Paper 12
Coagulation for SWRO Pretreatment: Eliminating SWRO Biofouling Potential

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THEME 3

HIGHLIGHTS

- TEP removal measured as biopolymers (by LC-OCD) with coagulation/filtration is effective.
- The effect of coagulation/filtration on TEP0.4 is high and on TEP10kDa is substantial.
- Filtration through 0.45μm significantly improves water quality for most parameters tested.
- Fouling potential (MFI-UF10kDa) of TEP solutions with biopolymer concentration of 0.5mgC/L is high
- Coagulation with iron (III) followed by 0.45μm filtration reduces the fouling potential (MFI-UF10kDa).

INTRODUCTION

Recent advances in technology, especially improvements in semi-permeable membranes, have made desalination a realistic water supply option and considered as an important alternative source for potable and non- potable water uses in many countries. Although seawater reverse osmosis (SWRO) technology has gained higher ground on water desalination in recent years, the operational cost is still high and not affordable for many countries due to several factors (Khawaji, et al., 2008).

One important factor is membrane fouling which results in both an increase in operational pressure and a short lifetime of the membrane elements and in an increased number of chemical cleanings to restore membranes permeability. Membrane fouling in SWRO can be caused by organic matter (lipids, proteins, and polysaccharides), microorganisms (algae, plankton, and unicellular organisms), colloids and suspended solids, salts and metal cations. Over the last years, there have been increasing episodes of membrane fouling that have been attributed to due to biopolymers (polysaccharides and proteins) and especially during algal bloom periods.

Algal blooms are a serious problem that desalination facilities need to tackle as algae release dissolved or colloidal extracellular polymeric substances (EPS). Transparent exopolymer particles (TEPs) are a planktonic type of EPS and have been identified as a major component of polysaccharide substances in seawater and other aquatic systems. TEPs are transparent, sticky, negatively charged and amorphous substances and may exist as strings, disks, sheets or flexible fibers (1-3 nm in diameter by 100's of nanometers long) originating from biological detritus and release of aquatic microorganisms (Passow, 2002). Many TEP provide a nutritious and sticky organic substrate for colonization by bacteria and other microorganisms and serve as "hot spots" of intense microbial and chemical activity within the water mass (Passow, 2012). In polysaccharides, nucleic acids, proteins and trace elements may be associated with these gel-like particles (Berman, et al., 2011).

Because large amounts of TEP found in most natural waters, it is likely that these hitherto neglected particles turn out to have important implications for biological fouling in many filtration applications. In addition to biofilm development on membranes, TEP may initiate or enhance biofilm development in RO membranes by creating a "conditioning layer" on the membrane surface (Berman and Holenberg, 2005). TEP may serve as "food packages" for microorganisms and stimulate "bacterial growth". The operational problem caused by algal bloom episodes in SWRO plants during the last 5-10 years have led to new concerns and an increased attention has been put on ad-hoc pretreatment systems.

The performance of RO relies upon the production of high quality water from pretreatment (conventional media filtration/ ultra-filtration). Therefore, TEP has to be removed from RO feed water to reduce (bio) fouling potential in RO. A recent study by Villacorte (2009) reported that smaller acidic polysaccharides were up to 5 times more abundant than those were larger than 0.40 μm. Typical sizes of TEP may cover the range from colloidal to particulate, suggesting that TEP is not only a potential foulants for organic fouling but particulate fouling as well (Villacorte, 2009). Just recently, the removal of TEP by Ultra Filtration (UF) pretreatment have been studied by Villacorte (2009) and concluded that it may not completely remove TEP from the RO feed water.

The coagulation of TEP is not been considered so far, even though extensive study on coagulation for colloids and algae is studied. Coagulation may agglomerate event the smaller particles and give rise to lower fouling potential of the RO. Therefore, the coagulation of TEP is focused on this research. The feed water consist of TEP is also to be characterized using the available analytical measurements.

GOAL AND OBJECTIVES

The goal of this research is to assess the performance of conventional pretreatment; coagulation/ flocculation/ sedimentation/ filtration to reduce biofouling potential of reverse osmosis feed water during algal bloom periods with high TEPs concentrations.

The specific objectives are:

- To characterize RO feed water quality in terms of TEP concentration, fouling potential (MFI-UF), biopolymer concentration (LC-OCD), DOC characterization (UV_{254}, FEEM), Turbidity and Iron residual for different conditions of coagulant dose and pH.
- To predict fouling potential in SWRO systems using a theoretical model with experimental data as input.

MATERIAL AND METHODOLOGY

The study involved laboratory experiments on conventional coagulation/filtration for TEP removal from high salinity water. Experiments were performed to investigate the effect of coagulation conditions such as dose and pH on solutions of laboratory produced TEP in synthetic seawater (SSW). Coagulation efficiency was estimated by measuring a suite of analytical parameters including turbidity, iron residual, $TEP_{0.4}$, TEP_{10kDa}, UV_{254}, FEEM, and MFI-UF. A portion of these samples was tested for LC-OCD analysis with DOC-Labor (Karlsruhe, Germany). The results were investigated to formulate findings on the link between TEP and conventional pretreatment in terms of biofouling potential in RO systems (Figure A.1).

