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Treating laundry waste water: Cationic polymers for removal of contaminants and decreased fouling in microfiltration

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ABSTRACT

The goal was to select coagulants and a coagulation process for treating laundry wastewater. The long-term goal is for application in Army mobile treatment units with solids removal using microfiltration (MF) and for which a robust operation with small coagulant volumes are desirable. Laundry wastewater usually has very high pH thus strong base cationic polymers are good coagulant candidates. Seven quaternary amine polymers were examined to determine effects of coagulant dose on zeta potential (ZP). Four of the polymers were further evaluated for sedimentation of contaminants, specific resistance to filtration, and cake compressibility during filtration. A low molecular-weight epichlorohydrin/dimethylamine (epi/DMA) polymer was tested further because of greatest increase in ZP with low polymer dose, lowest specific resistance to filtration, and good removal of contaminants. Flocculation for 10 min resulted in greatly improved removal of cake by hydraulic washing compared to 2 and 5 min flocculation. Fouling during multi-cycle membrane operation was greatly reduced with coagulant additions less than half the charge-neutralization (CN) dose. Low polymer dose results in decreased chemical demand and reduced sludge production. Successful treatment using from 50% to 100% of the CN dose provides more robust operation under field conditions.

1. Introduction

This paper deals with coagulation of laundry wastewater with quaternary amine polymers and solids removal by sedimentation or low-pressure membrane filtration. The research is motivated by the need to recycle laundry wastewater at Army forward operating bases using the Tricon Shower Water Reuse System (SWRS) in which microfiltration (MF) of laundry wastewater without prior coagulation can result rapid membrane fouling. The results will be useful for treatment of laundry wastewater in any venue.

The most widely employed strategies for treatment of laundry wastewater are coagulation, adsorption, flotation, adsorption, filtration with media, and membrane filtration [1–8]. Coagulation can be effective for removal of chemical oxygen demand (COD), phosphates, and anionic surfactants. Coagulation produces floc that must be removed by a solid separation process. MF or ultrafiltration (UF) membranes are increasingly used for solid separation and these processes are compatible with in-line application of coagulants [9].

Inorganic coagulants are typically effective only when a precipitate forms, usually with a net charge opposite to the charge on the contaminants. For example, alum or ferric chloride work best when the final pH results in precipitation of the metal oxides and when the initially formed precipitates have sufficient positive charge to neutralize negative charge on humic materials, clays, and other common constituents in water. Laundry wastewater, however, typically has very high pH and is well-buffered with respect to pH. Ge and coworkers [7] reported that contaminant removals from laundry wastewater were poor when using inorganic coagulants for pH <4 or >9. Similarly, electrocoagulation did not improve flux compared with raw water in polyvinylidine fluoride (PVDF) MF [10]. Strong base cationic polymers retain a high positive charge at high pH values are consequently are good candidates for coagulation of laundry wastewater.

The goal was to identify coagulants and coagulation processes to achieve the following objectives during treatment of laundry wastewater at high pH: (1) remove contaminants especially total suspended solids (TSS), total chemical oxygen demand (TCOD), and total phosphorus (TP); (2) effective removal of coagulated solids by sedimentation or MF; (3) substantial decrease in MF fouling compared to raw laundry wastewater; and (4) effective operation over a wide range of coagulant doses to achieve simple

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and robust operation. Experiments were conducted in three phases: (1) seven strong-base cationic polymers were screened to determine charge-neutralization (CN) effectiveness at pH 11; (2) four cationic polymers were selected for evaluation of contaminant removal by sedimentation, specific resistance to filtration, and cake compressibility; (3) one cationic polymer was selected for additional tests including effect of flocculation time and chemical dose on MF performance during multi-cycle tests meant to simulate continuous operation of the SWRS.

2. Materials and methods

2.1. Laundry wastewater

Wastewater was collected from an industrial laundry in Centre County PA during hours when only commercial uniforms were washed. Temperature and pH were measured onsite. The sample was immediately transported to the laboratory, filtered with 10 μm polypropylene mesh filters, pH adjusted to 11, and stored in a walk-in-refrigerator for further experiments. Table 1 shows the wastewater characteristics.

2.2. Coagulant titrations and jar tests

Seven quaternary amine (strong base) cationic polymers were initially selected to provide a range of apparent molecular weight, composition, and form (water solution, emulsion, and dispersion).

Table 1
The characteristics of laundry wastewater samples collected on six different dates from a local industrial laundry.

