to this variability scheme (**Table 3**, and **Figure 3** and **Figure 4**), the rate of COD removal is in gradual adaptation of microorganisms to the increase of feed water concentration. In fact, on the 1st and 2nd days, feed water's COD concentrations of HTS molecular sieves wastewater (HTS-COD) was 25 mg/L while glucose concentration (glucose-COD) was 600 mg/L corresponding to HTS-COD/glucose-COD ratio of 0.04:1. The COD removal rates were 69% and 70%, respectively. Thereafter, the sludge domestication continued, and from the 3rd to the 7th day, when the ratios were increased gradually by 0.08:1, 0.08:1, 0.15:1, and 0.25:1, respectively, COD removal rate remained stable at 69%. This indicates that sludge domestication started. On the 9th and 10th days, the ratio was increased by 0.35:1 and 0.45:1 with appropriate increase of HTS-COD.

The COD removal rate records from mixed wastewater were 85% and 89%, respectively, and the sludge domestication was relatively smooth. The sludge domestication continued and from the 11th to 15th day the HTS-COD concentrations were increased with related gradual ratios of 0.5:1, 0.6:1, 0.7:1, 0.8:1 until 1:1 and then the average removal rate of COD in wastewater became 86% which means that the biochemical properties of sludge are good. From 16th day to 23rd day,

Table 3. Feed water and domestication results of sludge from municipal wastewater treatment plant.

(a)							
Days	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Glucose (mg/L)	600	600	600	600	500	500	500
HTS water (mg/L)	25	25	50	50	75	100	125
Feed water COD (mg/L)	260	250	227	267	160	154	140
Effluent COD (mg/L)	80	74	27	42	50	47	43
COD removal rate (%)	69	70	88	84	69	69	69
SV ₃₀ (%)	76	79	81	81		83	
MLSS (mg/L)	5.7	6.1	6.3	6.3		6.7	
SVI	133	130	129	128		124	
pH	6.04	6.88	7.28	7.43	7.54	7.56	7.54

(b)							
Days	Day 8	Day 9	Day 10	Day 11	Day 12	Day 13	Day 14
Glucose (mg/L)	500	500	500	500	500	500	500
HTS water (mg/L)	175	175	225	250	300	350	400
Feed water COD (mg/L)		206	246	200	220	273	307
Effluent COD (mg/L)		31	27	48	28	33	28
COD removal rate (%)		85	89	76	87	88	91
SV ₃₀ (%)			82		82		85
MLSS (mg/L)			6.7		7.1		7.6
SVI			121		115		112
pH		7.58	7.58	7.54	7.54	7.56	7.54

(c)							
Days	Day 15	Day 16	Day 17	Day 18	Day 19	Day 20	Day 21
Glucose (mg/L)	500	500	500	500	500	400	400
HTS water (mg/L)	500	600	800	1000	1500	2000	2200
Feed water COD (mg/L)	400	446	547	547	633	747	700
Effluent COD (mg/L)	48	80	133	60	69	139	207
COD removal rate (%)	88	81	79	89	89	81	70
SV ₃₀ (%)		87		89		89	
MLSS (mg/L)		8.4		8.7		9.0	
SVI		104		102		99	
pH	7.56	7.58	7.58	7.58	7.54	7.59	7.61

(d)			
Days	Day 22	Day 23	Day 24
Glucose (mg/L)	300	100	0
HTS water (mg/L)	2500	1600	1600
Feed water COD (mg/L)		700	614
Effluent COD (mg/L)		54	80
COD removal rate (%)		92	87
SV ₃₀ (%)		90	90
MLSS (mg/L)		9.6	9.5
SVI		94	95
pH		7.58	7.62