Feed water was prepared with the ionic concentration of 35g/L, similar to North Sea water. TEP culture was prepared in the laboratory using a fresh strain of *Chaetoceros affinis* (CA) purchased from Culture Collection of Algae and Protozoa (CCAP), Oban, Scotland. TEP was obtained through the cultivation of

CA in Guillard's medium for diatoms (f/2+Si). Iron chloride ($FeCl_3.6H_2O$) from KEMIRA was used as coagulant. The amount of coagulant dose was estimated based on iron (Fe_{tot}) concentration of 13.7% by weight and a density of 1420 kg/m^3.

A jar test unit was used to simulate the conventional pretreatment steps: coagulation, flocculation and sedimentation. A Dual Syringe Pumps (Harvard Apparatus, USA) connected to the syringe with a filter (0.45m porous, Cellulose acetate, 25mm diameter) was used to simulate the conventional filtration step. Trial tests were performed to establish the experimental protocol and the conditions were fixed as, rapid mixing intensity of 1,100 S^{-1} (≈ 360 rpm) for 20 seconds, flocculation intensity of 45 S^{-1} (≈ 42 rpm) for 15 minutes, sedimentation time of 20 minutes. The experiment was carried out for the selected doses and pH whereas; the optimization of coagulant dosage and pH is not the scope of this study.

RESULTS & DISCUSSION

Conventional treatment at pH= 5 and 8

The experiment was carried out based on the protocol of the experimental procedure that has been tested in the trial experiment. This is in line with first specific objective.

MFI-UF constant flux test

The MFI-UF value was estimated using pressure developed at 10 seconds intervals by filtering through 10 kDa membranes at 60 LMH (L/m^2/h) and is shown in Figure A.3. Due to the lower profile at pH=5, the values are normalized in order to compare the results at both pHs. The MFI-UF value is highly reduced by the coagulation dose above 1 mg/L and the filtration process reduces more than 50% for any dose at both pHs.

Residual Fe measurements

The results of iron residual using Phenanthroline methods for range of coagulant dose are given in Figure A.4. The iron residual is not lowered below the membrane manufacturers recommended limit of 0.05 mg/L (more susceptible to oxidation damage of membranes) by the coagulation process at both pHs, however, the filtration process at pH=8 reduces below the limit.

This results comply with values by Robert F. Skinner Filtration Plant where the irons residual is below the detection limit of 20µg/L after filtration through 0.45 micron filter at pH8 and about 0.64 mg/L in settled water. The positive iron compounds at pH=5 in is very low i.e. 3.26*10-8 [Fe]/mole or 1.82µg Fe/L (very low solubility). Therefore, the high iron residuals are hardly being explained by the iron solubility criteria. Further, the zeta potential measurements for TEP are highly scattered based on the previous testing experience.

Residual turbidity

Residual turbidity for range of coagulant dose at pH= 8 and 5 for settled and filtered samples are depicted in Figure A.5. Turbidity is not reduced by coagulation process except dose above 5 mg Fe/L at both pHs below 1.0 NTU which is the recommended limit by the Hydranautics (a membrane manufacturer). However, Turbidity is reduced below the limit by filtration.

The SSW itself has turbidity 0.08 NTU and this may be due to the precipitates/ colloids from the salt used for the preparation of SSW. As TEP is transparent micro-particles, it must produce less turbidity to the water. However the TEP feed solution is of light muddy colour due to the algal residues and give raise to higher turbidity in feed water. Low turbidity of 0.1 - 0.2 NTU have been reported in literatures for conventional pre-treatment in seawater treatment(,).

UV_{254} absorbance

Ultra violet adsorption at 254 nm (UV_{254}) for range of coagulant dose at pH= 8 and 5 for filtered samples are shown in Figure A.6.The UV_{254} absorbance for TEP (biopolymer concentration of 0.5 mgC /L) is of 0.02 abs/cm. By the coagulant dose of above 5 mg Fe/L at pH=8, it was lowered by half, in contrast it was increased to 0.04 abs/cm at pH=5 for any coagulant dose.

Absorption of both visible and UV light is widely attributed to the aromatic chromophores present in NOM molecules (primarily humic) dissolved in the water. This may be hardly explained by the other parameters measured in filtered water.

LC-OCD measurements

The analytical results (biopolymer) from DOC-Labor and the percentage removal of biopolymers for filtered samples for range of coagulant dose at pH 8 and 5 are given in Figure A.7. Steady increase in biopolymers removal was observed with increase in coagulant dose at pH 8, up to approximately 67% at 20mgFe/L. At pH 5, maximum removal efficiency is about 55% and does not improve significantly beyond coagulant dose of 5mgFe/L.

Biopolymer concentration in SSW was measured at 32μgC/L (blank), which may arise from impurities in the salts used to prepare the SSW.The measured biopolymer in the feed water is from the TEP added to the SSW. The biopolymer concentration measured from the LC-OCD analysis was after filtering through 0.45μm filter as per the protocol for the measurements. Therefore, the biopolymer greater than this size were not taken into account in this results.

Fluorescence excitation-emission matrix (FEEM)

Figure A.8 shows the numerical representation of the FEEM plotting using Matlab program for settled and filtered water for range of coagulant. Two types of DOM fluorescence signals have been observed in the above spectra. Polysaccharides don't fluorescence when excited by light; therefore they only captured by LC-OCD. Polysaccharides being a potential membrane foulants, protein-like organic matter are hypothesized to be a principal membrane foulants.

