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Real Textile Wastewater Reclamation using a Combined Coagulation/ Flocculation/ Membrane Filtration System and the Evaluation of Several Natural Materials as Flocculant Aids

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ABSTRACT

A coagulation/flocculation/membrane filtration process was applied to two real textile wastewaters in Turkey. Aluminum sulfate and ferric sulfate were used as coagulants and several natural materials, namely limestone, magnesite, kaoline, pumice, and sedipür (polyelectrolyte), were used as flocculant aids. The effects of pH, coagulant dosage, and the type and dosage of flocculant aids on the color and chemical oxygen demand (COD) of wastewater were studied. The experimental results showed that the treatment with aluminum sulfate (0.5 g/L) and ferric sulfate (0.18 g/L) at a pH of 6 was very effective. The color removal for aluminum sulfate and ferric sulfate reached 81% and, 86%, respectively, and the COD was reduced by 70% and 47%, respectively. The natural flocculant aids behaved differently for color removal and COD reduction. The treatment with aluminum sulfate and limestone at pH 6 removed 89% of the color and reduced the COD by 80% in the presence of magnesite. The treatment with ferric sulfate aided with natural materials at pH 6 did not significantly remove the color and reduced the COD value by 50% in the presence of magnesite. Cellulose nitrate membranes can easily be cleaned using nitric acid.

Key Words: *Textile wastewater; coagulation; flocculation; membrane filtration.*

1. INTRODUCTION

Developing technologies and, rapid and unplanned industrialization are resulting in water pollution, which is important for human life [1]. The discharge of dyes into receiving waters is one major cause of water pollution. The textile industry is one generator of colored wastewater. Because the textile industry uses large amounts of water, large quantities of wastewater are produced with strong colour, large amounts of suspended solids, a highly fluctuating pH and a high chemical oxygen demand. The direct discharge of this wastewater into the environment affects its ecological status by causing various undesirable changes [2]. Therefore, treatment processes for removing dyes from textile effluents have become important for diminishing the environmental damage.

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Generally, color can be removed from wastewater by chemical and physical methods including adsorption, ion exchange, membrane-filtration, coagulation/flocculation, oxidation and electrochemical methods. Coagulation of dye-containing wastewater has been used for many years for primary treatment or pretreatment of wastewater due to its low capital cost. The effectiveness of dye coagulation can be enhanced by properly selecting of coagulant/flocculant aids, and optimizing the process parameters, such as initial pH, coagulant dosage, settling time, etc. [3-6]. High concentrations of dye and auxiliary chemicals can cause membrane fouling. Therefore, the coagulation/flocculation of the dye-containing wastewater can enhance the retention of dyes during membrane filtration [7].

Many studies have been conducted regarding the reclamation of dye wastewater by using coagulation/flocculation and membrane methods. Khayet et al. [4] studied the coagulation/flocculation of solutions with dye concentrations and tested the use of aluminum sulfate as a coagulant. Wang et al. [8] employed a cationic organic flocculant (epichlorohydrin-dimethylamine) for treat acidity and dye directly. The interactions between the cationic flocculant and the anionic dye were investigated using spectral analysis. In another study, Zahrim et al. [9] studied the removal of C.I. Acid Black 210 from a highly concentrated solution with aluminum sulfate as the primary coagulant and five commercial polymers as flocculant aids. The results of these studies showed that the aluminum sulfate is an important primary coagulant and that the settling time significantly affects the dye removal. Tan et al. [10] investigated the effectiveness of $MgCl_2$ as a coagulant for removing the reactive dyes and for treating industrial dye wastewater. Their results indicated that $MgCl_2$ is capable of removing more than 90% of coloring materials at a pH of 11 from a dye solution of 4 g $MgCl_2$/L. Following treatment of the industrial waste, the COD was reduced by 88% and the suspended solids content was reduced by 95%. El-Gohary and Tawfik [11] studied coagulation-flocculation for removing color and for reducing the COD values of dyes in wastewater. The chemically pre-treated wastewater was subjected to aerobic biological treatment using a sequential batch reactor process. The results showed that color removal reached 100% and the COD was reduced by 50%. Li at al. [12] studied magnesium hydroxide as a coagulant for treating reactive dyes wastewater assisted with kaolin. They found that kaoline clay had significantly influence on floc formation on reactive dyes removal. Many investigations attempted the use membrane filtration and nanofiltration systems for dyeing wastewater [13-16]. Although several studies have been published regarding the removal of dyestuff and reducing the COD values in dye wastewater, no published reports have evaluated natural materials as flocculant aids.

