Adsorption of organic micro pollutants with high silica zeolite in secondary wastewater effluent

Competition between OMP and NOM

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MSc thesis

Adsorption of organic micro pollutant with high silica zeolite in secondary wastewater effluent

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By

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ABSTRACT

This work investigated which NOM fraction from secondary wastewater effluent were causing competition with metoprolol and clarithromycin for adsorption site on high silica zeolites (HSZ). This thesis works with five commercially available HSZ frameworks (FAU, MOR, BEA, MFI and FER). Adsorption batch test were performed with demi water, wastewater and nano filtrated wastewater with molecular weight cutoff around 400 Da. The competition between two organic micro pollutant (OMP) metoprolol and clarithromycin in demi water were not obvious for FAU type high silica zeolite. Metoprolol is adsorbed much better than clarithromycin regardless of the water type or high silica zeolite framework. Adsorption of clarithromycin was the best with MOR and BEA in demi water, but the removal deteriorated severely in secondary wastewater effluent. Clarithromycin adsorption on BEA and MOR in micro filtrated wastewater and nano filtrated wastewater seems to be comparably impaired. Metoprolol on the other hand showed counter intuitive results. It adsorbs worse in nano filtrated wastewater compared to micro filtrated wastewater for MOR and BEA.

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1. INTRODUCTION

1.1 Water crisis

A continue supply of adequate good quality water is essential for every societies. However, 80% of the world population is facing high level threat to water security (Vorosmarty, 2010), which is resonated by many studies (Hanjra, 2010)(Nations, 2006)(Iglesias, 2007). To approach the problem, the water quality issues are set as a high priority in the environmental policy agenda (Sousa, 2018). In 2000, EU Water Framework Directive was established to improve water protection policy (Todo, RESEARCH, 2002). Subsequently, watchlist of priority substances Directive 2013/39/EU (European Commission, 2013) and a list of contaminants of emerging concern Decision 2015/495/EU (Commision, 2015) were published.

As human population continues to grow, problems related to water scarcity becomes more frequent and more serious (Systems, 1998). Over one third of the accessible renewable water resource are used for agriculture, industry and domestic purposes. These activities contaminate the water source with two important classes, the macro- and micro- pollutants of diverse chemical natures. Macro- and micro pollutants are pollutants that appear at high concentration (µg/l to mg/l) and very low concentration (ng/l to ug/l). They do not refer to the size of the pollutant. Macro pollutants like nutrients, salt, natural organic matter and acids appears in high quantities in the water. These pollutants represent a manageable problem because their origin, their environmental impacts, and their treatment are generally well understood and can be controlled accordingly (Anderson, 2006)(Men, 1997). On the other hand, micro pollutants, which mainly comprise of synthetic chemicals at very low concentration in the aquatic environment, are more difficult to handle and to assess their impact (Anderson et al., 2006).

Micro pollutants including pharmaceuticals, hormones and other organic wastewater contaminants are detected in water resources with residential, industrial and agricultural origins (Kolpin, 2002). The increasing number of these persistent recalcitrant organic micro pollutant accumulating in the environment bears high concern for both short- and long-term effects (Tijani, 2013) that could be harmful to human and ecological health (Daughton, 1999) (Jekel, 2013). The treatment of micro pollutants however is less developed compared to macro pollutants treatment, posing a pressing and continual problem in maintenance of good water quality.

1.2 Conventional treatment

There is general agreement that the majority of micro pollutants ending up in various water sources are of wastewater treatment plant (WWTP) origin (Tijani et al., 2013). WWTP supposes to act as a primary barrier to prevent the spread of micro pollutants. Unfortunately, current strategies fail to effectively remove micro pollutants because WWTP are not designed to treat them (Luo, 2014).

Many WWTP consist of preliminary (screening and grid removal), primary and secondary treatments (Verlicchi, 2012). The primary treatment is a process where suspended solids gets removed, but this is ineffective for removing micro pollutants (Luo et al., 2014). Some micro pollutants are removed in the secondary treatment through biodegradation and sorption. Most common technology applied are conventional activated sludge (CAS) and membrane biological reactor (MBR) (Verlicchi et al., 2012)(Radjenovic, 2009). Increasing the sludge retention time has a positive effect on the capacity to remove drugs due to promoting the growth of diverse slow growing microorganism that can treat micro pollutants (Verlicchi et al., 2012). MBR utilizes filters that allows to retain sludge much longer than CAS, and consequently remove more pharmaceutical. CAS has some removal for 25 compounds, but only two out of them were removed at an efficiency over 90%. MBR achieved higher removal for all compounds compared to CAS, but those are not high as only 5 out of 25 pharmaceutical were removed over 90% (Radjenovic et al., 2009) which is still far away from complete pharmaceutical treatment.

The WWTP treatment of micro pollutants may even result in negative removal efficiency (Verlicchi et al., 2012). It is thought that the metabolites in the influent get oxidized during the biological treatment. This in turn releases the parent compound resulting in higher concentration detection of this micro pollutant in the effluent compared to in the influent (Barbosa, 2016).

Overall, the current WWTP is not well equipped to handle micro pollutants. Alternative approaches should be explored to achieve a higher micro pollutant removal level.

1.3 Advanced treatment technology

The recent developed advanced treatment technology (reviewed by (Luo et al., 2014)(J. Wang, 2016)) holds promise in micro pollutants treatment. There are many variants of advanced treatment technology, among them the advanced oxidation process (AOP) and activated carbon (AC) are effective in eliminating micro pollutant (Yang, 2017).

AOP deploys strong oxidant hydroxyl radical •OH to convert micro pollutants into more biodegradable compound (Roberta Hofman-Caris, wolter Siegers, 2016) virtually capable of attacking any organic compounds (Sievers, 2010). This means that nearly anything in the wastewater are competing with micro pollutants to react with hydroxyl radicals which makes this type of treatment less efficient. (Lee, 2010) showed that the competition from the wastewater remains the same throughout the whole oxidation process and impairs the efficiency to target micro pollutant.

AC is an adsorbent with highly developed porosity which results in huge surface area (500-1500 m^2/g) (Çeçen, 2011). It is able to achieve high removal for a wide range of micro pollutants, but the efficacy is greatly reduced with the presence of natural organic matter (NOM) which competes for adsorption sites (Snyder, 2007)(Rossner, 2009). Both AC production cost (Dias, 2007) and reactivation of depleted granular activated carbon (GAC) are expensive; it takes up to 75% of the total operating and maintenance cost for fixed-bed GAC (Çeçen et al., 2011). The high financial cost of AC prohibits its general application for WWTP treatment. Furthermore AC are prepared from high carbon content materials like coconut shell, wood, peat, petroleum coke and coal (Çeçen et al., 2011). When the latter source was used for AC preparation, the environmental friendliness of it would be questionable.

These approaches are overall not efficient in the wastewater. Furthermore, the implementation of this tertiary treatment step will inevitably induce higher cost (Luo et al., 2014).

High silica zeolite (HSZ) has been proposed for adsorptive water treatment. It is less studied as a mean to remove micro pollutants, but its properties suggest it as a viable alternative for advance treatment. For example, HSZ has good ability to remove organic micro pollutant (OMP) (Jiang, 2018); adsorption of methyl-tert-butyl-ether and nitrosamines by HSZ framework MFI and MOR respectively saw no competition with NOM found in natural waters, presumably because NOM is too big to enter the pores from HSZ (Hsu Wen Hung, 2006)(de Ridder, 2012).

Furthermore, zeolite has the option to be regenerated with oxidation on site (Jiang et al., 2018). The adsorption efficiency of toluene on HSZ framework MFI (92%-99%) was not affected after four regeneration cycles (Zaitan, 2016). Other reported adsorption capacity improvement of HSZ framework FAU for trichlorophenol after three regeneration cycles (Zhang, 2016). This stability compared much more favorably to GAC, of which 5-10% are destroyed or lost for each cycle of reactivation and transportation (Çeçen et al., 2011).

These advantages underline the potential of HSZ to be a future alternative adsorbent for treating micro pollutant in NOM-rich waters.

1.4 Zeolite characteristics

Zeolite can be synthesized in different frameworks, each has selective behavior on the adsorption of molecules (Monneyron, 2008)(Mohanty, 1999) For instance, levofloxacin is adsorbed effectively by zeolite with framework FAU, but it shows no adsorption to zeolite with framework MOR. The reason for poor adsorption with framework MOR is ascribed to its physical structure such as insufficient pore size or impropriate pore shape (Martucci, 2012). The selection of the most appropriate zeolite framework for advanced treatment therefore requires prior knowledge on the structural and functional characteristics of the zeolite variants and the OMPs which are to be removed.

Zeolite is a crystalline aluminosilicate with 4-connected TO_4 tetrahedron (Figure 1 left) which creates open three-dimensional framework structure. Herein T can be Si or Al (International-Zeolite-Association, 2017)(Flanigen, 2010). By linking the tetrahedron in a periodical pattern a zeolite framework is constructed (Lobo, 2010). This gives zeolite uniform pore size and it can exclude molecules larger than the pore diameter completely, known as the molecular sieving effect (Breck, 1972). This is a beautiful exploitable characteristic that makes zeolite an interesting option as adsorbent which can exclude competition from NOM as described earlier.

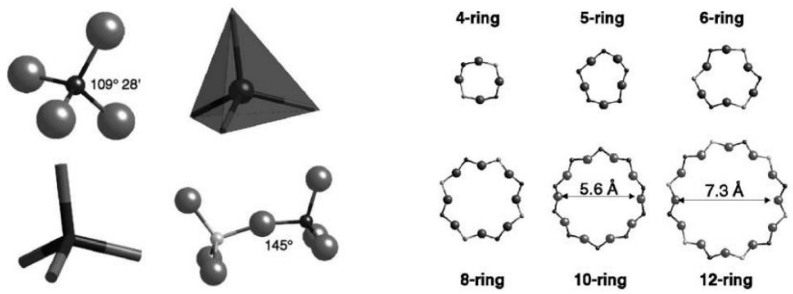

Figure 1 (Left) Different presentation of the tetrahedron; (Right) Pore aperture for 10-ring and 12-ring are given with a sense of scale (Lobo et al., 2010)

To date there are 248 zeolite framework identified (International-Zeolite-Association, 2017). Framework defines the pore size and shape, the channel dimensions, the volume and also cage orientations (Mccusker, 2007). This strongly effects the shape selectivity and sorption capacity (Mccusker et al., 2007). The pore size can be described by n-rings, where n is the amount of connected tetrahedrons (Figure 1 right). It determines what molecules can enter the zeolite. 6-ring are too narrow for any molecules larger than water to penetrate. 8-, 10- and 12-rings are considered as small, medium and large pore respectively. 8-rings are big enough for small molecules like CO_2, N_2 and linear alkanes to pass through (Lobo et al., 2010). Zeolite framework FAU with 12-rings can adsorb big molecules like levofloxacin with molecular weight (MW) of 361.4 (Martucci et al., 2012).

The variant HSZ has been mentioned as a potential adsorbent for wastewater treatment. HSZ are zeolites with Si/Al ratio above 10 (Flanigen et al., 2010). Increasing the ratio will make the zeolite more hydrophobic. At the same time the cation concentration and the ion exchange capacity will be reduced (Flanigen et al., 2010). The advantage of HSZ over low silica zeolite is the reduced pore blockage by water forming clusters. This gives more space to adsorb more OMP (Güvenç, 2012) (de Ridder et al., 2012).

In summary, zeolite has high selectivity due to its well-defined homogeneous pore size. Molecules larger than the pore will be excluded. High silica zeolite (HSZ) is hydrophobic and prevents water forming clusters inside taking up valuable space that would otherwise be used for adsorbing targeted pollutants.

1.5 NOM competition

Different zeolite framework can make a difference between an OMP being adsorbed or not (Martucci et al., 2012). Seeing NOM as a complex mixture of organic materials (Sillanpää, 2015), there could be compounds that may have the right characteristics to cause competition for adsorption site on the zeolites.

The number of papers about adsorption performance of zeolites in water sources with NOM are limited. When the subject about NOM is mentioned, it is often a small section of their research. For each of these papers a short summary, origin of NOM containing water, OMP and zeolite type are conveyed in Table 1. Methyl tert-butyl ether (MTBE) seems to be the most popular chemical for the studies and appeared in 5 out of 11 NOM and HSZ related papers. Zeolite with frameworks of MOR, MFI and HiSiv3000 can treat MTBE well even in the presence of NOM (H. W. Hung, 2005) (Knappe, 2005) (Rossner, 2008) (Hsu Wen Hung et al., 2006) (Abu-Lail, 2010). One paper showed great nitrosamine adsorption on MFI without noticeable NOM influence (de Ridder et al., 2012). Adsorption of sulfadiazine, sulfamethazine and sulfachloropyridazine by framework with FAU in the presence of dissolved organic content extracted from forest soil also saw no change in performance compared to distilled water adsorption test (Braschi, 2010). FAU has a complete removal for carbamazepine and erythromycin in wastewater effluent. Levofloxacin got removed for 96%. Though, the applied zeolite dosage is unclear (Martucci et al., 2012). Adsorption of atrazine improved in the presence of background organics. It was thought that atrazine has higher affinity towards the organics which is then adsorbed into MFI (Knappe et al., 2005).

However, sub-optimal outcomes for OMP removal in NOM-rich waters were also reported. MOR can adsorb fully or partially 15 out of 25 considered OMPs, while FAU only treated 3 (Rossner et al., 2009). Low adsorption efficiency is also the case for FAU adsorbing 2-methylisoborneol (MIB) in river water (Sagehashi, 2005a), even though FAU has high performance with MIB adsorption in ultra-pure water (Sagehashi, 2005b).