The protein-like peak observed in the feed water was from the TEP added to the SSW and it was removed by coagulation above 5mg Fe/L and the filtration through 0.45 micron can remove allmost all the protein-like peak from the water independent of the coagulant dose (refer Figure A.8).

$TEP_{0.4\mu m}$ measurements

The results for $TEP_{0.45\mu m}$ for settled and filtered water for pH 8 and 5 are shown in Figure A.9. The absorbance at 787nm of TEP retained on 0.45μm RC filters and stained with Alcian Blue (dye specific for acid polysaccharides), were converted to the weight of commercially available polysaccharide (Xanthan gum).

This shows higher removal of TEP in the settled supernatant by dosing coagulants of 1, to 20 mg Fe/L at both pHs. However, this measures the partial amount of TEP above 0.45 micron and the smaller sizes are not able to measure and are probably responsible for fouling. However, It was found that acidic polysaccharides smaller were up to 5 times more abundant in surface water than those larger than 0.40 μm ().Therefore, the TEP_{10kDa} measurement was proposed to cover the smaller particles.

TEP_{10kDa} measurements

The results for TEP_{10kDa} for settled and filtered water are depicted in Figure A.10. The absorbance at 787nm of permeate through 0.1μm polycarbonate filters after staining the TEP (extracted from the TEP retained on 10kDa RC filters used for MFI-UF) were measured.The absorbance was converted to the weight of commercially available polysaccharide (Xanthan gum) binding with Alcian Blue (dye specific for acid polysaccharides).

The results show very low removal of TEP targeting particle above 0.05 microns by the coagulation and filtration process. This can give rise to two issues; firstly there can be polymer release from either Cellulose Acetate (CA) used to simulate media filtration or Regenerated Cellulose (RC) used for TEP_{10kDa} analytical test. Secondly, this can represent the TEP_{10kDa} measurements issues such as limit of detection or accuracy of the method of measurements.

Fouling prediction using theoretical model

The parameters that are considered in the fouling prediction model are targeted to represent RO particulate fouling. The outcome of the model is to obtain the time to perform cleaning of the RO membrane. The model predicts the time required to calculate the pressure increase due to RO membrane fouling (at constant flux).

The cleaning frequency of the settled supernatant and filtered water of different coagulant dose at pH 5 and 8 are presented in Table A1. There is a significant difference between the cleaning frequency for settled and filtered water. Similarly a considerably high frequency cleaning is observed at pH5 compared to pH8. In general, RO cleaning frequency is 2 to 3 times per year (every 4 to 6 months) for smaller plants and should preferably not exceed once a year in large plant. unfortunately, the experimental setup has no RO unit to compare with, However, they are comparable with the results published by).

'CONCLUSION & RECOMMENDATIONS

Conclusion

- TEP removal measured as biopolymers (by LC-OCD) with coagulation followed by 0.45μm filtration is effective.The higher the coagulant dose the higher the effect, particularly at pH 8
- Effect of coagulation/filtration on $TEP_{0.4}$ is high. This result was expected since $TEP_{0.4}$ is collected by filtering through 0.45μm filters
- The effect of coagulation/filtration on TEP_{10kDa} is substantial. However doubt about the blanks due to release of polymers from different membranes used in the analyses prevent firm conclusions
- Filtration through 0.45μm significantly improves water quality for most parameters tested, even at low coagulant concentrations
- Fouling potential ($MFI\text{-}UF_{10kDa}$) of TEP solutions with biopolymer concentration of 0.5mgC/L is high
- Coagulation with iron (III) followed by 0.45μm filtration reduces the fouling potential ($MFI\text{-}UF_{10kDa}$). The higher the coagulant dose the lower the fouling potential.
- Cleaning frequency of RO membranes (estimated using the theoretical UNESCO-IHE model), can be significantly reduced with coagulation/filtration.

Recommendations

- Testing protocol for TEP_{10kDa} to be revised as proposed considering salinity effect and the biopolymer release from the membrane used for filtration.
- Cleaning frequency estimated from the theoretical model is to be validated through existing operation of the RO system.
- Studying the efficiency of coagulation/UF, inline coagulation/UF, etc., can reveal more information on the most suitable pretreatment option for SWRO in algal blooms.
- A measuring protocol is to be developed considering the suitable MWCO, flux, pressure recoding

intervals, moving average duration and selection of flushing water (milli-Q or SSW) depending on the type of water sample to be tested and the volume of flushing etc.

The effect of MFI-UF on storage of TEP may be possible and to be investigated with sufficient experimental results.