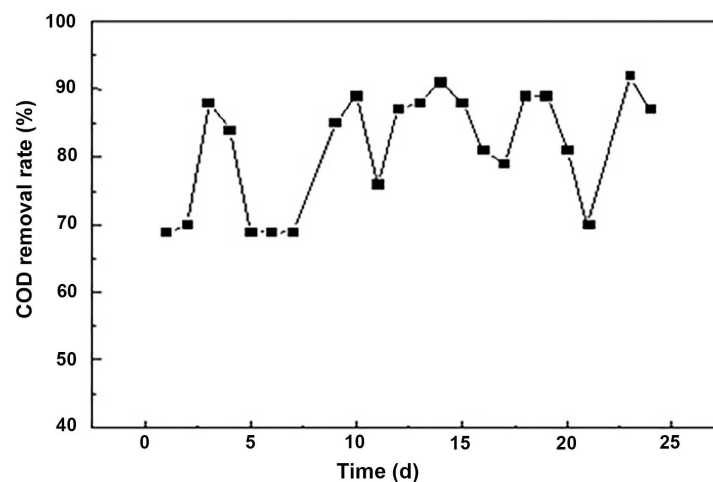


Figure 3. Variation of COD removal rate.

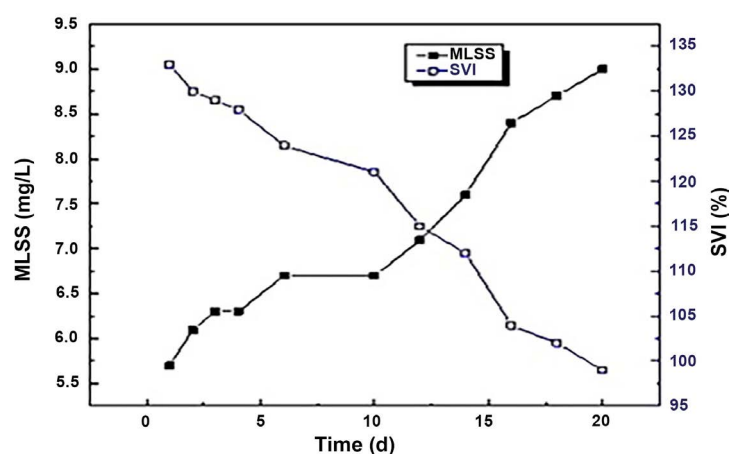


Figure 4. Variation of sludge characteristics.

the HTS-COD concentrations were gradually elevated than that of glucose-COD with the ratios of 1.2:1, 1.6:1, 2:1, 3:1, 5:1, 5.5:1, 8.3:1 until 16:1, respectively. At the end of reactions, the recorded average of COD removal rate was 83%. Thereafter, the HTS-COD concentrations were increased again and the average removal rate of COD was between 83% up to 92% which indicates that the sludge domestication is effective. This stage achieves the adaptation period of sludge's microbial community to the high organic matter of HTS molecular sieves wastewater.

From above **Figure 3**, it is also noted that on the 23rd day, the rate of removal of COD was 92%; on the 24th day, glucose was no longer added, and 614 mg/L HTS-COD was supplemented. At the end of this step, effluent showed 80 mg/L COD concentration corresponding to 87% COD removal rate. Following some early evidence based on better sedimentation index of the domesticated sludge, we show here (**Figure 4**) that the degradation of COD is better biochemical treatment performance. This implies enhanced the COD removal rate in HTS molecular sieves wastewater is significantly improved, and an increased contri-

bution of microorganisms' biodiversity living in the sludge of municipal sewage plant.

3.2. HTS Molecular Sieves Wastewater Treatment by Domesticated Sludge

Some of the specific parameters of feed water, the treatment efficiency and the sludge's properties are summarized in **Table 4**. The capability of the SBR has been evaluated by following the process of COD removal from HTS molecular sieves wastewater and conducting experiments during three months overall to acquire data.

While the effluent's COD concentration is greater than that of feed water's COD, the initial treatment effect is abnormal in the first few days (**Table 4** and **Figure 5**). In fact, the previous stage of water shortage has caused the sludge to self-decompose which was resulted to an increase of effluent's COD. Thereafter, on 11.05, the COD removal rate began to increase. At the 25th day, the COD removal efficiency remained more stable reaching about 50%. From the 25th day to the end of operations, the COD removal rate fluctuated between 47% to 67%. In addition, unlike the case where glucose was a carbon source, and because of the low C/N ratio of wastewater, the COD removal rate can be considered as moderate justifying the difficult biodegradation of COD of this kind of wastewaters. In fact, this situation is particularly related to the proprieties of high salinity and refractory to treatment of high salt organic wastewater (Cao et al., 2019).