Table 1 Literature review with summary specifically related to NOM competition

Zeolite framework (Si/Al)	NOM source	OMP (Dalton)	Summary	Reference
MOR (90)	River DOC 1.2 mgL^{-1} Groundwater DOC 2.1 mgL^{-1}	Methyl tert-butyl ether (88.15)	Superior OMP adsorption, probably due to comparable methyl tert-butyl ether kinetic diameter (6.2 Å) with pore size (6.5x7.0 Å). Adsorption isotherm from river, groundwater and deionized water are the same. Different OMP initial concentration didn't change the isotherm. Might be due to exclusion of big NOM that couldn't pass through the pores	(H. W. Hung et al., 2005)
MOR (90)	Groundwater DOC 8.0 mgL^{-1} pH 8.0 Surface water DOC 2.1 mgL^{-1} pH 7.7	Methyl tert-butyl ether (88.15)	Adsorption isotherm in both waters is nearly identical to the isotherm in deionized water. Changing the initial concentration in both waters also show identical isotherm.	(Hsu Wen Hung et al., 2006)

MFI (240)	River water DOC 6.1 mgL^{-1} pH 7.8	Methyl tert-butyl ether (88.15)	Preloading MFI with NOM or co-adsorption shows neglectable influence on OMP adsorption capacity	(Knappe et al., 2005)
HiSiv 3000 (-) ***Pore size 5.3*5.6* Å**	River water TOC 6.1 mgL^{-1} pH 7.8	Methyl tert-butyl ether (88.15)	Adsorption of OMP in ultrapure water and river water was similar, especially at high adsorbent dosage	(Rossner et al., 2008)
MFI (280)	Quote: "*Natural organic matter (humic acid, Sigma-Aldrich, Saint Louis, MO)"*	Methyl tert-butyl ether (88.15)	Adsorption of OMP on granular zeolite. NOM is 5 mgL^{-1} and the initial MTBE concentration varied between 85-5000 μgL^{-1} MFI has great adsorption and showed no influence of NOM on the OMP adsorption performance	(Abu-Lail et al., 2010)
MFI (80)	Surface water TOC 5.4 mgL^{-1} pH 8.1	Nitrosamine (158; 130; 102)	Adsorption of 3 types of nitrosamines in demi water and surface water are similar. NOM components are excluded effectively and do not block the zeolite pores	(de Ridder et al., 2012)
FAU (200)	Top 10 cm of forest soil layer Freeze dried solution: 240 mgL^{-1} pH 5.8	Sulfadiazine (250.3) Sulfamethazine (278.3) Sulfachloropyridazine (284.7)	Adsorption test has 40 µM of each OMP with zeolite: OMP solution ratio of 1mg:2ml No change in performance observed by comparing distilled water with dissolved organic matter	(Braschi et al., 2010)
FAU (200)	Wastewater from a treatment plant outlet	Levofloxacin (361.4) Carbamazepine (236.3) Erythromycin (733.9)	Out of the three tested HSZ (FAU 200, MOR 200 and MFI 500), FAU has the best adsorption for the three considered OMP. Short wastewater (WW) test has been conducted. Dosage of OMP, zeolite and the amount WW used is not clear. FAU has 100% removal for all considered OMP except for Levofloxacin which is 96%	(Martucci et al., 2012)
MFI (320) **FAU (30)**	River water Synthetic mineralized water	Atrazine (215.68)	Atrazine is a low soluble molecule. It is adsorbed better in river water with background organics compared to synthetic mineralized water. The background organics can host atrazine which is then adsorbed into the zeolites. MFI does better than FAU.	(Botteroi, 1994)

			Synthetic mineralized water composition is 53.84 mgL^{-1} $CaCl_2$, 65.1 mgL^{-1} Na_2SO_4 and 349.48 mgL^{-1} $NaHCO_3$	
MOR (230) **FAU (830)**	Lake Mead water TOC 2.5 mgL^{-1} pH 8.1	Acetaminophen (151.2) 23 OMP (194.2-318.1) Iopromide (791.1)	At 100 mgL^{-1} adsorbent dosage: MOR removed 15 out of 25 OMPs completely or partially. This is only 3 for FAU No demi water adsorption test was done	(Rossner et al., 2009)
FAU (70)	River water DOC 1.0 mgL^{-1}	2-methylisoborneol (168.28)	OMP adsorbs quickly, but gets desorbed overtime by NOM. Gel chromatograph shows NOM is mostly between 100-1000 molecular weight for this river water. Author hypothesize low molecular weight NOM are responsible for OMP desorption	(Sagehashi et al., 2005a)

1.6 Metoprolol and clarithromycin characteristics and social relevance

OMPs are chosen for this research based on, (1) social relevance and (2) consistent OMP adsorption capacity of HSZ where pH changes don't have a major impact. For these reasons, clarithromycin and metoprolol were selected.

Many pharmaceuticals are either weak organic acid or weak organic base. The degree of ionization highly depends on pH (Florence, 2005). It was shown for five sulfa drugs that pH strongly influences the adsorption of it on HSZ. For example, sulfamethoxazole has a pka of 5.7 (Fukahori, 2011). The pka is the pH in which the compound exists for 50% in neutral form and the other half in ionized form. If the compound is a weak base and the pH is below the pka, then the fraction of ionized form increases. For weak acid like sulfamethoxazole the neutral form increases with lower pH compared to its pka (Fukahori et al., 2011).The adsorption of it on HSZ at pH 5.7 is around 95% but drops to 10% at pH 8. On the other hand, the neutral form are better adsorbed then the ionized form (Fukahori et al., 2011). To keep the results comparable, the fraction between neutral and ionized form of the OMP should remain comparable in all experiment through adjusting pH precisely. However, this may be challenging when working with secondary wastewater effluent containing very complex mixtures of molecules. I therefore monitored two chemicals, the clarithromycin and metoprolol. Both clarithromycin and metoprolol are weak bases and has pka of 9.2 and 9.6 respectively (Goddard, 1996)(Bittner, 2018). When pH is below 8 then over 90% of these two compounds are in ionized (cation) form (Florence et al., 2005). It is more convenient to keep the solution below this pH to maintain similar adsorption capacity throughout all adsorption test than accurately adjust the pH for demi water and secondary wastewater effluent.

Clarithromycin is an antibiotic (S. Wang, 2018) that constitutes an emerging concern in water security as indicated on the Watchlist of Decision 2015/495/EU. Antibiotics are often discussed as they may play a role in development of antibiotic resistant bacteria (Xekoukoulotakis, 2010). Metoprolol is a beta blocker that is top 6 most prescribed drugs in USA (ClinCalc, 2019). With poor conventional WWTP treatment (0-26%), metoprolol is commonly detected in the sewer and surface water (Wick, 2009). Ecotoxicity study shows that it can be harmful to the aquatic environment (Maszkowska, 2014).

1.7 Objectives

Based on the advantageous properties of high silica zeolite (HSZ), this zeolite may be a good alternative for treating OMP in natural organic matter (NOM) rich waters compared to advanced treatment like advanced oxidation process (AOP) and activated carbon (AC). Surprisingly, so far there is only a single report on the usefulness of HSZ on OMP treatment where NOM is present (Sagehashi et al., 2005a). This was done with one high silica zeolite FAU, and one micro pollutant Methyl tert-butyl ether. They speculated that the small NOMs are responsible for the competitions with the adsorption sites in HSZ. Though, the fraction of competing NOM were not investigated.

This work will explore the competition from NOM for five HSZ frameworks (FAU, MOR, BEA, MFI and FER) that has different pore dimensions with two OMPs, namely metoprolol and clarithromycin. For the first time, the competing fraction of NOM will be investigated through fractionation. NOM will be treated with nanofiltration to exclude the bigger molecules. The produced permeate with smaller molecules will be used for the adsorption test, and compared against the un-fractionated original NOM

The competition of NOM will be investigated through answering three research questions:

- **Do OMPs compete with each other for HSZ adsorption site in demi water?**
- **Which zeolite framework experiences competition from NOM?**
- **Which fraction of NOM is responsible for the competition?**

2. STUDY APPROACH

This research works with 5 commercially available HSZ frameworks with different pore dimensions (TOSOH, 2019; Zeolyst, 2019). Two OMPs were chosen for this study which is metoprolol and clarithromycin based on social relevance and low influence from pH chances on the adsorption capacity of the considered compound.

I study three aspects of the HSZ for micro pollutants removal, which are summarized in Figure 2. The first part investigates the competition between OMPs on FAU. This part consists of three batch tests on clarithromycin, metoprolol as single solutes and a binary solute batch test with both OMP, respectively. The single solute test results will be compared with binary solute test to examine if there are adsorption competition between micro pollutants.

The second part investigates which zeolite framework experience competition from NOM in secondary wastewater effluent. This part conducts 10 batch tests with binary OMP solution. Five batch adsorption tests were done in demi water with five considered HSZ frameworks. Then five tests were repeated in secondary wastewater effluent. Comparing the results between the test with demi water and wastewater effluent shows the extend of competition from NOM in different frameworks.

The last part investigates which molecular size class of NOM is the main factor of competition in HSZ through size fractionation with nano filtration. As the amount of wastewater that could be treated is limited, adsorption test for only two zeolites could be done. The choice of these two are based on the results from previous experiment with “NOM competition”. The zeolites that has the best and worst adsorption performance of OMPs in demi water and wastewater respectively were chosen, which results into using Z2 (BEA) and Z3 (MOR) in the last experiment.

The choice of molecular weight cut-off for nano filtration was based on the findings from other research which showed that NOM from river water competed strongly with micro pollutant MIB for adsorption site on FAU (Sagehashi et al., 2005a). Gel permeation chromatography revealed the molecular size of NOM spanning mainly between 100 to 1000 molecular weight (MW). It was suggested that the main factor of competition originates from small NOM. However, which fraction of this were not investigated. I therefore used nanofiltration with a molecular weight cut off within 100-1000 MW range to size fractionate the NOM constituents. The collected fractions were tested for competition with OMP.

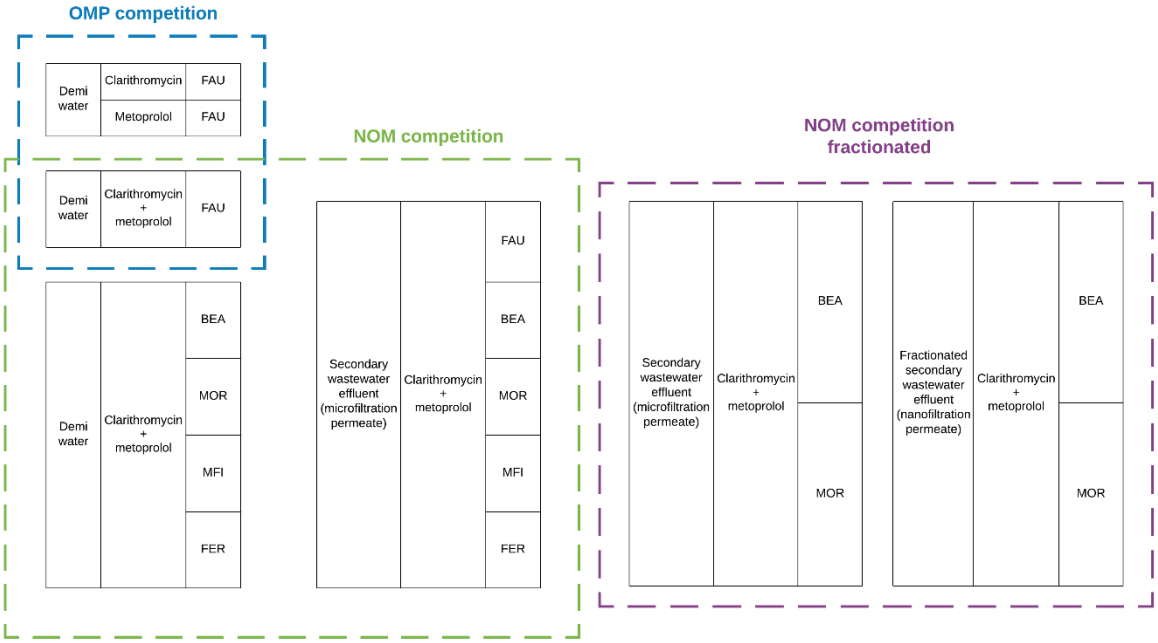

Figure 2 Batch experiment overview. Left column depicts the water source, middle column shows the applied organic micro pollutant and the right columns states which high silica zeolite framework has been used.

3. MATERIALS AND METHOD

3.1 Setup

Equilibrium adsorption batch test were carried out with four water types: demi water, wastewater-1, wastewater-2 and the nano filtrated permeate of wastewater-2. Each batch has 8 bottles with C8 containing the highest amount of zeolite and C1 the lowest zeolite dosage. Three additional bottles have no zeolite in it (C0). A water type was dosed into all 11 bottles and contains equal OMP concentration (metoprolol and clarithromycin). The average OMP concentration in three C0 is the initial concentration for all bottles (C8 to C1). Each bottle has a magnetic stirrer. The adsorption tests were carried out in a dark room and the samples were stirred for 2.5 days.

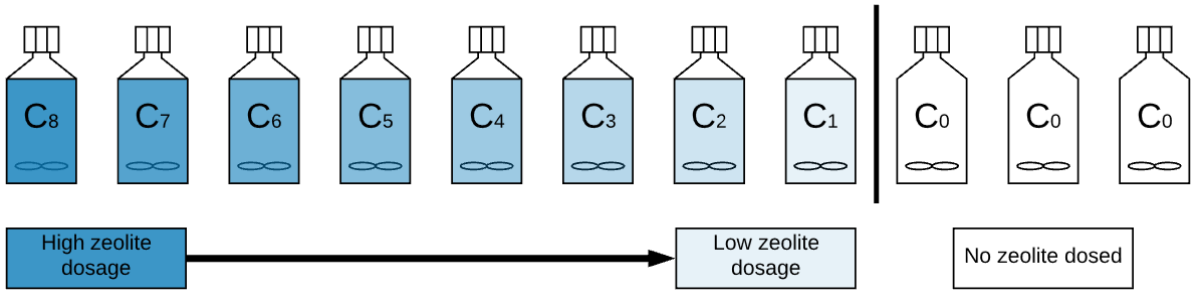

Figure 3 Adsorption batch test setup where 8 bottles has decreasingly lower zeolite dosage. Three bottles without zeolites (C0) are used to determine the initial OMP concentration.

3.2 Water type

Four water type were used for the adsorption test. Demi water was available in the lab through the tap. Other water types required treatment prior used for adsorption test which will be discussed here. Figure 4 shows an overview where the water types originates and how some of them were prepared.

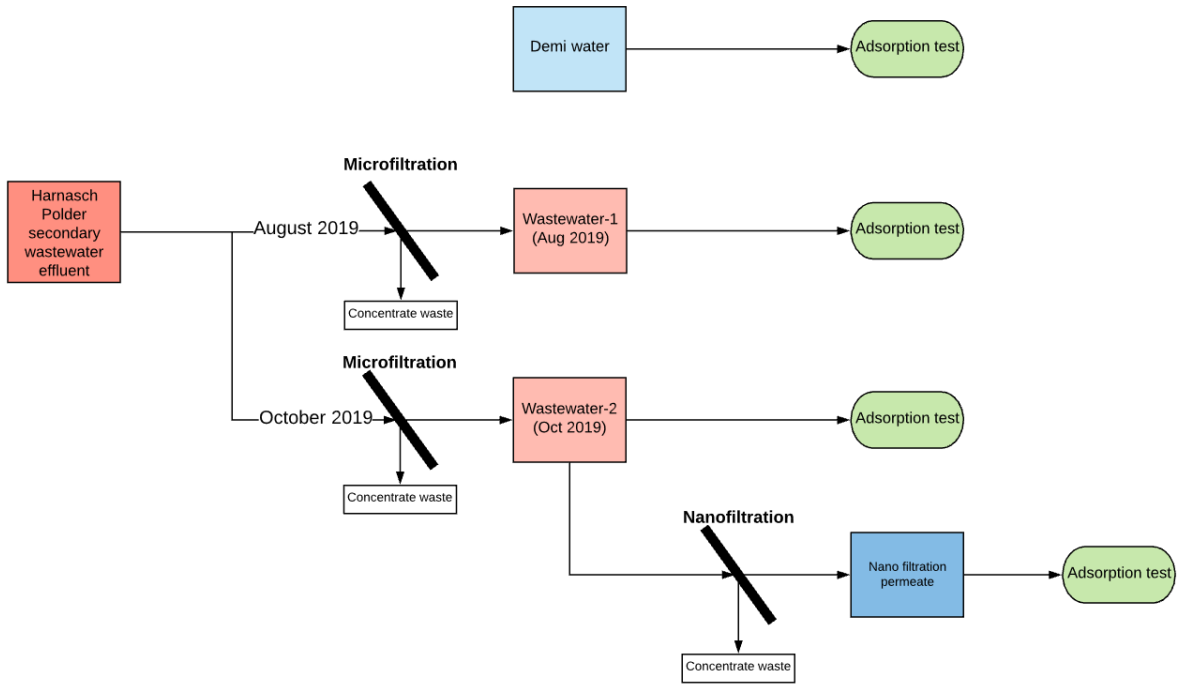

Figure 4 Graphical overview of water type and their treatment

3.2.1 Wastewater-1

Secondary wastewater effluent was retrieved from Harnasch polder on 8th of August 2019 at 14:00. Their treatment consists of primary treatment to remove coarse objects, followed by primary clarifier to let big particles settle down. After this is the secondary treatment with activated sludge, here after is the secondary clarifier to let the sludge settle down (Delft Services, 2019). The effluent is taken after the secondary clarifier.