Methodology

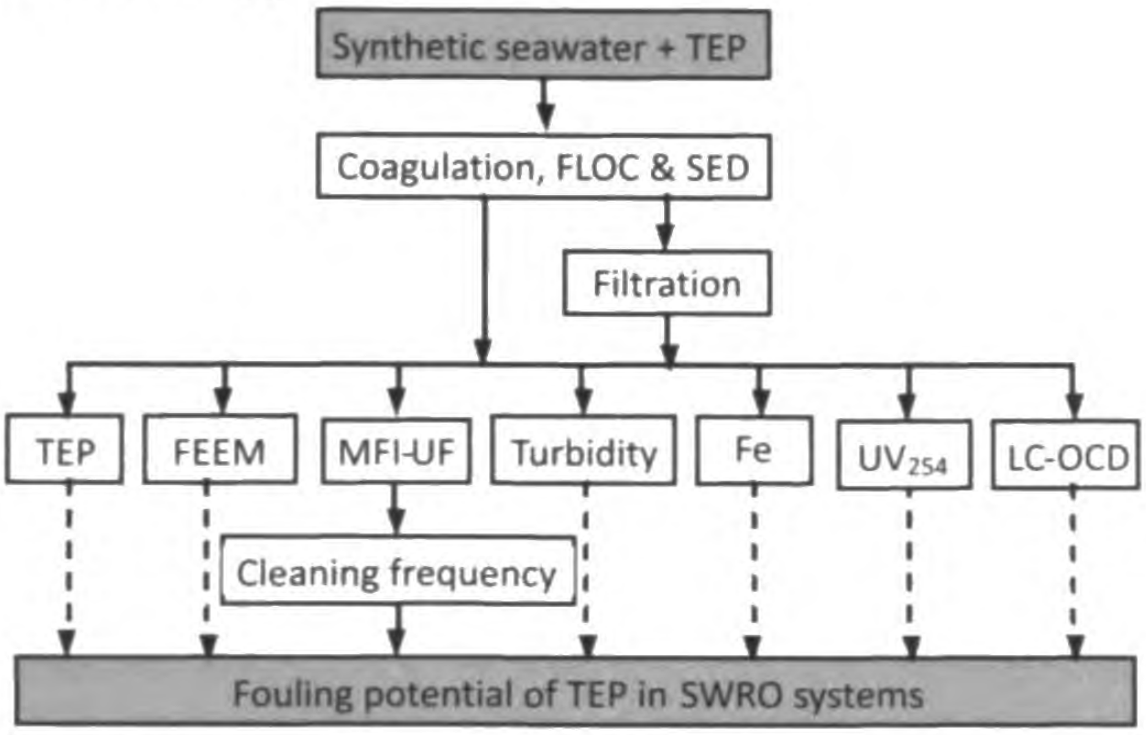

Figure A1: Research methodology scheme

Figure A.2:Diatom species of CA (Villacorte et al,2010)