Moreover, the persistence of high organic pollutants concentrations is also favored by HTS molecular zeolite cavities which do not promote the accessibility of bulk organic molecules to inner tetrahedral framework Ti sites (Xia et al., 2017). In addition, HTS molecular sieves like QACs species have high surface activity and moderate-high activity which are proved to be harmful to microorganisms even at low concentration (Xiang et al., 2016). Furthermore, such species have great influence on the bioavailability and mobility of the other coexisting pollutants (Xiang et al., 2016). Hence, the COD removal rate is an average value which can be considered acceptable knowing that such organic matters, even after pretreatment by physicochemical methods, are very difficult to manage (Herney-Ramirez et al., 2010).

These results could be useful for the petroleum and petrochemical industries in the design of further COD treatment processes of high COD and high salinity wastewaters. In fact, they could be useful to determine additional procedures which can consider the fact to decompose or to reduce HTS surfactants from such wastewaters prior to any COD removal.

3.3. SBR Nitrification Process

The results of nitrification process are detailed in **Table 5** and **Table 6** below.

There are some fluctuations of COD concentrations while the changes of ammonia-nitrogen, nitrate-nitrogen and total nitrogen concentrations are fairly

small with less 16% TN removal efficiency (Table 5). The slow nitrification reaction can be probably attributed to low temperature. In fact, the registered high sludge concentration can be explained by the death of certain microorganisms due to low temperature conditions. Thereafter, 3 L of wastewater (1.5 L HTS molecular sieves raw water +1.5 L deionized water) and heating rods were added into the reactor. The following analysis of sludge proprieties gave MLSS of 4.6 mg/l and MLVSS/MLSS ratio of 0.9. The aeration was continued at room temperature with dissolved oxygen (DO) of above 2 mg/L and the results of COD, ammonia-nitrogen, nitrate-nitrogen and total nitrogen tests are shown in the following Table 6.

Table 4. Feed water and experimental results.

(a)							
Date	10.31	11.01	11.02	11.03	11.04	11.05	11.06
Feed water COD (mg/L)	880	1500	2167	2900	2400	1666	1033
Effluent COD (mg/L)	1000	1800	1300	3123	2780	666	400
COD removal rate (%)	--	--	40	--	--	60	61
SV30 (%)	80		79		78		60
MLSS (g/L)	3320		3178		3024		2842
SVI (ml/g)	240		249		258		211
pH	7.86	7.79	7.98	7.93	7.89	7.92	7.89
(b)							
Date	11.07	11.08	11.09	11.10	11.11	11.12	11.13
Feed water COD (mg/L)	693	737	400	667	707	1120	873
Effluent COD (mg/L)	373	480	140	180	400	280	540
COD removal rate (%)	46	39	65	73	43	75	38
SV ₃₀ (%)		58		57		55	
MLSS (g/L)		2780		2865		2859	
SVI (ml/g)		209		199		192	
pH	7.94	7.98		7.86	7.78	7.89	7.93
(c)							
Date	11.14	11.15	11.16	11.17	11.18	11.19	11.20
Feed water COD (mg/L)	950	1187	880	680	840	820	947
Effluent COD (mg/L)	500	480	370	490	540	560	640
COD removal rate (%)	47	60	60	30	36	32	32
SV ₃₀ (%)	54		52	53		52	
MLSS (g/L)	2854		2877	2756		2759	
SVI (ml/g)	189		181	192		192	
pH	7.86	7.92	7.89	7.89	7.96	7.89	7.96

(d)

Date	11.21	11.22	11.23	11.24	11.25	11.26	11.27
Feed water COD (mg/L)	987	933	1093	1300	800	680	1027
Effluent COD (mg/L)	640	640	700	680	520	273	407
COD removal rate (%)	35	31	36	48	35	60	60
SV ₃₀ (%)	51		50	45		43	
MLSS (g/L)	2754		2777	2756		2746	
SVI (ml/g)	192		180	163		157	
pH	7.85	7.92	7.96	7.96	7.97	7.93	7.96