This effluent has been treated with microfiltration once arrived at the lab to make the water more stable for longer storage. I've built a microfiltration setup kit which works with any peristaltic pump, appendix 8.1. A dead-end 1 micron pleated polypropylene filter cartridge rated 5000 Beta from TechnoFilter (1 in 5000 compounds bigger than 1 micron can pass through) were used. The pump (Watson-Marlow 520S) provided a flowrate about 680 ml/min with feed pressure around 0.3 bar. This water type will be called wastewater-1. The dissolved organic carbon (DOC), pH and EC are 10.46 mg/L, 8.0 and 960 µS/cm respectively.

3.2.2 Wastewater-2

New secondary wastewater effluent from Harnasch polder was retrieved on 8th of October 2019 at 15:00 for NOM competition experiment. This effluent was subjected to microfiltration upon arrival in the lab. Same setup was used only with another pump (Marlow-Watson 504U). The flowrate is roughly 200ml/min with feed pressure around 0.4 bar. This water type will be called wastewater-2. The DOC, pH and EC are 11.34 mg/l, 7.5 and 661 µS/cm respectively.

3.2.3 Nano filtration permeate

Part of wastewater-2 were used to treat further with crossflow nanofiltration. The setup was already built, and the schematic setup is shown in Figure 5. Before the feed goes into the membrane, it goes through one of the two 125-micron filter to remove big particles. The product specification is not known. One filter is used for flushing while the other is for NOM-rich feed. The nano filtration membrane is from NXFiltration membrane type dNF40-0.7 with molecular weight cutoff of 400 Da. The initial and final flux end is roughly 17 and 21 l/m^{2}h respectively. The flux chart can be found in appendix 8.2. The feed temperature was initially 4 degrees Celsius and increased over time to 24 degrees. The feed pressure and concentrate pressure is 4.5 and 4 bar respectively. The permeate is called here nano filtrated wastewater. The DOC, pH and EC of nano filtrated wastewater is 3.071 mg/L, 7.0 and 503 µS/cm respectively. The recovery of nanofiltration was 95% (10L to 0.5L).

Wastewater-1, wastewater -2 and nano filtrated wastewater were stored in the refrigerator at 4 degrees Celsius.

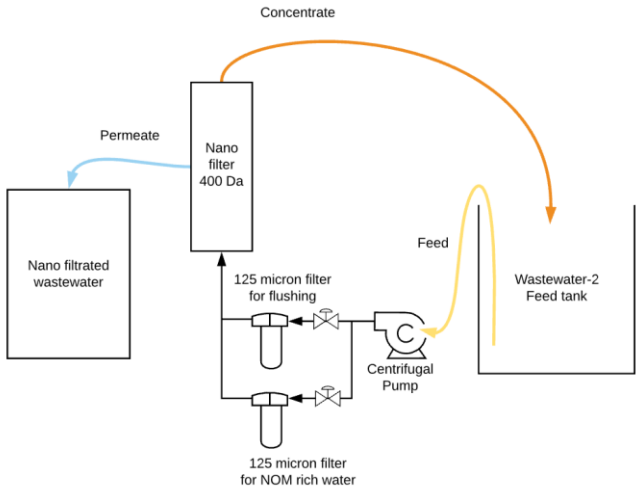

Figure 5 Schematic representation of the nano filtration setup

3.2.4 Wastewater characteristics overview

The pH, EC, DOC and two micro pollutant metoprolol and clarithromycin concentration are given in Table 2.

Table 2 Wastewater characteristics

	pH [-]	EC [µS/cm]	DOC [mg/l]	Metoprolol [µg/l]	Clarithromycin [µg/l]
Wastewater-1	8.0	960	10.46	2.93	0.16
Wastewater-2	7.5	661	11.34	1.69	1.17
Nano filtrated wastewater	7.0	503	3.071	0.44	0.01

3.3 Adsorbate (OMPs)

Clarithromycin (≥98%, Sigma-Aldrich) stock solution is prepared at 10 mg/L in 1L demi water acidified to pH 6 with 0.5M HCl for improved solubility (McCusker, 2007). Metoprolol-tartrate salt (≥98%, Sigma-Aldrich) is used as a source of metoprolol. In 1L demi water 12.8 mg of metoprolol-tartrate has been dissolved to get 10 mg/L metoprolol.

Both stock solutions were placed in sonication bath for one hour in the dark. Afterwards they were stirred 2 days in the dark climate room at 20 degrees Celsius. These were then filtered through 0.45 µm syringe filter and stored in 40 ml vials in the refrigerator at 4 degrees.

Table 3 Chemical characteristics of considered OMP

Chemical name	Molecular weight (Dalton)	Water solubility (mgL^{-1})	Log (K_{ow})	pKa	3D structure bound-box dimension (Å)
Clarithromycin	748	90	3.16	9.2	10.44 * 12.12 * 14.80
	Ref. 1	Ref. 2	Ref. 3	Ref. 4	Ref. 5
Metoprolol	267.36	50000	-1.10	9.6	5.84 * 5.26 *15.80
	Ref. 1	Ref. 6	Ref. 7	Ref. 8	Ref. 9

Ref. 1 (Pupchem, 2019)
Ref. 2 (NAKAGAWA, 1992)
Ref. 3 (Le-minh, 2010)
Ref. 4 (Goddard et al., 1996)
Ref. 5 This is the minimum distances along the cartesian axis of the model (CCDC, 1998)
Ref. 6 Metoprolol Tartrate salt solubility (Sigma Aldrich, 2019)
Ref. 7(Schaffer, 2012)
Ref. 8 (Bittner et al., 2018)
Ref. 9 This is the minimum distances along the cartesian axis of the model(CCDC, 2019)

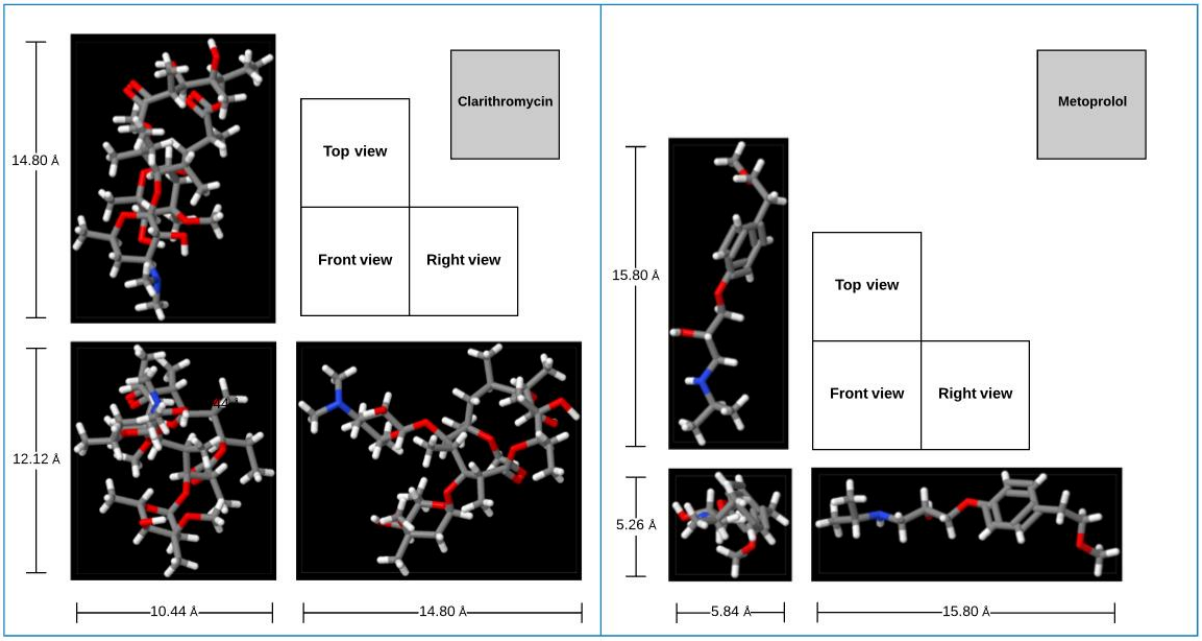

Figure 6 Dimensions of clarithromycin (left) and metoprolol (right) given in Å (CCDC, 1998) (CCDC, 2019)

3.4 Adsorbent (HSZ)

Five high silica zeolites are considered in this work, Table 4. Zeolite FAU has only one type of pore. Other zeolites have two main diffusional path ways with another pore size which is depicted as pore size 1 and pore size 2. The zeolites are arranged from the largest pore (FAU) to the smallest pore (FER). This thesis depicts the biggest pore sized zeolite framework with Z1 and the smallest with Z5. The Si/Al ratio ranges from 20 to 1500 of the considered zeolites. FAU, BEA and MOR has 12-rings pores. FAU has the largest pore, followed by BEA and then MOR. MFI and FER has 10-rings pores were the pores from FER are smaller than MFI (Internation Zeolite Association, 2017), Figure 7. All HSZ are manufactured by Tosoh except FER which is produced by Zeolyst.

Table 4 Zeolite characteristics provided by the manufacturer

Thesis acronym	Zeolite framework	Zeolite type	Product name	*SiO2/Al2O3 mole ratio*	Nominal cation form	Surface area (m2/g)	Pore size 1 (Å)	Pore size 2 (Å)
Z1	***FAU***	USY zeolite	390HUA	***500***	H	630	7,4*7,4	
Z2	***BEA***	zeolite β	980HOA	***500***	H	500	6,6*7,7	5,6*5,6
Z3	***MOR***	Mordenite	690HOA	***240***	H	450	6,5*7,0	2,6*5,7
Z4	***MFI***	ZSM-5	890HOA	***1500***	H	310	5,1*5,5	5,3*5,6
Z5	***FER***	Ferrierite	cp914c	***20***	NH4	400	4,2*5,4	3,5*4,8

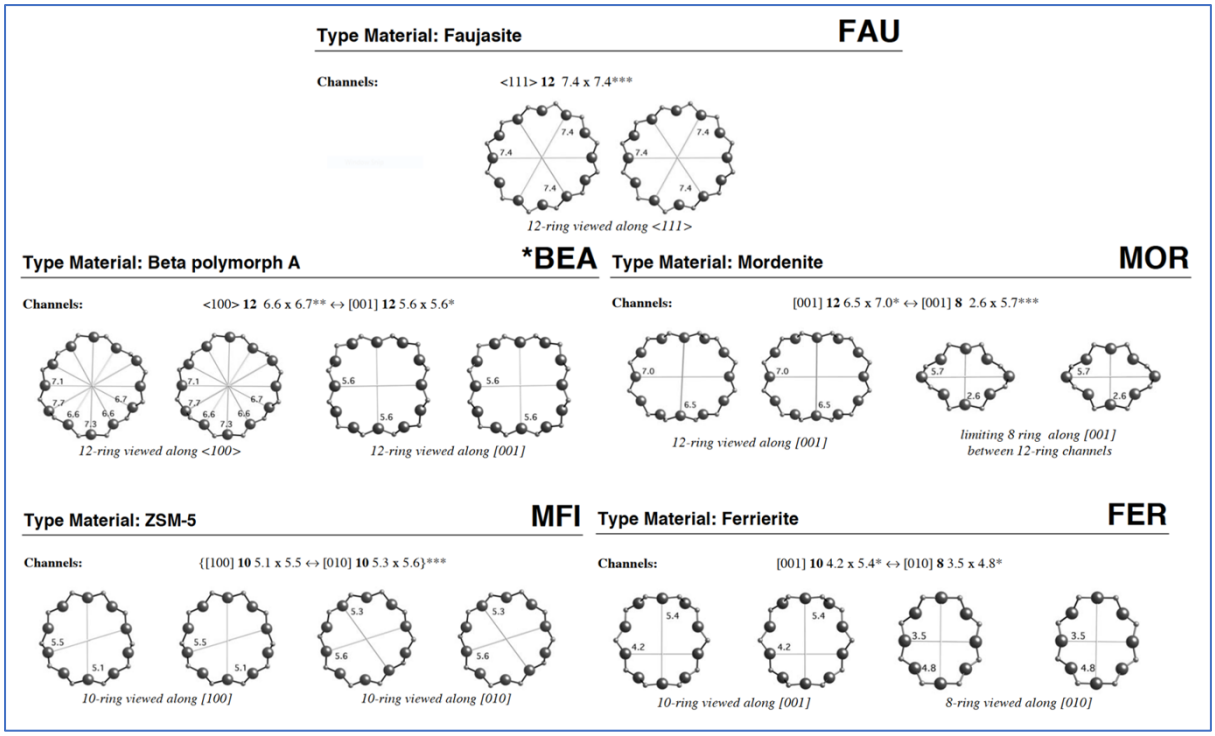

Figure 7 Pore dimension in Å for five considered HSZ. Illustrations from (Internation Zeolite Association, 2017)

3.5 Adsorption test

3.5.1 Adsorption test with demi water

First, all glass wares are cleaned with laboratory dish washer.

For each adsorption test all glassware were washed thoroughly in the following order

- Ethanol
- Demi water
- 0.5 M HCl
- Demi water
- 0.5 M NaOH
- Demi water

Then the glassware is dried overnight in the oven at 100 degrees Celsius.

Prior doing adsorption isotherm experiments, the adsorbent (HSZ) was oven dried overnight at 105 degrees Celsius. The zeolites are then placed into the desiccator for half an hour to cool down to room temperature. The experiments were performed using adsorbent doses between 0.2 and 1,000 mg/L with C0 (no zeolites) in triplicates. Depending on the targeted adsorbent dose, adsorbents were transferred into 500 mL or 1000 mL glass bottles. High adsorbent doses use the 500 ml bottles. Each bottle is spiked with OMP. The adsorption test duration is 2.5 days and are stirred continuously with a magnet stirrer in a dark room at room temperature. The stirring speed is set such that a vortex can be observed in the samples.

3.5.2 Adsorption test with wastewater

The jerrycan with filtered wastewater (WW) were spiked with OMP and homogenized. The pH for MFp_1 were acidified with 0.5 M HCl from 8 till around pH 7. This was not needed for MFp_2 and NFp as they were pH 7.5 and 7 respectively. Adsorbent were oven dried overnight at 105 degrees Celsius prior usage. Adsorbent doses between 1 and 1000 mg/L were applied for the adsorption isotherm experiment with C0 (no zeolite) in triplicate. Glass bottles 80, 250 and 500 mL were used. Smaller bottles were for high adsorbent dosage. The adsorption test takes place in a dark room at room temperature and are stirred continuously with magnetic stirrer at a speed with a vortex for 2.5 days.