Experimental Results

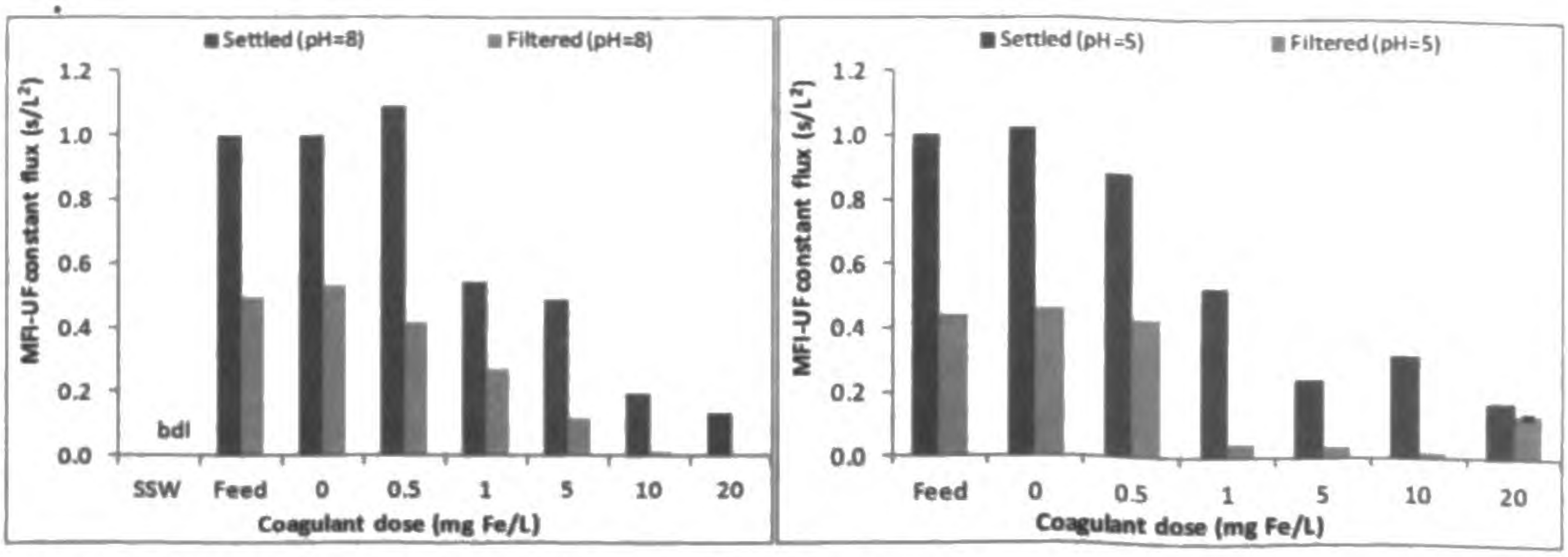

Figure A.3: MFI-UF Vs coagulant dose (Normalized) at pH= 8 and 5

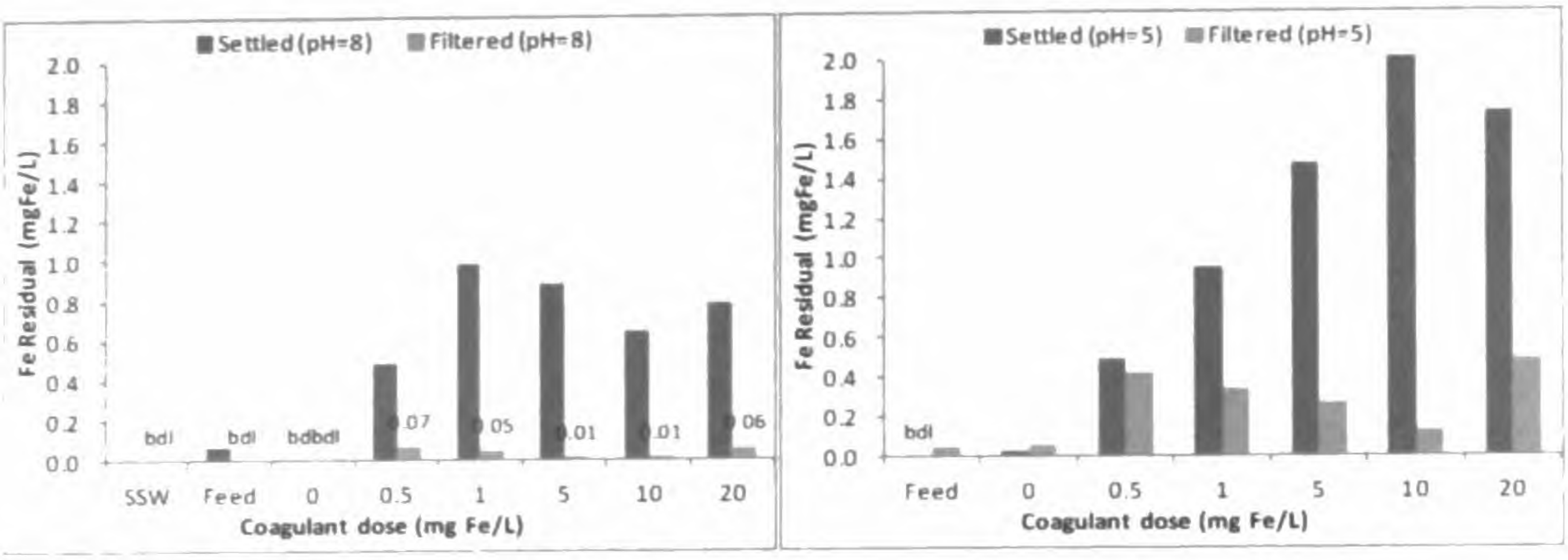

Figure A.4: Fe residual Vs coagulant dose at pH= 8 and 5

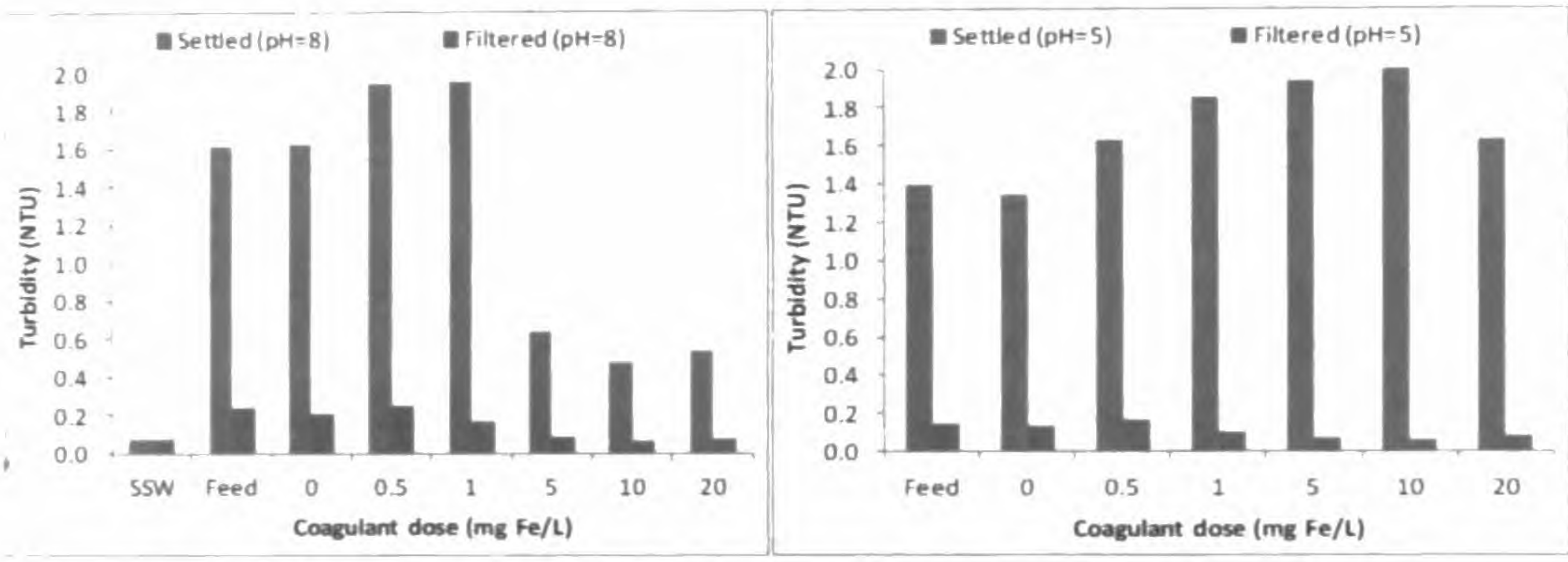

Figure A.5: Residual turbidity Vs coagulant dose at pH= 8 and 5

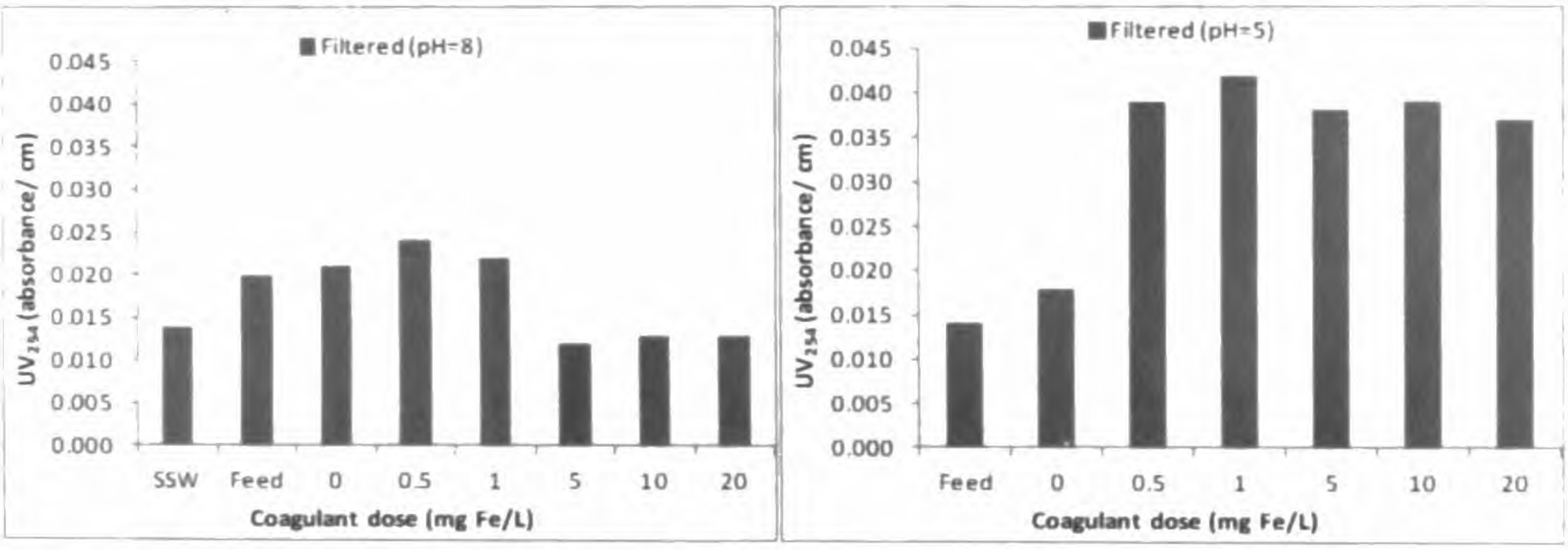

Figure A.6: UV_{254} Vs coagulant dose at pH= 8 and 5

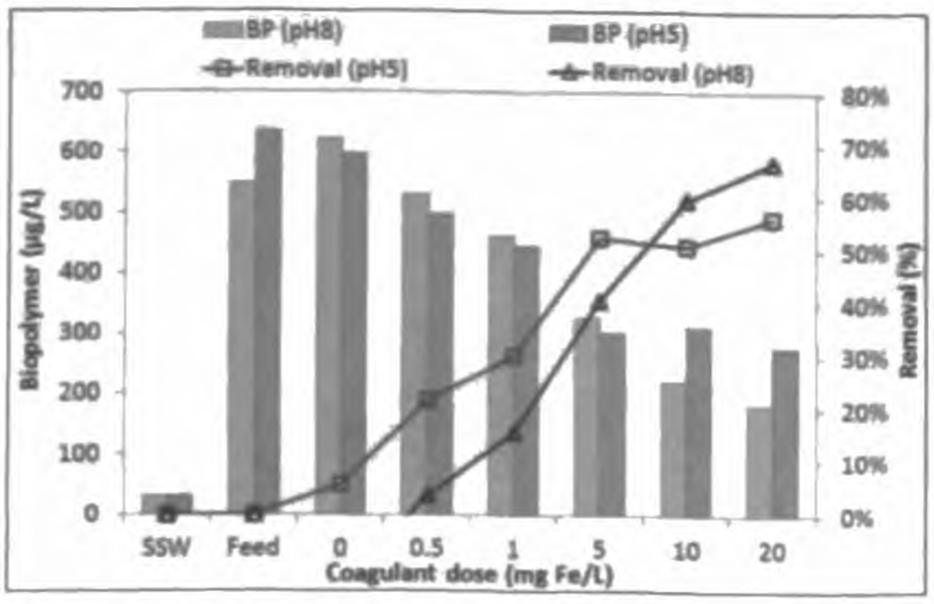