(e)

Date	11.30	12.03	12.07	12.10	12.15	12.20	12.24
Feed water COD (mg/L)	967	913	975	987	989	973	973
Effluent COD (mg/L)	356	453	400	512	478	422	397
COD removal rate (%)	63	50	59	48	52	57	59
SV ₃₀ (%)	41		43		42		
MLSS (g/L)	2756		2765		2789		
SVI (ml/g)	148		156		154		
pH	7.87	7.95	7.96	7.94	7.97	7.93	7.96

(f)

Date	12.27	01.01	01.05	01.07	01.10
Feed water COD (mg/L)	900	893	934	987	891
Effluent COD (mg/L)	377	473	322	497	401
COD removal rate (%)	58	47	66	50	55
SV ₃₀ (%)	42		41		42
MLSS (g/L)	2768		2798		2799
SVI (ml/g)	152		147		150
pH	7.86	7.95	7.96	7.94	7.97

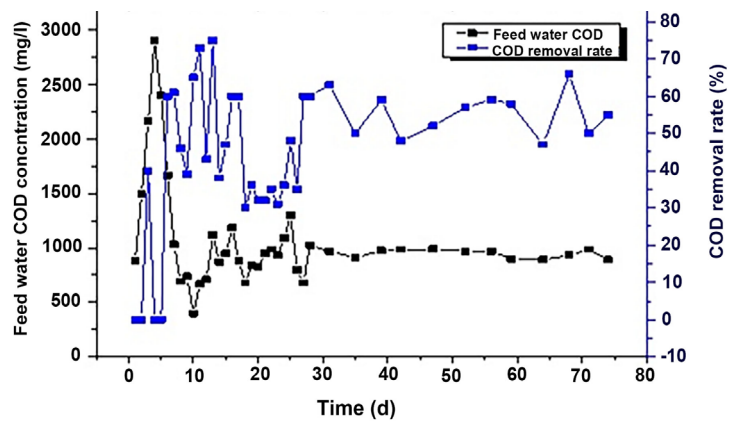


Figure 5. Variation of COD removal rate vs Feed water COD concentrations.

Table 5. Analysis of water quality of HTS molecular sieves wastewater.

Time	COD (mg/L)	Ammonia-N (mg/L)	Nitrate-N (mg/L)	Total N (mg/L)
0 h	967	147	48	165
1 h	1833	143	52	175
2.5h	667	145	51	179
4 h	667	148	53	189
6 h	833	149	58	211
8 h	500	125	54	105
10 h	800	141	47	171
24 h	333	128	43	139

Table 6. Quality analysis of HTS molecular sieves wastewater.

Time (h)	COD (mg/L)	Ammonia-N (mg/L)	Nitrate-N (mg/L)	Total N (mg/L)
0	1300	80	53	277
2	900	159	52	293
4	1000	158	48	300
7.5	833	169	43	300
10	600	151	30	275
21.5	633	150	30	242
25	500	148	25	250
29	350	144	30	258
40	370	145	36	265
50	386	147	35	268

According to **Table 6**, during the 25 hours of operations some fluctuations are observed for all parameters. This situation can be explained by the process of microorganisms' reconstitution and adaptation to new operational conditions. Thereafter, COD decreases gradually up to 70% elimination at the end of operation showing the presence of microorganisms suitable for organic matter removal along with favorable operational conditions. Unfortunately, any improvement of the other parameters has been registered at the end of experiments. Thus, less than 35% nitrate-nitrogen was removed while ammonia-nitrogen concentration increased and TN removal remained completely low. This may be due, on the one hand to high operational temperature (about 40°C) and, on the other hand to high concentration of HTS molecular sieves wastewater which after being adsorbed by the sludge's surface can hinder the nitrification reaction. In fact, high temperature values have been proved to influence many biological and chemical processes (Chapman, 1996) and this has probably an impact on dissolved oxygen