3.5.3 Sampling

The samples are filtered through 0.45 µm syringe filter (CHROMAFIL®Xtra RC45/25) and stored in 40- and 60-mL vials. These are wrapped into aluminum foil to avoid contact with light and is stored in the fridge at 4 degrees Celsius till the samples were used for analysis.

3.6 Calculations

The loading (q_e) [ng/mg] is the amount of OMP adsorbed per mass zeolite (M_a) [mg]

determined with the following equation:

$$q_e = \frac{(C_0 - C_e) * V}{M_a}$$

C_0 [µg/L] is the average OMP concentration of three samples without zeolite dosed. C_e [µg/L] is the final concentration of the OMP after 2.5 days adsorption duration. V is the volume [L] in which zeolite are dosed (M_a) [mg]. The Freundlich parameters are obtained through linearizing the Freundlich equation.

The Freundlich isotherm is given by

$$q_e = K_F * c_e^{n_F}$$

The linearized Freundlich formula through logarithmizing is

$$\log q_e = \log(K_F) + n_F \log(C_e)$$

K_f and n_f are the Freundlich parameter which are obtained through the linearized Freundlich equation. K_f indicates the strength of the adsorption. With higher value, the adsorbent can achieve a higher loading. The lower exponent n_f is the higher the loading is at low concentration. This value is typically below 1 (Worch, 2012). This is favorable as OMP are present in low concentration.

3.7 Analysis

3.7.1 pH and electrical conductivity

The initial pH and at the end of the adsorption test were measured. The electrical conductivity (EC) were measured for each water type. The EC sample (5 zeolite frameworks, each with 11 samples) from wastewater-1 were measured and found no significant changes with varying zeolite dosage, so EC for wastewater-2 and nano filtrated wastewater were not done.

3.7.2 Dissolved organic carbon (DOC)

All organic carbon in the water sample filtered through 0.45µm filter are dissolved organic carbon (DOC). This is a convenient way to analyze the NOM removal (Sillanpää, 2014).

TOC-C_{CPH} analyzer from Shimadzu was used to determine the total organic carbon (TOC) through NPOC method. The sample was first acidified with HCl manually. The instrument will then sparge the sample with N_2 to remove inorganic carbon that were converted to CO_2. Afterwards the sample will be combusted at 680 degrees Celsius (Shimadzou, 2019). TOC is the sum of particulates and dissolved organic carbon without inorganic carbon. General definition for DOC is the organic carbon that passes through the 0.45 µm filters (Sillanpää et al., 2014). Since all samples were filtered 0.45 µm syringe filter (CHROMAFIL®Xtra RC45/25), the TOC analyzer is measuring the DOC.

3.7.3 HPLC-MS/MS

High performance liquid chromatography combined with tandem mass spectrometry (HPLC-MS/MS) were used to quantify organic micro pollutants. For HPLC, gradient elution using aqueous (resistivity >18 MΩ cm, ELGA/Germany) and organic (methanol, ULC grade, Carl Roth/Germany or Biosolve/France) phases, both

acidified with 0.1% ULC grade formic acid (Biosolve/France), was applied on an ACQUITY UPLC® BEH C18 (1.7µm particle size, 2.1x50 mm, Waters Ireland) column, at a flowrate of 0.35ml/min, pumped by an ACQUITY UPLC I-Class Plus (Waters/USA). MS/MS was conducted on a Xevo TQ-S micro (Waters/USA), equipped with electrospray ionization in positive mode (ESI^+), detecting two fragments (quantifier & qualifier, verified against the Metlin or Massbank MS/MS databases) of each analyte and deuterated internal standards (Torronto Research Chemicals/Canada), with quantification by 10-point calibration at levels from 0.0025 µg/L to 10 µg/L. Data were evaluated with MassLynx software.

4. RESULTS

4.1 Adsorption isotherm of singular and binary solute on Z1 (FAU) in demi water

Three adsorption tests have been performed with Z1 (FAU) to elucidate the role of competition between the two selected OMP. Two single component tests where only metoprolol or clarithromycin, respectively, were present and one binary mixture test where both metoprolol and clarithromycin were adsorbing simultaneously, were performed.

The adsorption isotherm of Z1(FAU) in liquid phase with single and binary solute is shown in Figure 8. Two metoprolol in binary solute are not shown because the concentration was measured to be below the limit of quantification (LoQ). One adsorption isotherm point from clarithromycin in binary solute was removed as an outlier. The left graph shows the metoprolol adsorption isotherms. The initial metoprolol concentration in single and binary solute is 9.57and 10.84 µg/l respectively. The single and binary solute adsorption isotherm falls inside 2 to 4 log range for the loading (qe) as well as for the concentration (Ce). For most cases little to no differences could be observed, only two adsorption points on the far right from binary solute lies 0.5 log below the single solute adsorption isotherm. The adsorption isotherm on the upper right area are more prone to errors (Zietzschmann, 2016).The right graph shows logarithmized clarithromycin adsorption isotherm. The loading (qe) falls inside 1.5 and 3 log, concentration (Ce) is within 2.5 to 4 log. Clarithromycin initial concentration for single and binary solute are 12.98 and 12.64 µg/l respectively.

The adsorption isotherm described with Freundlich isotherm has R^2 between 0.928 and 0.988. Single solute with metoprolol and binary solute for clarithromycin has n_f value above 1 which is unusual (Worch, 2012). At last, the pH for single solute and binary solute is around 6 with small deviation between the initial and final condition Table 6.

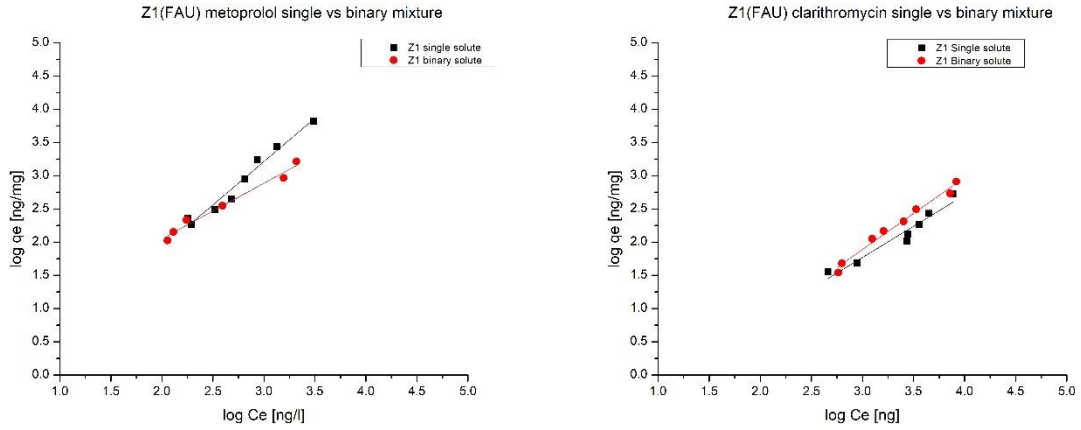

Figure 8 Z1(FAU) adsorption test with metoprolol (left) and clarithromycin (right) in single compound and binary mixture

Table 5 Freundlich parameters K_F ((ng/mg)(l/ng)^n) and n_F (-); N is the number of datapoint

Z1(FAU)	Freundlich parameters	Number of data points and R^2
Metoprolol (single solute)	K_F = 0.201; n_F = 1.303	N = 8; R^2 = 0.967
Metoprolol (binary solute)	K_F = 2.394; n_F = 0.836	N = 6; R^2 = 0.975
Clarithromycin (single solute)	K_F = 0.090; n_F = 0.938	N = 7; R^2 = 0.928
Clarithromycin (binary solute)	K_F = 0.043; n_F = 1.085	N = 8; R^2 = 0.983

Table 6 The initial and final pH are given along with the standard deviation for metoprolol and clarithromycin in single and binary solute with Z1(FAU) in demi water.

	Mean pH_0	St.dev pH_0	Mean pH_e	St.dev pH_e
Metoprolol (single solute)	6.05	0.04	6.08	0.08
Clarithromycin (single solute)	6.07	0.09	6.03	0.07
Metoprolol (binary solute)	6.20	0.12	5.99	0.10
Clarithromycin (binary solute)				

4.2 Adsorption in demi water and wastewater-1

The experiments here are meant to elucidate the proneness to NOM competition of different zeolite frameworks. First the results from metoprolol adsorption in demi water and wastewater-1 will be shown then clarithromycin. Afterwards the adsorption of dissolved organic carbon (DOC) will be present.

4.2.1 Metoprolol

Figure 9 shows logarithmized adsorption isotherm of metoprolol for five HSZ in demi water and wastewater-1. The average C_0 concentration in demi water and wastewater-1 is 9.98 and 30.92 µg/l respectively, Table 9. The elevated dosage in wastewater-1 is a result of miscalculation of the dosage. Some measurements were not displayed due to the metoprolol concentration being below the limit of quantification (LOQ), an outlier or above C0. The reason for removal of measured points are collected in Table 7. The LOQ for metoprolol in demi water and wastewater-1 is 0.005 and 0.05 µg/L respectively.

Z1(FAU) metoprolol loading (qe) and concentration (Ce) in demi water is within 2 to 3.5 log. The band is larger in wastewater-1 were the loading is between 1.4 to 3.7 log and concentration ranging between 1.9 to 4.5 log. The loading for Z2(BEA), Z3(MOR) and Z4(MFI) is mostly above 3.5 log in demi water as well as in wastewater-1. Most of the measured points were not shown as they were below LOQ Table 7. The loading of Z5(FER) is lowest of all five HSZ ranging from 2 to 3 log in demi water and wastewater-1. The concentration of metoprolol in demi water is from 2 to 4 log and in wastewater-1 from 3.1 to 4.5 log. The loading (qe) in wastewater-1 is mostly lower than in demi water for all five HSZ.

Table 7 Removed measurement points for metoprolol test in demi water and wastewater-1 for 5 HSZ. There are three types of removed measurement points. One is the value measured below the limit of quantification (LOQ), one is the measured value is above C_0 and one is an outlier.

Removed measurement points	Demi water	Wastewater-1
Z1(FAU)	2 LOQ	1 outlier
Z2(BEA)	4 LOQ	5 LOQ
Z3(MOR)	6 LOQ	6 LOQ
Z4(MFI)	6 LOQ	5 LOQ
Z5(FER)	1 above C_0; 3 LOQ	3 LOQ

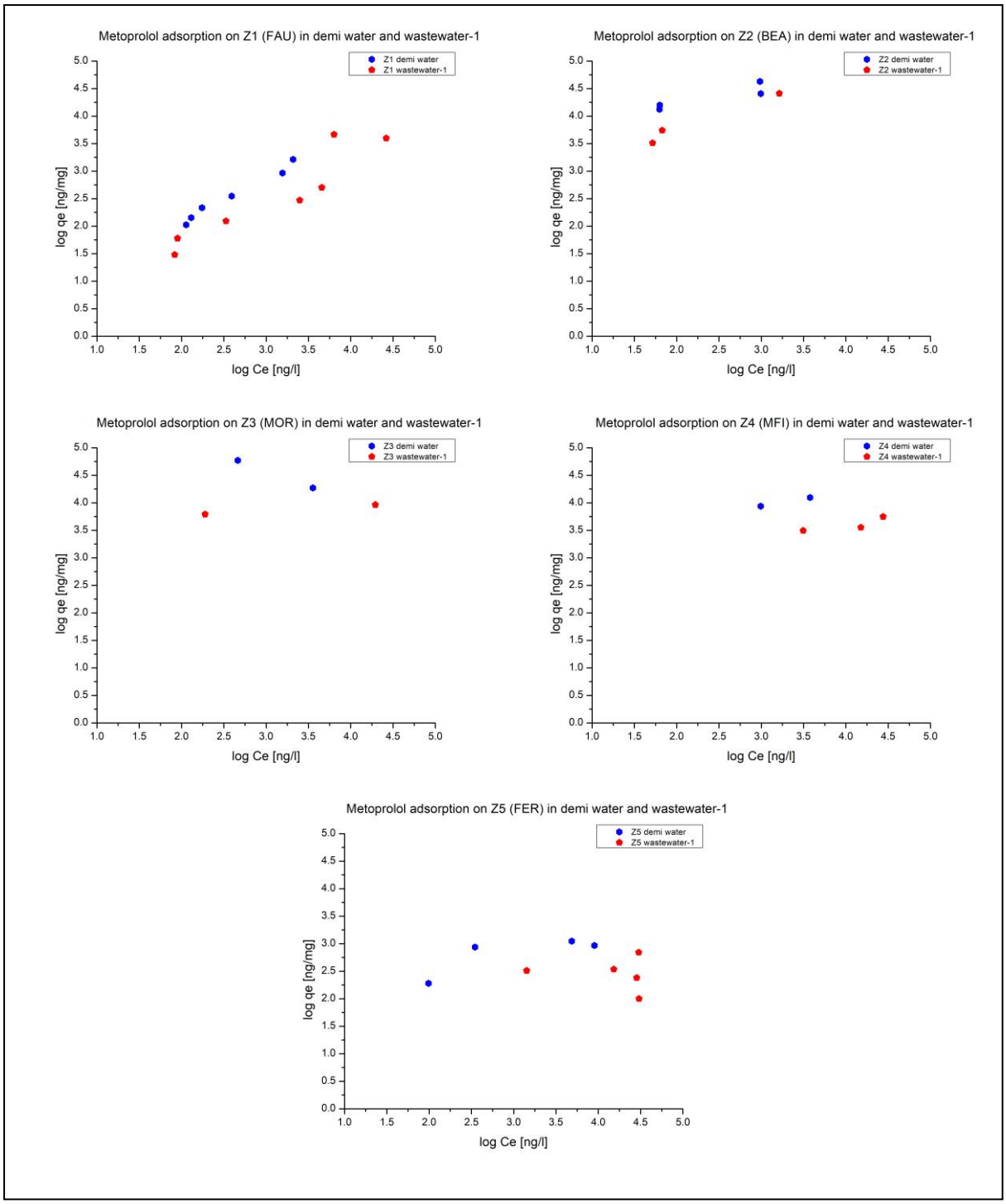

Figure 9 Adsorption isotherm of metoprolol on five HSZ in demi water and wastewater-1

4.2.2 Clarithromycin

The number of measured points varies per HSZ due to the clarithromycin concentration being below the limit of quantification (LOQ), an outlier or above C0. The reason for removal of measured points are summarized in Table 9Figure 8Table 7. When investigating all the C_0 from metoprolol and clarithromycin in demi water and wastewater-1 it shows that the metoprolol results has less deviation (~1) compared to clarithromycin (~3 to 6), Table 9. The C_0 in wastewater-1 is higher than in demi water because of miscalculation with spiking in which three times the volume is dosed.

Despite of these fluctuations, some observation could be made in Figure 10. The loading (qe) of clarithromycin on all five HSZ are in general lower than metoprolol, Figure 9. The loading in wastewater-1 is lower than in demi water and the concentration (Ce) is higher for Z2(BEA), Z3(MOR) and Z4 (MFI).

Table 8 Removed measurement points for clarithromycin test in demi water and wastewater-1 for 5 HSZ. There are three types of removed measurement points. One is the value measured below the limit of quantification (LOQ), one is the measured value is above C_0 and one is an outlier.