Parameter	Value
pH	12.5 ± 0.5
Temperature (°C)	40 ± 1.0
Zeta potential (mV)	-57.4 ± 8.5
Conductivity (μS cm^{-1})	724 ± 123
Total dissolved solids (mg L^{-1})	357 ± 52
Turbidity (NTU)	858 ± 111
TSS (mg L^{-1})	359 ± 82
TCOD (mg L^{-1})	1138 ± 58
TP (mg P L^{-1})	22 ± 4

Removals of turbidity, TSS, TCOD, and TP by pre-filtration with 10 μm polypropylene mesh filters were 17 ± 6, 34 ± 3, 14 ± 6, and 2 ± 1%, respectively.

All polymers were diluted according to manufacturer's specifications with deionized water to 1% (v/v) just before use. The 1% solutions were typically stored at room temperature. Prior to some experiments the 1% solutions were stored at 4 °C or 40 °C. All polymer doses are expressed in ppm (v/v). Characteristics of the polymers are shown in Table 2.

Coagulant titration tests were conducted by adding increasing volume of polymer beneath the water surface in the vortex of a rapidly stirred wastewater sample and measuring pH and zeta potential (ZP). Polymer doses were increased until several positive ZP readings had been recorded. Zero ZP is an indicator for the CN condition, i.e., the negative charge on contaminants has been exactly titrated by positive charge from the coagulant. Under-dosing (UD) refers to coagulant additions less than the CN dose resulting in residual negative charge on the coagulated flocs, while over-dosing (OD) means coagulant addition greater than the CN condition resulting in net positive charge on the flocs. Four significantly different polymers were selected based on the titration tests for jar tests and specific resistance to filtration tests.

Jar tests were performed using the four selected polymers to measure removals of turbidity, TSS, TCOD, and TP after sedimentation. Total means dissolved plus suspended contaminants after 1 hr sedimentation. Tests were conducted with a Phipps & Bird stirrer with conventional blades (Model 7790-400) by adding selected volumes of 1% solutions of polymer into wastewater with 1 min high speed mixing and then 30 min mixing at a velocity gradient of 200 s^{-1}. Samples were collected at the end of the mixing for ZP measurement. Supernatant was collected for the other analyses from just below the water surface after 1 h quiescent settling. Most jar tests were conducted at room temperature (≈ 22 °C) but some tests were conducted in water baths at 40 °C.

2.3. Effects of coagulants on specific resistance to filtration and compressibility

Flat-sheet hydrophobic 0.22 μm PVDF MF membranes (GVHP04700, Millipore) were used. Membranes were wetted in methanol and then soaked in deionized water overnight. A dead-end filtration system was used to estimate cake characteristics (Fig. 1a). Head loss from velocity head ($v^2/2g$) and elevation (Δh) were negligible, where v is the fluid velocity (m s^{-1}) and g is gravitational acceleration (9.8 m s^{-2}).

The pre-wetted membrane was placed in a commercial filtration cell (polycarbonate filter holder, Pall Sciences) with 9.6 cm^2

Table 2
The characteristics of polymers (in alphabetic order) provided by manufacturer.

Polymer brand	Ionicity	Charge density		Molecular weight	Composition	Form
		(%)[a]	(meq g^{-1})[b]			
Cat-floc 8102 plus	Cationic	100	6.2	Medium	PolyDADMAC	Water solution
Cat-floc 8108 plus	Cationic	100	6.2	High	PolyDADMAC	Water solution
Core shell 71301	Cationic	50–80	3.8–4.7	High	AcAm/DMAEA.MCQ	Emulsion
Core shell 71303	Cationic	20–50	2.1–3.8	Very high	AcAm/DMAEA.MCQ	Emulsion
Core shell 71305	Cationic	1–30	0.1–2.8	Very high	AcAm/DMAEA.MCQ	Emulsion
Nalcolyte 8105	Cationic	100	7.3	Low (< 50 K)	Epi/DMA	Water solution
Ultimer 1460	Cationic	50–80	4.3–5.6	High	AcAm/DADMAC	Dispersion

(Poly)DADMAC=(poly)diallyldimethyl-ammonium chloride ($C_8H_{16}NCl$).
AcAm=acrylamide (C_3H_5ON).
DMAEA.MCQ=dimethylaminoethylacrylate methyl chloride salt ($C_8H_{16}O_2NCl$).
Epi/DMA=epichlorohydrin and dimethylamine ($C_5H_{12}ONCl$).

[a] Mole percent of charged groups (e.g., the mole% of DMAEA.MCQ in AcAm/DMAEA.MCQ).
[b] The amount of cationic charge per gram of polymer was calculated with the mole percent of charged groups.