(DO) concentration which becomes low. In addition, saline wastewaters have also an influence on the solubility of DO. Besides, the decrease of DO solubility in water may impacts nitrifying bacteria activities so that ammonia-nitrogen may not be easily degraded. Likewise, the persistence of high salt organic pollutants concentrations (high COD and high salt concentrations) may be harmful to microorganisms which death can increase nitrogen species concentration. In fact, the activated sludge's microorganisms should be disturbed by the high salt content (about 3%) of this type of wastewater. Their activities could also be affected by the difficult access to nitrogenous materials since these wastewaters contain surfactants in the form of HTS' micelles.

3.4. Denitrification Process

All over the experiment, the results of COD, nitrate-nitrogen and total nitrogen for denitrification were determined as shown in **Table 7**.

In **Table 7**, the left data are the experimental results without glucose, and the right data are the experimental results with the initial addition of 500 mg/L glucose. For both cases, the COD concentrations decrease somewhat at the beginning from 0 h to 3.5 h, and then increase gradually. The removal rates of ammonia-nitrogen (ammonia-N), nitrate-nitrogen (nitrate-N) and total nitrogen (total N) concentrations were fairly small. The possible reason is that microorganisms in the presence of high concentrations pollutants are hibernated, and eventually some of them are disintegrated so that pollutants and nitrogen species concentrations remain high in the system. Furthermore, the persistence of high organic pollutants concentrations is also favored to HTS molecular zeolite cavities which do not promote the accessibility of bulk organic molecules to inner tetrahedral framework Ti sites (Xia et al., 2017). According to the data of the two situations (*i.e.* with and without glucose addition), neither case allows the promotion of the denitrification reaction. Therefore, the specific characters of the HTS molecular sieves wastewaters have a great effect on the denitrification efficiency.

Table 7. Quality analysis of the HTS molecular sieves wastewater.

Time	Without glucose (mg/L)			With glucose (mg/L)		
	COD	NO ₃ -N	TN	COD	NO ₃ -N	TN
0 h	1733	63	363	2555	65	351
1.5 h	1380	55	377	2300	67	333
3.5 h	970	52	378	1610	52	356
8 h	1667	50	364	1833	55	363
11 h	1900	52	357	1966	77	353
24 h	2500	50	362	2568	76	358
28 h	2466	49	364	3000	78	353
33 h	2469	48	371	3000	83	364

4. Conclusion

SBR intermittent domestication tests of sludge were successfully performed with wastewater from one municipal sewage treatment plant giving 87% COD removal rate. The results of HTS molecular sieves wastewater's COD treatment showed partial efficiency with a removal rate fluctuating around 47% to 67%. In addition, unlike the case where glucose is a carbon source, the COD removal rate can be considered as passable.

The nitrification process showed no changes in $\text{NH}_3\text{-N}$ and TN concentrations. Under temperature below 10°C (winter condition), less than 16% TN was removed. When temperature was increased to 40°C , TN removal efficiency remained worse. These observations mean that the change in temperature had no effect on the TN elimination. Problems still exist in the choice of suitable operational conditions along with the impact of HTS molecular sieves on activated sludge's surface which hinders the nitrification reaction. Suitable operational conditions such as pH, temperature, DO and low C/N ratio should be redefined after reducing the salinity of this wastewater which probably disturbed activated sludge's efficiency. The renewal of activated sludge capable of oxidizing TN in salty conditions should be an option.

Regarding the denitrification process, changes in $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$ and (TN) concentrations were fairly small. This can be the result on one hand of the hibernation of microorganisms because of high concentrations of contaminants which lead to their disintegration and an increase of nitrogen, and on the other hand due to the lack of specific activated sludge which could be capable to oxidize nitrogen species. It can be also concluded that this HTS molecular sieves wastewater's salinity had a great effect on the nitrification and denitrification reactions.

Further studies should be directed towards the choice of specialized activated sludge along with suitable operational parameters which could improve TN removal. Experimental conditions should be changed and additional physicochemical pretreatment on HTS molecular sieves wastewater could help reduce their impact on activated sludge.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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