Removed measurement points	**Demi water**	**Wastewater-1**
Z1(FAU)	Nothing removed	2 above C_0; 1 LOQ; 1 outlier
Z2(BEA)	4 above C_0	2 outliers
Z3(MOR)	2 above C_0	1 above C_0; 3 outliers
Z4(MFI)	4 above C_0	2 above C_0; 1 LOQ
Z5(FER)	1 above C_0	4 above C_0; 2 outliers

Table 9 Average of all C_0 from metoprolol and clarithromycin in demi water and wastewater-1

	Mean C_0 (µg/l)	**St.dev C_0 (µg/l)**
Metoprolol in demi water	9.98	1.12
Metoprolol in wastewater-1	30.92	1.34
Clarithromycin in demi water	9.84	3.37
Clarithromycin in wastewater-1	17.78	6.36

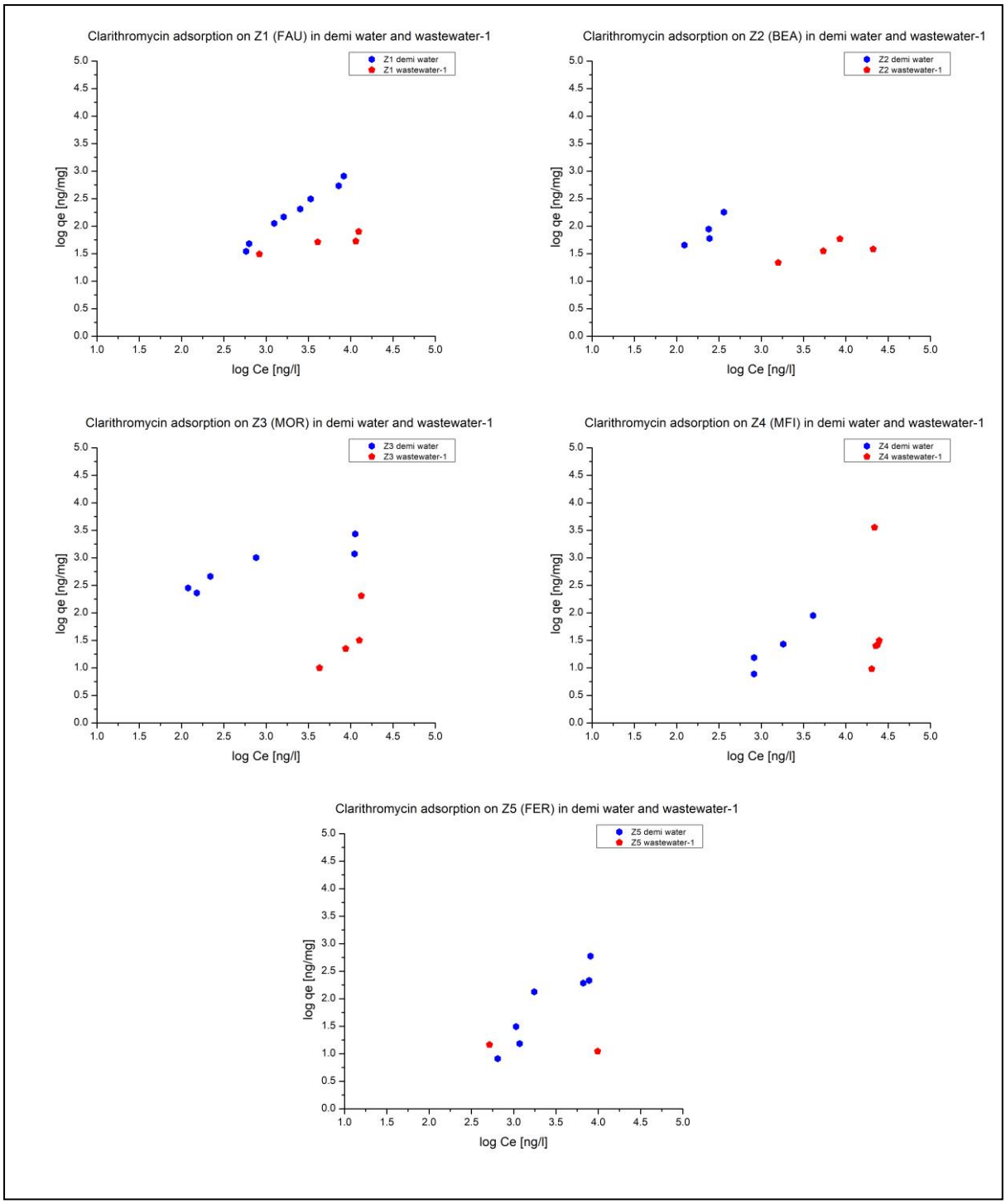

Figure 10 Adsorption isotherm of clarithromycin on five HSZ in demi water and wastewater-1

4.2.3 pH and Electrical conductivity

The pH in demi water is mostly around 6 and only Z4(MFI) has slightly higher pH average, Table 10. Wastewater-1 was acidified with HCl. The starting pH after acidifying is nearing 7. At the end of the experiment the pH is around 7.5, Table 11.

Table 10 The initial and final pH are given along with the standard deviation in demi water

Demi water	Mean pH_0	St.dev pH_0	Mean pH_e	St.dev pH_e
Z1 (FAU)	6.20	0.12	5.99	0.10
Z2 (BEA)	6.09	0.16	5.91	0.14
Z3 (MOR)	6.04	0.05	5.97	0.15
Z4 (MFI)	6.41	0.55	6.26	0.36
Z5 (FER)	6.22	0.32	6.02	0.22

Table 11 The initial and final pH are given along with the standard deviation in wastewater-1

Wastewater-1	Mean pH_0	St.dev pH_0	Mean pH_e	St.dev pH_e
Z1 (FAU)	6.88	0.10	7.59	0.25
Z2 (BEA)	6.85	0.10	7.52	0.28
Z3 (MOR)	6.80	0.07	7.51	0.38
Z4 (MFI)	6.86	0.06	7.50	0.29
Z5 (FER)	7.02	0.05	7.69	0.20

The electrical conductivity of each samples was measured for wastewater-1 at the end of the adsorption test.

Table 12 Electrical conductivity of all samples with wastewater-1

Wastewater-1	Mean EC (µS/cm)	St.dev EC (µS/cm)
Z1 (FAU)	974.45	22.35
Z2 (BEA)	976.64	5.97
Z3 (MOR)	979.27	8.78
Z4 (MFI)	977.64	5.17
Z5 (FER)	957.64	8.00

Details of pH and EC measurements results can be found in appendix 8.7.

4.2.4 DOC

Table 13 shows the DOC removal ("DOC_{delta}") for 1 g/L zeolite concentration. Shown alongside are the removal of clarithromycin and metoprolol in percent. Limit of quantification (LoQ) indicates that there is near complete removal of the considered OMP.

The average starting DOC_0 is 10.39 mg/L and the average DOC_{delta} removal of the five considered HSZ is 1.39 mg/L. The DOC removal and OMP removal for Z1(FAU), Z2(BEA), Z4(MFI) and Z5(FER) at 1 g/L dosage are about the same. Only Z3(MOR) has less DOC (1.08 mg/L) and clarithromycin (70%) removal.

Table 13 Initial DOC concentration (DOC_0), equilibrium DOC concentration (DOC_{eq}) with DOC removal (DOC_{delta}) with 1 g/l adsorbent dosage in wastewater-1. Limit of quantification (LoQ) for clarithromycin and metoprolol is 0.5 µg/l and 0.05 µg/l respectively.

	DOC_0 (mg/L)	DOC_{eq} (mg/L)	DOC_{delta} (mg/L)	Clarithromycin removal (%)	Metoprolol Removal (%)
Z1(FAU)	10.17	8.69	1.48	≤LoQ	99.7
Z3(MOR)		9.09	1.08	70.0	≤LoQ
Z2(BEA)	10.43	8.85	1.58	93.1	≤LoQ
Z4(MFI)		8.96	1.47	≤LoQ	≤LoQ
Z5(FER)	10.56	9.20	1.36	96.6	≤LoQ

4.3 Adsorption in wastewater-2 and nano filtrated wastewater

This section investigates the adsorption of clarithromycin and metoprolol onto Z2(BEA) and Z3(MOR) in three water types (demi water, wastewater-2 and nano filtrated wastewater).

4.3.1 Metoprolol

The adsorption isotherm has been plotted in logarithmized scale for metoprolol adsorption on Z2(BEA) and Z3(MOR) in Figure 11. The metoprolol loading (qe) for both HSZ are above 4 log. Z2(BEA) and Z3(MOR) has 4 and 2 measured values while other measured concentration was below the limit of quantification (LOQ: 0.01 µg/l). In wastewater-2 three adsorption isotherm points were shown for Z2(BEA) and Z3(MOR) and others were below the LOQ. In nano filtrated wastewater one measured value was removed as an outlier for Z3(MOR). No measured concentration reached below the LOQ. Most adsorption isotherm load from nano filtrated wastewater is below the adsorption isotherms in demi water and wastewater-2.

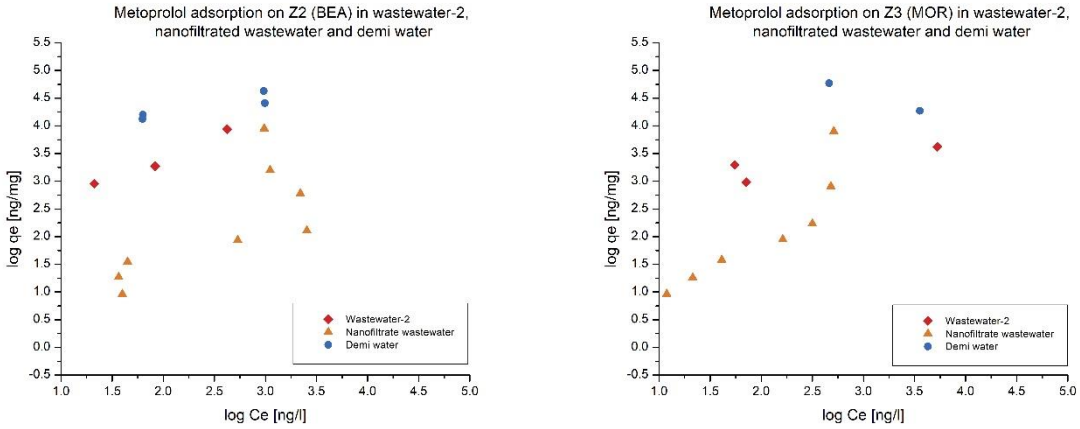

Figure 11 Metoprolol adsorption on BEA (left) and MOR (right) in wastewater-2 (red), nano filtrated wastewater (orange) and demi water (blue)

Removed measurement points	Demi water	Wastewater-1	Nano filtrated wastewater
Z2(BEA)	4 LOQ	6 LOQ	Nothing removed
Z3(MOR)	6 LOQ	5 LOQ	1 outlier

4.3.2 Clarithromycin

Figure 12 shows the adoption isotherm of clarithromycin in Z2(BEA) and Z3(MOR) in demi water, wastewater-2 and nano filtrated wastewater. The clarithromycin loading (qe) on Z2(BEA) and Z3(MOR) is above 1.5 log and 2.2 log in demi water. The missing points from demi water measurements are described in Table 8. The measured clarithromycin concentration in wastewaters for both zeolites are all above the LoQ. Only the adsorption results in wastewaters in which the measured concentration is higher than C_0 were not shown in Figure 12. The wastewaters results are strongly scattered, so a trend is difficult to derive. Therefore, no measurement points could be removed as an outlier. The average C_0 and standard deviation of clarithromycin and metoprolol are included in Table 14. The mean of clarithromycin in nano filtrated wastewater is 7.14 µg/l with standard deviation of 5.33. The standard deviation for others is around 1 or lower.

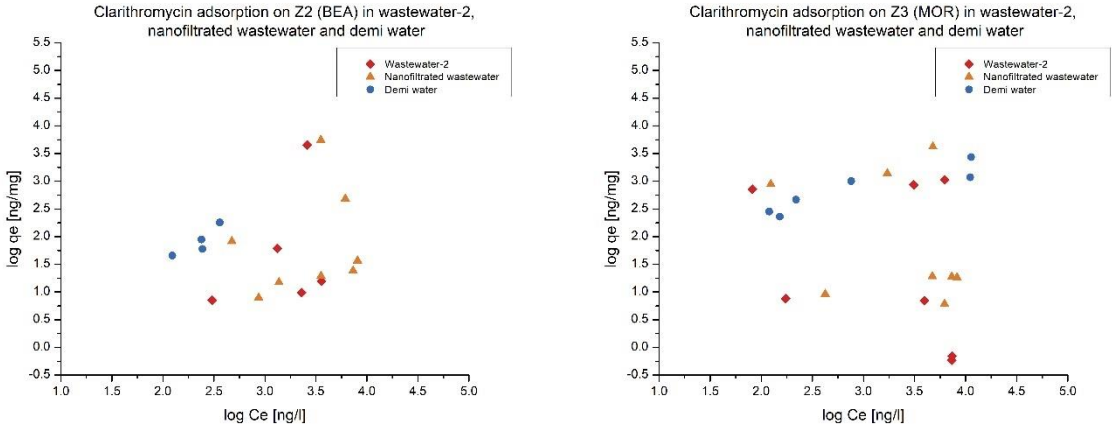

Figure 12 Clarithromycin adsorption on Z2 (BEA) (left) and Z3 (MOR) (right) in wastewater-2 (red), nano filtrated wastewater (orange) and demi water (blue). Only concentrations above C_0 are not shown in the graph

Table 14 Average of all C_0 from metoprolol and clarithromycin in wastewater-2 and nano filtrated wastewater

	Mean C_0 (µg/l)	St.dev C_0 (µg/l)
Metoprolol in wastewater-2	9.83	0.27
Metoprolol in nano filtrated wastewater	8.47	0.94
Clarithromycin in wastewater-2	6.98	1.02
Clarithromycin in nano filtrated wastewater	7.14	5.33

4.3.3 pH and Electrical conductivity

The characteristics from nano filtrated wastewater and wastewater-2 are different. After nano filtrating wastewater-2, the EC dropped from 661 to 503 µS/cm. The EC for each sample was not measured as there was no significant changes observed relating to different zeolite dosage, Table 12. The pH changed from 7.5 to 7.0 after nano filtrating wastewater-2. The samples in wastewater-2 has a pH around 7.5, Table 15. The initial pH in nano filtrated wastewater is close to 7 and the pH rise close to 8 at the end of the adsorption test Table 16.

Table 15 The initial and final pH are given along with the standard deviation in wastewater-2

Wastewater-2	Mean pH_0	St.dev pH_0	Mean pH_e	St.dev pH_e
Z2 (BEA)	7.36	0.07	7.59	0.20
Z3 (MOR)	7.40	0.18	7.66	0.25

Table 16 The initial and final pH are given along with the standard deviation in nano filtrated wastewater

Nano filtrated wastewater	Mean pH_0	St.dev pH_0	Mean pH_e	St.dev pH_e
Z2 (BEA)	6.98	0.14	7.74	0.2
Z3 (MOR)	6.82	0.15	7.91	0.15

4.3.4 DOC

The DOC changed from 11.34 to 3.07 mg/l after nano filtrating wastewater-2, Table 17. Z2(BEA) and Z3(MOR) dosage of 1 g/l adsorbed about 3.4 mg/l DOC. Z2(BEA) removed 0.07 mg/L DOC and Z3(MOR) removed about 7 times less DOC in nano filtrated wastewater compared to wastewater-2 with 0.54 mg/L.