Figure A.7: Residual biopolymer Vs coagulant dose at pH= 8 and 5

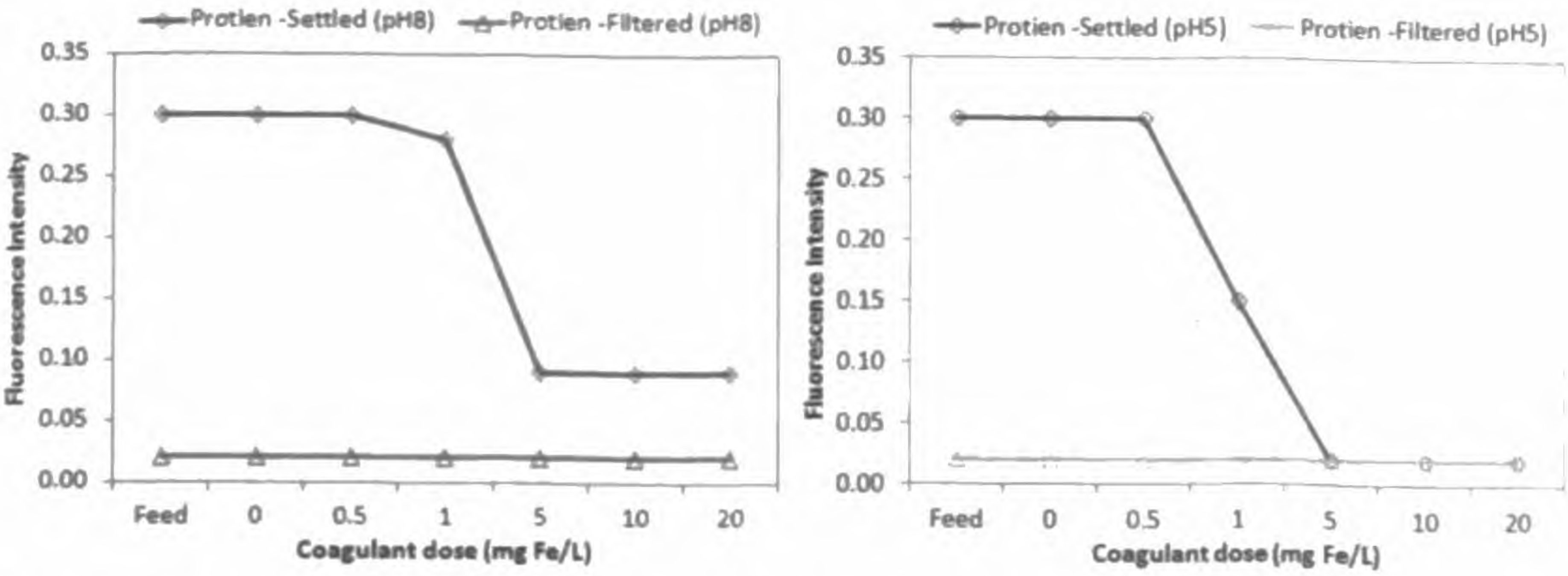

Figure A.8: Fluorescence Intensity Vs coagulant dose at pH= 8 and 5

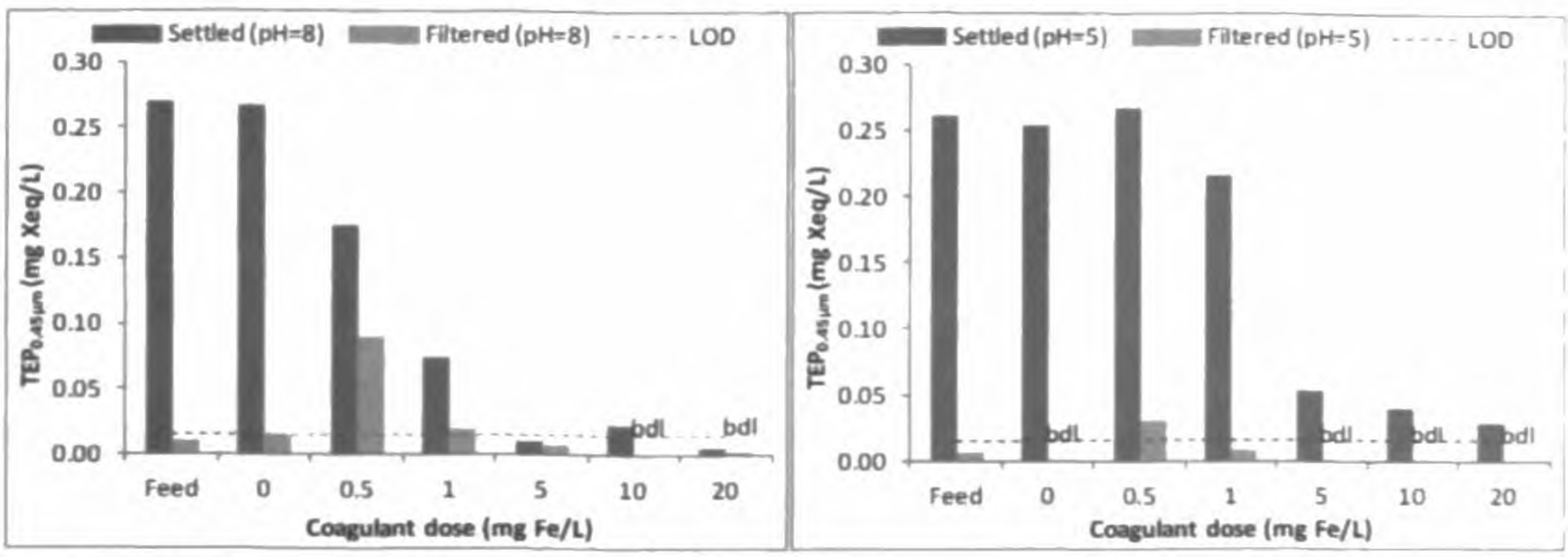

Figure A.9: TEP0.4µm Vs coagulant dose at pH= 8 and 5

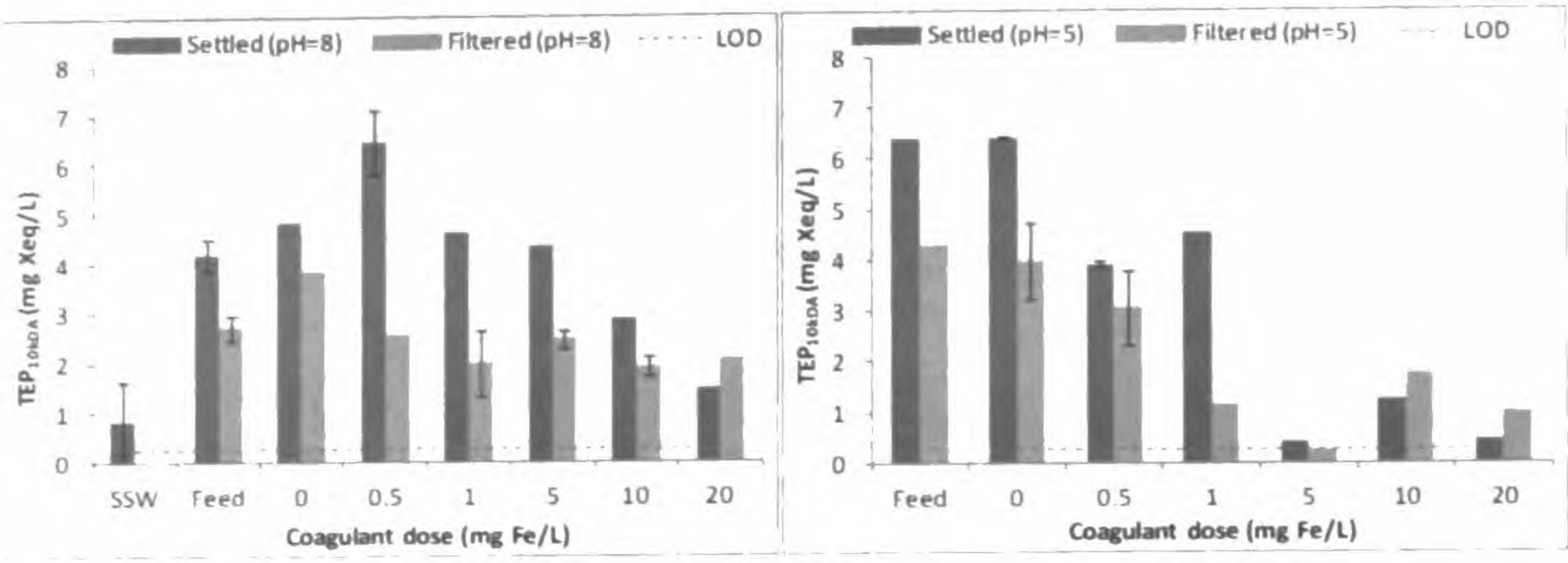

Figure A.10: TEP10kDa Vs coagulant dose at pH= 8 and 5

Table A.1: Estimated time for 15% increase in NDP for settled and filtered water