Table 17 DOC_{delta} shows the DOC adsorption by dosing 1g/L HSZ. DOC0 is the blank without adsorbent and DOCeq is the remaining DOC after 2.5 days stirring with 1g/L zeolite.

	Water type	DOC_0 (mg/L)	DOC_{eq} (mg/L)	DOC_{delta} (mg/L)
Z2(BEA)	Wastewater-2	11.34	7.90	3.44
Z3(MOR)			7.97	3.37
Z2(BEA)	Nano filtrated wastewater	3.07	3.00	0.07
Z3(MOR)			2.53	0.54

5. DISCUSSION

5.1 Reliability of clarithromycin data

The experiment with Z1(FAU) single and binary solute shows good dose response ratio 7/8 and 8/8 respectively. Furthermore, these adsorption isotherms could be borderline reasonably be modeled with Freundlich with R^2 0.92 and 0.98, Table 5. The results after this experiment are more unstable.

The binary solute experiment in demi water and wastewater-1 with five HSZ frameworks results for clarithromycin in general seem to be more unstable compared to metoprolol. There was often higher concentration measured in samples with zeolite then in C_0 samples without zeolites, Table 8. Previously there were many problems with measuring clarithromycin with the HPLC-MS/MS in acetonitrile (ANC) eluent. Clarithromycin were detected (with good peaks) in ultrapure water (purer than demi water) from two produced sources. There was carry over. Later eluent was switched to acidified methanol and no clarithromycin were detected in ultrapure water. It is uncertain if something went wrong during the analysis for clarithromycin despite of changing the eluent. Despite of these uncertainty, the results does indicate strong influence from wastewater-2 on the adsorption of clarithromycin onto five HSZ, Figure 10.

The results from wastewater-2 and nano filtrated wastewater are scattered strongly such that no trend from the adsorption isotherm could be derived. At the lowest Z2 (BEA) dosage of 1 mg/l in Wastewater-2 2.60 ug/l clarithromycin were detected, Table 18 left. At Z2 (BEA) dosage from 5.13 till 49.59 mg/l the clarithromycin concentration was higher than the blank average. At 98.37 mg/l there is a drop in clarithromycin concentration. In case with Z3 (MOR) (Table 18 right), the clarithromycin concentration doesn't seem to go down with increasing Z3 (MOR) dosage between 1 and 250 mg/l. The detected clarithromycin concentration has substantial scattering, so making a clear statement regarding the adsorption differences in the three waters is hardly possible.

Table 18 Clarithromycin concentration for Z2 (BEA) (left) and Z3 (MOR) (right) with varying zeolite dosage ranging from 1 to 1000 mg/l in Wastewater-2. Near the bottom are three blanks, at the bottom is the average of these blanks calculated. The red numbers were excluded from making graphs as their values are above the C0 average or is an outlier in the C0

Clarithromycin in wastewater-2			
Z2 (BEA)		**Z3 (MOR)**	
mg/l	Ce ug/l	mg/l	Ce ug/l
991.86	0.30	959.84	0.17
523.83	2.29	502.93	3.96
241.40	3.58	243.35	7.31
98.37	1.33	96.91	7.38
49.59	7.96	44.91	8.50
10.68	8.83	10.31	0.08
5.13	9.57	5.06	3.11
1.06	2.60	1.12	6.26
0.00	7.59	0.00	4.87
0.00	6.65	0.00	7.43
0.00	7.87	0.00	7.47
C0 avg.	**7.37**	C0 avg.	**7.45**

The results from nano filtrated wastewater show more randomness compared to Wastewater-2, Table 19. The C_0 deviation in Nano filtrated wastewater is much larger. One full 10 L jerry-can with Nano filtrated wastewater were spiked with clarithromycin and metoprolol. Ten liter is enough for Z2 (BEA) and Z3 (MOR) adsorption experiment. As the experiment takes place simultaneously and the used water are from the same jerrycan, the C_0 from Z2 (BEA) and Z3 (MOR) should be comparable. This didn't happen as low concentration like 0.25 and 0.75 ug/l and high concentration like 15.64 ug/l were observed in C_0 of nano filtrated wastewater. When C_0 has such fluctuation then the initial concentration for each varying zeolite dosage could be different. This affects the reliability of the results.

Table 19 Clarithromycin concentration for Z2 (left) and Z3 (right) with varying zeolite dosage ranging from 1 to 1000 mg/l in nano filtrated wastewater. Near the bottom are three blanks, at the bottom is the average of these blanks calculated. The red C0 numbers were excluded from calculating the adsorption isotherm points

Clarithromycin in nano filtrated wastewater			
Z2 (BEA)		**Z3 (MOR)**	
mg/l	Ce ug/l	mg/l	Ce ug/l
971.85	0.87	952.89	0.42
478.92	1.38	481.87	6.22
253.67	3.55	230.49	4.73
97.40	0.47	96.71	7.33
49.71	7.31	49.47	8.25
11.16	8.10	10.29	0.12
4.92	6.13	5.35	1.71
0.89	3.53	1.04	4.79
0.00	7.54	0.00	0.75
0.00	9.48	0.00	9.16
0.00	0.25	0.00	15.64
C0 avg.	**8.51**	C0 avg.	**9.16**

Thus far the clarithromycin adsorption results for Wastewater-2 and Nano filtrated wastewater seems unreliable. It is uncertain if there were problems during the analysis. Great calibration lines for HPLC-MS/MS were obtained. The signal-to-noise ratio (S/N) were higher than 10 for all clarithromycin measurements which is good (ABsciex, 2010). These data can be found in appendix 0. Furthermore, the peaks were checked manually on the MassLynx software and they were all good.

The fluctuating changes of clarithromycin results may not be due to inaccuracy of pipetting internal standard solutions. Here each sample was spiked with an internal standard mixture (deuterated OMP). Figure 13 shows big variation in signal intensity for clarithromycin-d3, but carbamazepine-d8 and sufamethoxazole-d4 has very small changes indicating that pipetting was done right.

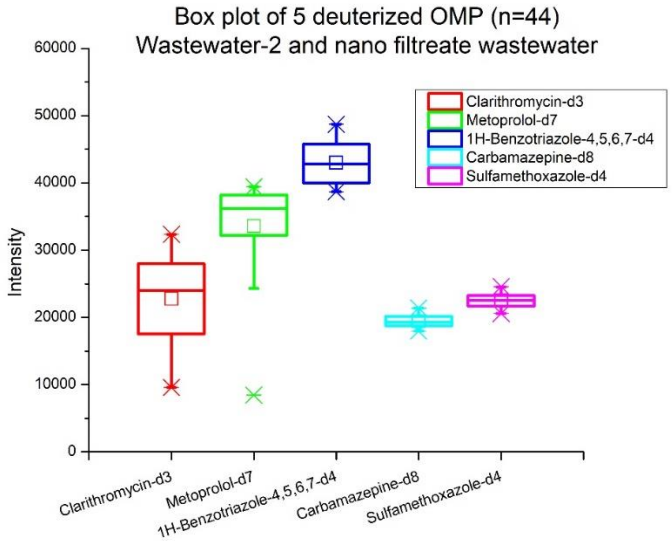

Figure 13 Intensity of the measured deuterated OMPs for wastewater-2 and nano filtrated wastewater experiment. Carbamazepine-d8 and sulfamethoxazole-d4 shows pipetting the internal standard mixture was done right

The pH differences between the samples are not huge to explain why clarithromycin data is scattered as much, Table 15 and Table 16. This should not affect the solubility of clarithromycin too much. At pH 8 about 80 µg/L is soluble in water at 37 degrees Celsius. Clarithromycin is more soluble at lower temperature and lower pH (NAKAGAWA et al., 1992). The clarithromycin concentration here is below 10 µg/L and the pH is below 8.

The methodology of my experiment setup seems unreliable. However, the results from metoprolol shows that the method were executed correctly. Table 9 and Table 14 shows the standard deviation of C_0 for metoprolol is around 1 µg/L opposed to 3, 5 and 6 µg/L with clarithromycin.

At the very beginning with single and binary solute tests were done with Z1(FAU), the clarithromycin adsorption isotherm seems fine. However, it got worse after that. It might be that the clarithromycin stock solution got older and started to degrade. The stock solution concentration of metoprolol and clarithromycin should be the same and the spiked volume is the same. Table 9 shows that the C_0 of clarithromycin and metoprolol in demi water are comparable around 10 µg/L, Table 9. The difference between them are bigger in wastewater-1. Clarithromycin concentration was around 17 µg/L compared to 30 µg/L with metoprolol while the same amount of volume was dosed, Table 9. The clarithromycin stock solution is 1.5 months old when used for wastewater-1 experiment.

When doing experiment with wastewater-1, three jerrycans were used. Two 10L and one 5L jerrycans. Table 20 shows metoprolol concentration is consistent for all three jerrycans, indicating that the correct amount of stock solution was added. Clarithromycin was added in a similar manner, but the results from jerrycan 2 is more different than from jerrycan 1 and 3. This shows that controlling clarithromycin concentration is difficult.

Table 20 Average clarithromycin and metoprolol concentration in wastewater-1 for each HSZ related to the used jerry-can

	Jerry-can with wastewater-1	Clarithromycin Mean C_0 (µg/l)	Metoprolol Mean C_0 (µg/l)
Z1(FAU)	Jerrycan 1 (10L)	16.86*	30.31
Z3(MOR)		14.28	29.27
Z2(BEA)	Jerrycan 2 (10L)	22.96	31.51
Z4(MFI)		25.06	32.70
Z5(FER)	Jerrycan 3 (5L)	15.32	30.80

*One outlier of 0.8093 µg/l was removed from calculating the average concentration

5.2 OMP competition

The competition between OMP was investigated on Z1(FAU). The adsorption isotherm of single and binary solute for metoprolol and clarithromycin shows no significant differences to indicate competition between them. It could be that there are excess adsorption sites available due to the low concentration of the dosed OMP (µg/l).

5.3 NOM competition

Z2(BEA), Z3(MOR) and Z4(MFI) have great adsorption capacity for metoprolol in demi water and wastewater-1, Figure 9. A study showed that OMP at concentration in the range of ng/L and µg/L are preferable adsorbed to closely fitted pores because of stronger interaction between OMP and HSZ (de Ridder et al., 2012). Z2(BEA), Z3(MOR) and Z4(MFI) has channels (Internation Zeolite Association, 2017) and these may coincide with the linear molecular shape of metoprolol (Figure 6) which could provide the strong interaction with these three HSZ for great adsorption capacity. Metoprolol may fit better than most of the compounds from natural organic matter (NOM) in wastewater-1. This might be the reason why metoprolol didn't experience significant competition in wastewater-1. Despite of Z1(FAU) having the largest pore size and surface area per mass (630 m^2/g while others are below 500 m^2/g) out of the five HSZ, the adsorption capacity is moderate in demi water and wastewater-1. Z1(FAU) is the only zeolite that doesn't have the channel structure out of the five HSZ. It has super cages instead (Internation Zeolite Association, 2017). This may not be a good fit for the linear structure of metoprolol to provide strong interaction. Some competition was observed here, and it could be due to some NOM having a better fitting structure that competes stronger for Z1(FAU) adsorption site. Z5(FER) does have channels, but the

adsorption capacity is moderate in demi water. Z5(FER) has the smallest pore size out of the five HSZ which is slightly smaller (10-ring pore size 4.2*5.4 Å) than metoprolol (5.84 * 5.26 *15.80 Å). Yet, metoprolol is moderately adsorbed. This could be explained with the fact that molecules and crystal structure are not rigid. Pores becomes larger with increasing temperature and vibrations allows slightly bigger molecules to "wriggle" through somewhat narrow pores (Csicsery, 1984). The competition in wastewater-1 was stronger and there could be more favorable NOM structures that can enter more easily and fit better in the channel system of Z5(FER) then metoprolol.

The adsorption capacity of all five HSZ for clarithromycin (Figure 10) is lower than metoprolol (Figure 9). It could be since clarithromycin is a bigger compound (748 Da) than metoprolol (267.36 Da) and has a bulkier shape Figure 6. In demi water Z2(BEA) and Z3(MOR) has the best adsorption capacity for clarithromycin, Figure 10. Z1(FAU) adsorbs clarithromycin less compared to Z2(BEA) and Z3(MOR). The reason could be like why metoprolol adsorption capacity is lower in Z1(FAU) because of the super cages providing less ideal fit for strong zeolite compound interaction. Adsorption of clarithromycin onto MFI and FER is surprising, because clarithromycin is much larger than their largest pore size. Clarithromycin has a dimension roughly 10.44*12.12*14.80 Å and the largest pore size between MFI and FER is 5.3*5.6 Å. It was not expected to adsorb clarithromycin due to size exclusion. (Martucci et al., 2012) observed moderate adsorption of carbamazepine and erythromycin on MFI despite that both OMP has bigger molecular dimension then the accessible pore. Through X-ray diffraction combined with Rietveld refinement, they determined that both pollutants were not adsorbed inside the zeolite and suggested that they were adsorbed onto the surface grains. This surface adsorption might also apply for the adsorption of clarithromycin onto MFI and FER.

Clarithromycin adsorption capacity for all HSZ got impeded significantly by NOM from wastewater-1. (Sagehashi et al., 2005a) showed that affinity of the compound plays an important role with adsorption. Despite of 2-methylisoborneol rapid adsorption onto FAU in river water, it desorbs over time and got replaced by NOM with higher affinity. Clarithromycin may have a lower affinity than NOM and therefore show a lower adsorption capacity with all five concerned HSZ. There is an interesting observation on the adsorption of clarithromycin with around 1g/l adsorbent dosage. Z3(MOR) has lower adsorption efficiency (70%) for clarithromycin opposed to other HSZ (above 90%) and slightly lower DOC adsorption, Table 13. The Z3(MOR) structure may have played a role in this. It is essentially a one-dimensional pore channel structure. The 8-rings adjacent to the 12-rings are displaced such that there are limited access from one channel to other channel (McCusker et al., 2007). This cause a single line diffusion which is slow and is prone to pore fouling (blocking) (Lobo et al., 2010).

5.3.1 Summary

Metoprolol adsorbs onto the five HSZ better than clarithromycin whether it is in demi water or wastewater-1. The impact of NOM on clarithromycin adsorption is noticeable especially for BEA and MOR. The adsorption of clarithromycin on MFI and FER was unexpected as their pore should be too small to fit clarithromycin. However, this might be due to surface adsorption.

5.4 Fractionated NOM competition

New wastewater was obtained for this experiment which is noted as wastewater-2. This water was treated further with nano filtration to obtain "nano filtrated wastewater". Earlier was shown that the results of clarithromycin adsorption data were not very reliable. Therefore, only adsorption data of metoprolol will be discussed.

The loading of metoprolol on Z2(BEA) and Z3(MOR) is high in demi water with above 4 log, Figure 11. The loading is lower in wastewater-2 which is between 3 to 4 log. The initial DOC concentration of it is 11.34 mg/L. At 1g/L Z2(BEA) and Z3(MOR) dosage 3.44 and 3.37 mg/L DOC were adsorbed, which may explain the lower adsorption capacity for metoprolol in wastewater-2.

The lower adsorption capacity of metoprolol on Z2(BEA) as well as on Z3(MOR) in nano filtrated wastewater is surprising. The average final pH in nano filtrated wastewater is roughly 0.2 higher than in wastewater-2 for both HSZ which may not be a significant difference to explain the drop in metoprolol adsorption capacity, Table 15 and Table 16. After treating wastewater-2 with nano filtration around 73% of DOC were rejected. The DOC test showed that Z3(MOR) adsorbed 0.54 mg/L DOC (opposed to 3.44 in wastewater-2), Table 17. Z2(BEA) adsorbed virtually no DOC with only 0.07 mg/L. It seems like that the negative effect on the metoprolol adsorption capacity from the nano filtrated wastewater became more pronounced after rejecting the bigger NOM fraction.

(Martucci et al., 2012) showed with X-ray diffraction and Rietveld refinement that zeolite structure will deform when a compound is adsorbed inside through strong interaction with the structure. For instance, FAU structure was deformed after adsorbing erythromycin. Carbamazepine caused FAU pore size to become elliptical. Levoflaxin was also adsorbed onto FAU in which the pore size got larger and enhances levoflaxin adsorption. The zeolite crystal structure didn't change in the adsorption test for carbamazepine with MFI and levoflaxin with MOR, confirming they were not adsorbed inside. For this case it could be that adsorption of the small NOMs changes the zeolite structure in such a way that is unfavorable for metoprolol to be adsorbed. When the bigger NOMs are present, they could be preferentially be adsorbed due to higher affinity compared to small NOMs. With higher affinity they will have stronger interaction with the zeolite structure and may be the dominant factor for deforming the zeolite structure. The deformation caused by the bigger NOMs may be less obstructive to metoprolol adsorption compared to when the deformation was caused by smaller NOMs. (Botteroi et al., 1994) showed that atrazine adsorption was improved when the NOM are present. He suggests that atrazine has a higher affinity to NOM then to high silica zeolite FAU in which NOM plays a role like a host for atrazine. NOM is then adsorbed in FAU. It could be that metoprolol has a higher affinity to the larger NOM and together they adsorb better than the small NOMs from nano filtrated wastewater. Furthermore, that author states that Ca^{2+} to NOM ratio plays an important role in conformation. High Ca^{2+} to NOM ratio is favorable and creates coil-like conformation which is known to be favorable for adsorption (Botteroi et al., 1994). The EC from wastewater-2 dropped from 661 to 503 µS/cm. A proportion of Ca^{2+} may have been removed in the process of nano filtration reducing the favorable coil-like conformation.

6. CONCLUSION

In this study, competition of OMP and NOM for adsorption site for five HSZ were instigated. The competition between metoprolol and clarithromycin in demi water was not obvious for FAU. Competition from NOM found in secondary wastewater effluent were apparent but varied, depending on the OMP and zeolite. Metoprolol saw minor drop in adsorption capacity for all five HSZ in micro filtrated wastewater. Clarithromycin on the other hand encountered strong competition. BEA and MOR were used for the subsequent experiments with fractionated secondary wastewater effluent. Clarithromycin adsorption seems to be comparably bad in secondary wastewater and in nano filtrated water. Though, results may not be fully reliable. There were problems with quantification by HPLC-MS/MS in the past. Counter intuitive results were obtained with metoprolol. BEA and MOR adsorbs metoprolol worse in nano filtrated wastewater (DOC~3.5 mg/L) compared to micro filtrated wastewater (DOC~10mg/L). The fractionated small NOMs may have changed the zeolite structure in an unfavorable way such that metoprolol became less adsorbed. The interaction between metoprolol and the larger NOMs (rejected from nano filtration) and the waters with higher Ca^{2+} could have played a role with providing a more favorable metoprolol adsorption condition.

7. RECOMMENDATION

Controlling clarithromycin was difficult in this thesis which deteriorated the credibility of the results. When one has to work with clarithromycin, it is advised to make fresh clarithromycin stock solution and use them within a month. When OMP needs to be spiked into any water type, try to use one big volume when possible.

The results in which metoprolol adsorbs worse in nano filtrated wastewater compared to wastewater has been reported for the first time as far as the author knows. Additional comparable experiments need to be conducted to assure that this result is not a coincident.

The new experiment could be expanded with a broader variety of OMP compounds as this work showed that there isn't a noticeable competition between them. This may show if the worsening adsorption in nano filtrated wastewater is an exclusive behavior for metoprolol.

In the discussion it was mentioned that high Ca^{2+} to DOC ratio can create coil-like conformation which is favorable for adsorption. Unfortunately, this work only measured EC and no Ca^{2+}, so no statement could be made if there is likely more coil-like conformation created or less after nano filtrating the wastewater. Ca^{2+} measurement would therefore be recommended.

8. APPENDIX

8.1 Microfiltration setup

Figure 14 Microfiltration setup front view (left) and top view (right). The blue holder contains the filter cartridge and a pressure meter is at the feed flow. The green apparatus is the peristaltic pump.

Figure 15 Microfiltration kit (no peristaltic pump)

8.2 Nano filtrating wastewater-2 flux graph

Wastewater-2 came out of the fridge and was 4 degrees Celsius. It gradually increased to 24 degrees Celsius during the filtration session. The flux started to drop near the end, because the feed tank is nearly empty, and the system started to suck small amount of air. The feed tank started with 10 liters and by the end there was roughly 500 ml remaining.

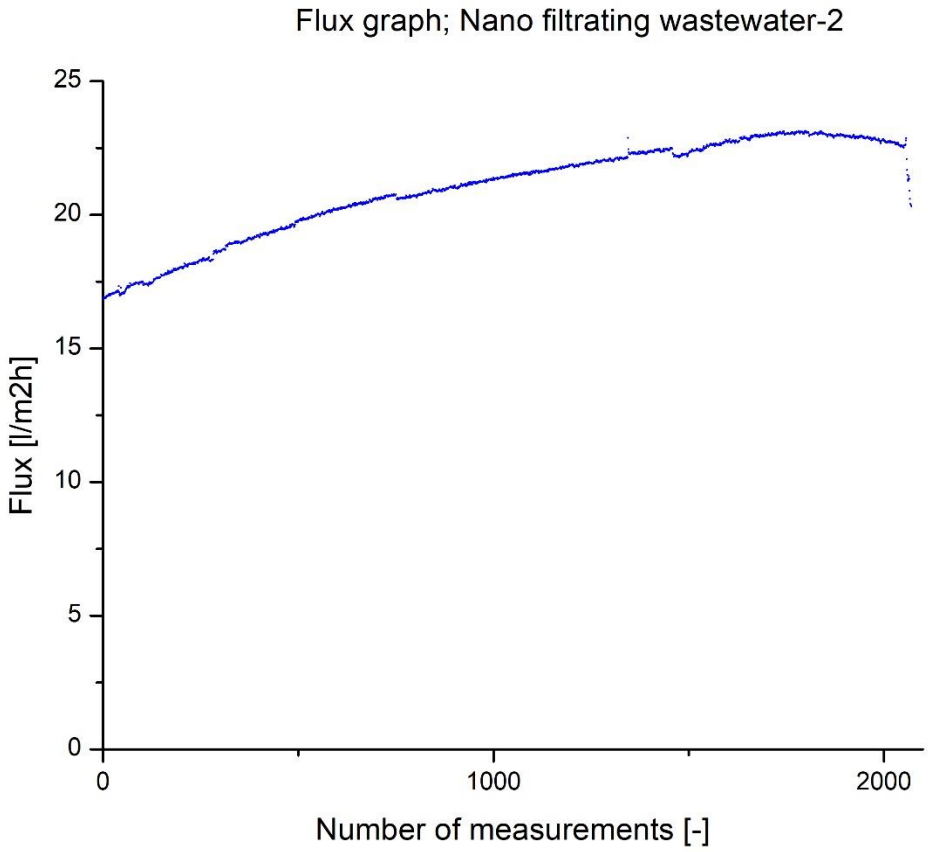

Figure 16 Nano filtrating wastewater-2 flux graph; Feed water started with 4 degrees Celsius and increased to 24 degrees; Small amount of air was sucked near the end due to depletion of the feed tank

8.3 Elaboration on choosing Z2 (BEA) and Z3 (MOR) for wastewater-2 and nano filtrated wastewater experiments

In order to assess the influence of fractionated NOM, it is best of interest to use zeolite framework for which its adsorption capacity got most impaired by NOM in wastewater-1 while having high adsorption capacity in demi water.

Unfortunately, metoprolol is not offering the sought big difference in adsorption performance between experiments in demi water and wastewater-1, Figure 9. Metoprolol is adsorbed very well by MOR, BEA and MFI in demineralized water as well as in wastewater-1. FAU and FER adsorption performance of metoprolol in demineralized water are not as high and the impact of NOM isn't that major compared to what can be observed with clarithromycin, Figure 10.

The selection of HSZ should therefore be based clarithromycin. MOR and BEA offers the biggest difference in adsorption performance between demi water and wastewater-1, Figure 10. I therefor chose these two zeolites to be used for the next experiments with wastewater-2 and nano filtrated wastewater.

8.4 Nano filtrated metoprolol concentration results

Metoprolol in NFp			
BEA mg/l	Ce ug/l	**MOR** mg/l	Ce ug/l
971.85	0.04	952.89	0.01
478.92	0.04	481.87	0.02
253.67	0.04	230.49	0.04
97.40	0.54	96.71	0.16
49.71	2.55	49.47	0.32
11.16	2.20	10.29	0.48
4.92	1.11	5.35	#0.069
0.89	0.97	1.04	0.51
0.00	8.93	0.00	8.12
0.00	8.96	0.00	9.16
0.00	#6.52	0.00	9.14
Blank avg.	**8.95**	Blank avg.	**8.81**

Metoprolol in MFp_2			
BEA mg/l	Ce ug/l	**MOR** mg/l	Ce ug/l
991.86	#0.0282	959.84	#0.0138
523.83	#0.0274	502.93	#0.0089
241.40	#0.0144	243.35	#0.0032
98.37	#0.0147	96.91	#0.0087
49.59	#0.112	44.91	#0.0007
10.68	0.02	10.31	0.07
5.13	0.08	5.06	0.06
1.06	0.42	1.12	5.29
0.00	9.47	0.00	9.70
0.00	9.73	0.00	10.36
0.00	9.79	0.00	9.90
Blank avg.	**9.66**	Blank avg.	**9.99**

8.5 Literature review acidity of HSZ

8.5.1 Introduction

It is generally assumed that the pH doesn't change the adsorption capacity of the high silica zeolites (HSZ). The manufacturer advertise it as highly resistant to acid and chemical reactivity is not to be expected (Tosoh, 2017)(Zeolyst, 2013).

This research will conduct experiment in demi water and wastewater effluent. The pH in demi water can become very low as the zeolite is acidic (Coster, 1994). pH around 3.9 were reported by a bachelor thesis when 500 mg/l MOR or FAU were used in demi water. I was recommended to wash the zeolite with demi water first. However, the results show that the zeolite this research uses is not that acidic and found out that zeolites should be prepared freshly before doing adsorption experiment.

8.5.2 Acidity

(Venkatesha, 2016) dealuminated BEA with three different acids and observed that the strength of the acid site on the zeolite increases with increasing Si/Al ratio, but the total acidity (mmol) decreases Table 21.

Table 21 Higher Si/Al ratio has stronger acidic sites as less amonium were desorbed. The total acidity decreases on contrary. BEA treated with 1 mol para-toluenesulfonic acid (pTSA); 1 mol methanesulfonic acid (MSA); 1 mol phenoldisulfonic acid (PDSA)

Zeolite	Si/Al ratio	Amount of NH_3 desorbed (mmol)	Total acidity (mmol)
BEA	25	0.64	1.11
1.0 pTSA BEA	48	0.45	0.96
1.0 MSA BEA	69	0.29	0.87
1.0 PDSA BEA	96	0.19	0.68

The total acidity seems to increase much more at lower Si/Al ratios.

8.5.3 Stability

Zeolites with lower Si/Al ratio are less stable in acidic solution. Zeolite type A and F with SiO_2/Al_2O_3 2 and 2.1 respectively dissolved at pH 4 that is controlled by dosing sulfuric acid. Zeolite type Y with SiO_2/Al_2O_3 100 did not dissolve (Fukahori et al., 2011). Other study showed that zeolite type 4A (Si/Al 1) dissolved in 8 M HCl and zeolite analcime (Si/Al 2) dissolved partially. Zeolite type Y (Si/Al 3) has insufficient aluminum to weaken the structure so silica dissolves into the HCl (Hartman, 2007).

8.5.4 Acidity results

The HSZ were kept in the desiccator for 1 day and 3 days. It seems like the HSZ became more alkaline when it stays longer in the desiccator.

	Zeolite in desiccator 1 day Duplicate **750**mg/500ml	Zeolite in desiccator 3 days Single **500**mg/500 ml
FAU	6.4	7.33
BEA	5.15	8.79
MOR	4.65	8.36
MFI	7.27	9.05
FER	6.28	8.48

Another test run was done with same dosage in duplicates (set A and B). One test in which the HSZ stayed half an hour in the desiccator and one after a day. FAU and MFI seemingly become more alkaline.

	Zeolite in desiccator half an hour Duplicate 500mg/500ml		Zeolite in desiccator 1 day Duplicate 500mg/500ml	
	Set A	Set B	Set A	Set B
FAU	5.98	6.07	6.46	6.57
BEA	5.4	5.55	5.67	5.61
MOR	5.22	5.2	5.3	5.26
MFI	6.29	6.3	7.25	7.44
FER	6.61	6.46	6.66	6.65

8.6 Adsorption binary mixture in demi water measured data

pH0 is the initial pH and pHe is the final pH. Samples without zeolite dosage are C0 which were done in triplicates. The average OMP concentration from these is the initial OMP concentration for all samples with zeolite dosage. The values with a "#" were not plotted in the graph. They could be outliers, below LoQ or higher than the average initial concentration.