Sample	MFI-UF (s/L²) at 60 L/m²/h	MFI-UF (s/L²) at 20 L/m²/h	tr at 20 LMH (months)	MFI-UF (s/L²) at 60 L/m²/h	MFI-UF (s/L²) at 20 L/m²/h	tr at 20 LMH (months)	MFI-UF (s/L²) at 60 L/m²/h	MFI-UF (s/L²) at 20 L/m²/h	tr at 20 LMH (months)	MFI-UF (s/L²) at 60 L/m²/h	MFI-UF (s/L²) at 20 L/m²/h	tr at 20 LMH (months)
	Settled (pH8)			**Filtered (pH8)**			**Settled (pH5)**			**Filtered (pH5)**		
Feed	26820	4926	**1.0**	14129	2595	**1.9**	18413	3382	**1.4**	8085	1485	**3.3**
0	28559	5246	**0.9**	12962	2381	**2.0**	18800	3453	**1.4**	8414	1545	**3.1**
0.5	29224	5368	**0.9**	11137	2046	**2.4**	16243	2984	**1.6**	7904	1452	**3.3**
1	14444	2653	**1.8**	7189	1320	**3.7**	9774	1795	**2.7**	736	135	**36**
5	12925	2374	**2.0**	3092	568	**8.6**	4458	819	**5.9**	696	128	**38**
10	5198	955	**5.1**	355	65	**75**	5900	1084	**4.5**	501	92	**53**
20	3454	634	**7.7**	0	0	**infinite**	3199	588	**8.3**	2524	464	**10.5**