Z1 (FAU)			**Clarithromycin**	**Metoprolol**
pH0	pHe	Zeolite mg/l	Ce ug/l	Ce ug/l
6.4	6.17	346.01	0.58	#0.0492
6.39	6.02	250.37	0.63	#0.0419
6.16	6	101.32	1.25	0.11
6.11	5.86	74.98	1.61	0.13
6.1	6.13	49.42	2.53	0.17
6.24	5.88	29.71	3.36	0.39
6.07	6.03	10.04	7.20	1.56
6.05	5.96	5.37	8.28	2.08
6.22	6.06	0.00	13.37	10.79
6.12	5.87	0.00	14.16	10.89
6.3	5.93	0.00	10.40	10.84
Average of three C0			**12.64**	**10.84**

Z2 (BEA)			**Clarithromycin**	**Metoprolol**
pH0	pHe	Zeolite mg/l	Ce ug/l	Ce ug/l
5.86	5.66	200.23	0.12	0.07
5.77	5.63	150.03	0.24	0.11
6.09	5.89	101.34	0.24	0.14
6.2	5.9	49.16	0.36	0.08
6.04	6.02	0.74	#10.5605	0.06
6.02	5.89	0.62	#10.2385	0.06
6.09	5.95	0.35	#9.9506	0.99
6.34	6.1	0.21	#11.0279	0.96
6.07	6.1	0.00	9.67	8.71
6.22	5.95	0.00	10.90	10.43
6.29	5.89	0.00	7.00	10.56
Average of three C0			**9.19**	**9.90**

Z3 (MOR)			**Clarithromycin**	**Metoprolol**
pH0	pHe	Zeolite mg/l	Ce ug/l	Ce ug/l
5.95	5.64	50.50	0.15	#0.1434
6.05	5.87	41.06	0.12	#0.0487
6.02	5.92	25.06	0.22	#0.0192
6.02	5.92	10.89	0.76	#0.043
6	6.02	0.82	#13.2284	#0.0259
6.04	5.97	0.57	11.08	#0.0233
5.98	6.16	0.37	12.68	#3.5707
6.07	6.08	0.17	11.29	0.46
6.1	5.95	0.00	10.09	10.64
6.09	6.21	0.00	13.43	10.46
6.08	5.94	0.00	#4.7079	10.31
Average of three C0			**11.76**	**10.47**

Z4 (MFI)			**Clarithromycin**	**Metoprolol**
pH0	pHe	Zeolite mg/l	Ce ug/l	Ce ug/l
7.65	7.06	1004.76	0.82	#0.0244
7.06	6.76	504.82	0.82	#0.0275
7.12	6.68	251.29	1.82	#0.026
6.17	6.08	50.51	4.10	#0.0266
6.07	6.1	3.12	#10.8215	#0.0157
6.04	5.99	1.91	#8.9226	#0.0211
6.09	6.05	1.07	#9.7226	0.98
6.12	6.15	0.52	#9.2267	3.78
6.08	5.94	0.00	9.69	9.26
6.02	6.12	0.00	8.50	10.72
6.11	5.97	0.00	7.61	10.80
Average of three C0			**8.60**	**10.26**

Z5 (FER)			**Clarithromycin**	**Metoprolol**
pH0	pHe	Zeolite mg/l	Ce ug/l	Ce ug/l
6.75	5.45	1000.05	0.65	#0.0216
6.75	6.25	499.79	1.17	#0.0225
6.7	6.37	248.94	1.07	#0.0371
6.15	6.04	52.74	1.75	0.10
6.05	6.12	11.28	6.63	0.35
6.03	6.09	4.75	7.78	4.86
6.01	5.95	1.23	8.07	9.00
5.95	6.02	0.48	#10.6094	#10.2177
6.05	6.1	0.00	#0.9932	#6.2703
5.95	5.92	0.00	8.98	10.19
6	5.93	0.00	8.63	10.09
Average of three C0			**8.80**	**10.14**

8.7 Adsorption binary mixture in wastewater-1 measured data

pH0 is the initial pH and pHe is the final pH. Samples without zeolite dosage are C0 which were done in triplicates. The average OMP concentration from these is the initial OMP concentration for all samples with zeolite dosage. The values with a "#" were not plotted in the graph. They could be outliers, below LoQ or higher than the average initial concentration.

All zeolites were dosed with 120 µl of 0.5M HCl per 50ml sample except (Z5) FER which is 60 µl.

Z1 (FAU)				**clarithromycin**	**metoprolol**
pH0	pHe	EC	Zeolite mg/l	Ce ug/l	Ce ug/l
6.81	7.44	980	995.77	#0.216	0.08
6.82	7.70	980	503.08	0.83	0.09
6.85	7.43	990	241.35	4.07	0.34
6.85	7.47	987	93.87	11.49	2.49
6.85	7.61	962	51.12	12.42	4.55
6.84	7.96	982	10.14	#0.2616	#1.4892
6.83	7.17	984	5.16	13.24	6.35
6.74	7.43	983	1.02	14.25	26.27
7.01	7.46	990	0.00	#0.8093	29.50
7.01	7.97	908	0.00	16.86	30.62
7.09	7.89	973	0.00	16.13	30.81
Average of three blanks				**16.49**	**30.31**

Z2 (BEA)				**clarithromycin**	**metoprolol**
pH0	pHe	EC	Zeolite mg/l	Ce ug/l	Ce ug/l
6.58	7.66	962	983.72	1.59	#0.0429
6.87	7.64	975	496.31	5.41	#0.0253
6.87	7.58	974	246.20	8.50	#0.024
6.85	7.51	974	104.91	21.80	#0.0443
6.86	7.51	978	51.28	20.99	#0.0497
6.92	7.38	973	9.68	#0.4098	0.05
6.91	7.2	977	5.70	#7.1434	0.07
6.75	6.89	983	1.16	#23.7797	1.63
6.94	7.52	983	0.00	20.24	31.11
6.94	8.02	980	0.00	25.84	31.79
6.91	7.81	984	0.00	22.79	31.64
Average of three blanks				**22.96**	**31.51**

Z3 (MOR)				**clarithromycin**	**metoprolol**
pH0	pHe	EC	Zeolite mg/l	Ce ug/l	Ce ug/l
6.67	7.16	960	1002.10	4.28	#0.0779
6.72	7.71	971	488.85	#10.6892	#0.0434
6.77	7.71	966	248.92	8.71	#0.0269
6.80	7.49	983	106.95	#3.7139	#0.021
6.81	7.98	982	51.33	12.65	#0.0188
6.80	7.12	984	9.88	#15.0339	#0.0324
6.80	7.26	984	4.69	13.33	0.19
6.74	6.80	985	1.06	#3.5812	19.53
6.91	8.13	983	0.00	14.70	28.91
6.89	7.60	987	0.00	13.19	30.91
6.89	7.62	987	0.00	14.96	28.00
Average of three blanks				**14.28**	**29.27**

Z4 (MFI)				**clarithromycin**	**metoprolol**
pH0	pHe	EC	Zeolite mg/l	Ce ug/l	Ce ug/l
6.92	7.51	966	999.40	#0.4247	#0.0253
6.89	7.51	975	506.71	20.19	#0.024
6.88	7.72	977	247.01	#25.9447	#0.0262
6.87	7.57	976	99.98	22.54	#0.0359
6.88	7.85	977	49.26	23.75	#0.0188
6.95	7.26	975	9.44	24.76	3.13
6.93	7.29	975	4.93	#28.5517	15.05
6.76	6.86	983	0.92	21.78	27.57
6.79	7.97	981	0.00	25.70	32.47
6.79	7.52	984	0.00	25.70	33.54
6.8	7.49	985	0.00	23.77	32.10
Average of three blanks				**25.06**	**32.70**

Z5 (FER)				**clarithromycin**	**metoprolol**
pH0	pHe	EC	Zeolite mg/l	Ce ug/l	Ce ug/l
6.92	7.78	942	1010.62	0.52	#0.0154
6.96	7.63	944	496.15	9.81	#0.021
7.01	7.53	950	262.65	#15.6245	#0.0377
7.04	7.53	958	90.48	#15.6179	1.42
7.10	7.68	960	45.15	#15.6041	15.23
7.02	7.93	963	9.76	#0.308	28.45
7.01	7.34	966	4.99	#9.7229	30.29
7.03	7.61	964	1.06	16.24	30.06
7.04	7.64	964	0.00	15.73	31.33
7.03	8.03	961	0.00	14.74	30.65
7.06	7.92	962	0.00	15.48	30.41
Average of three blanks				**15.32**	**30.80**

8.8 Comparison between wastewater-1 and wastewater-2

Adsorption isotherm with new wastewater (wastewater-2) and previous wastewater (wastewater-1) were compared to see how much the adsorption capacity deviates for BEA and MOR. However, this comparison might be undermined due to great differences with initial OMP concentration for the adsorption tests. The initial concentration can play an important role with determining the adsorption capacity. (H. W. Hung et al., 2005) Showed for various activated carbons that the lower the initial concentration of MTBE is, the higher the competition would be with NOM. They also conducted experiment with MTBE adsorption with MOR. There was no difference in adsorption capacity observed with varying initial concentration. This phenomenon was ascribed to the molecular sieving effect. The NOM molecules were thought to be too big to enter the pores.

Although my thesis utilizes MOR, the idea were different initial concentration of metoprolol and clarithromycin doesn't influence the adsorption capacity in NOM-rich water may not be applicable in this study. Minor competition was observed for metoprolol and a significant competition for clarithromycin, paragraph 5.3. The results from wastewater-1 and wastewater-2 are compared Figure 17.

The initial OMP concentration of all experiments should be around 10 ug/l, comparable to the experiments with demi water. Unfortunately, a mistake was made calculating the amount of OMP to spike for wastewater-1. This resulted in three times higher initial concentration of metoprolol in wastewater-1 compared to demi water and wastewater-2 tests. The adsorption capacity of MOR and BEA in wastewater-1 is higher than wastewater-2, Figure 17. This could be due to the difference in the used wastewater matrix or because of the difference in the initial concentration.

The initial clarithromycin concentration of MOR and BEA in wastewater-1 are 14.28 ug/l and 22.96 ug/l respectively, Figure 18. Despite of pipetting the appropriate volume from the stock solution, they both differs greatly. Metoprolol didn't show this problem while working in the same way. Adsorption isotherm of clarithromycin with MOR shows lots of scattering which is difficult to determine a trend.

In general metoprolol adsorbs better than clarithromycin regardless of the zeolite framework or wastewater type. Metoprolol adsorption capacity is lower in wastewater-2 compared to wastewater-1 which might be due to lower initial concentration or due to different wastewater matrix. Clarithromycin shows much differences in

initial concentration and has scattering with MOR making it difficult to compare the effect between the two wastewater matrices.

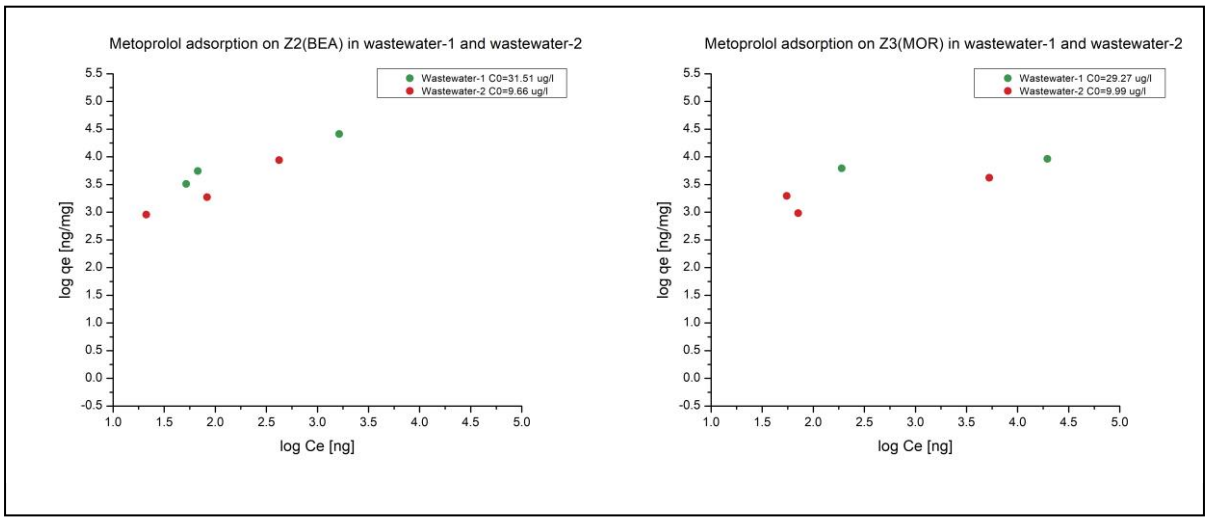

Figure 17 Metoprolol adsorption in wastewater-1 and wastewater-2 on Z2(BEA) left graph and Z3(MOR) right graph

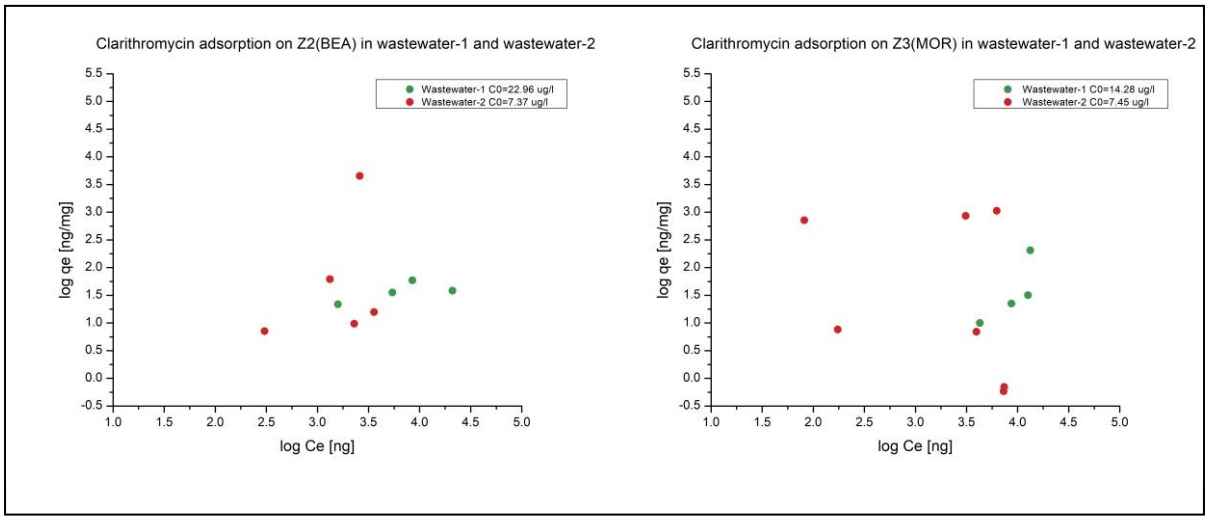

Figure 18 Clarithromycin adsorption in wastewater-1 and wastewater-2 on Z2(BEA) left graph and Z3(MOR) right graph

8.9 Clarithromycin measurement signal/noise ratio

All signal to noise is above 10 which is good (ABsciex, 2010). All peaks were checked manually on the MassLynx software and they were all good as well.

Table 22 Signal to noise ratio of clarithromycin during LC/MS measurement in wastewater-2 and nano filtrated wastewater

Z2 (BEA) wastewater-2	
Zeolite dosage [mg/l]	S/N [-]
991.86	589
523.83	1239
241.40	4374
98.37	1355
49.59	5308
10.68	1476
5.13	2158
1.06	1569
0.00	3580
0.00	3214
0.00	7520

Z3 (MOR) wastewater-2	
Zeolite dosage [mg/l]	S/N [-]
959.84	559
502.93	1575
243.35	4993
96.91	3477
44.91	4313
10.31	301
5.06	1068
1.12	3737
0.00	2064
0.00	5923
0.00	3935

Z2 (BEA) nano filtrated wastewater	
Zeolite dosage [mg/l]	S/N [-]
971.85	655
478.92	1780
253.67	1861
97.40	284
49.71	2665
11.16	4040
4.92	3345
0.89	1639
0.00	2654
0.00	1799
0.00	586

Z3 (MOR) nano filtrated wastewater	
Zeolite dosage [mg/l]	S/N [-]
952.89	402
481.87	1568
230.49	1270
96.71	1615
49.47	3529
10.29	222
5.35	762
1.04	3277
0.00	1011
0.00	4927
0.00	7231

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