This study was conducted using on two textile wastewaters to evaluate the efficacies of aluminum sulfate and ferric sulfate coagulation and membrane filtration. The effects of the initial wastewater pH, the coagulant dosage, and the type and dosage of the natural flocculant aids were investigated.

2. EXPERIMENTAL

Textile wastewater that consisted of reactive dye was collected from a textile factory in Bursa, Turkey on different days. Table 1 shows the characteristics of samples 1 and 2. In this case, it appeared that the wastewater had very high color and COD values. The samples were refrigerated at 4 ^{o}C prior to performing subsequent experiments. The chemicals used in this study were analytical grade Merck products.

Table 1. Characterization of textile wastewater samples

Parameter	Sample 1	Sample 2
COD (mg/L)	1409.7	974.8
Conductivity (mS/cm)	1.117	2.91
pH	7.6	8.7
Colour (Pt-Co)	1500	830
Suspended Solid (mg/L)	2.99	1.94
Alkalinity (mg $CaCO_3$/L)	600	520

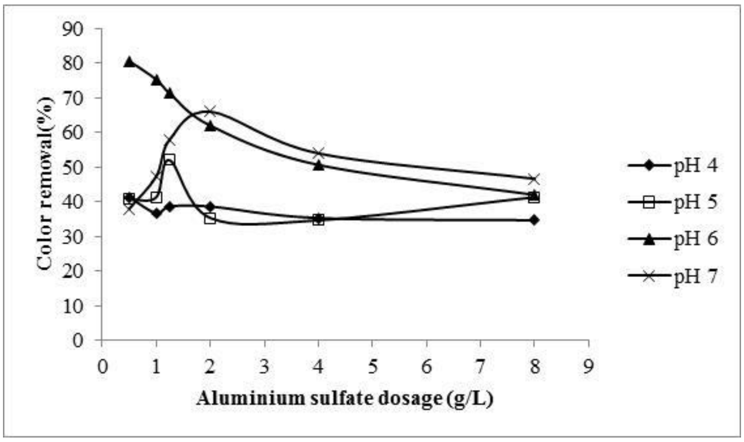
The membrane filtration experiments were conducted by using 0.45 μm pore sized cellulose nitrate filter papers. Conductivity and pH were measured using a CMD630 digital model conductivity meter and a Thermo Orion model pH meter, respectively. Alkalinity measurements were performed according to the Standart Methods [17]. The color concentration was measured using a HACH DR/2000 spectrophotometer in units of point color (Pt/Co). The COD was determined with a Thermoelectron Aquamate Model spectrophotometer.

Coagulation-flocculation experiments were conducted by running a series of jar tests using aluminum sulfate ($Al_2(SO_4)_3.18H_2O$) and ferric sulfate ($Fe_2(SO_4)_3.7H_2O$) as coagulants for wastewater samples 1 and 2, respectively. To improve the performance of the coagulants, limestone, magnesite, kaoline, pumice and cationic polyelectrolyte (sedipür) were used as flocculant aids. The experiments were performed at room temperature (20±2 ^oC) using 250 mL of the wastewater sample by adding 6 different coagulant doses that ranges from 0.5 to 8 g/L and from 0.18 to 1.248 g/L for samples 1 and 2, respectively. A period of fast agitation for 2 min at 120 rpm was followed by a period of slow agitation for 30 min at 30 rpm. The flocculant aid was added to the sample during the slow mixing step. After allowing settling to occur (60 min), the sample was prefiltered before subjecting to membrane filtration. The supernatant was collected for analysis.

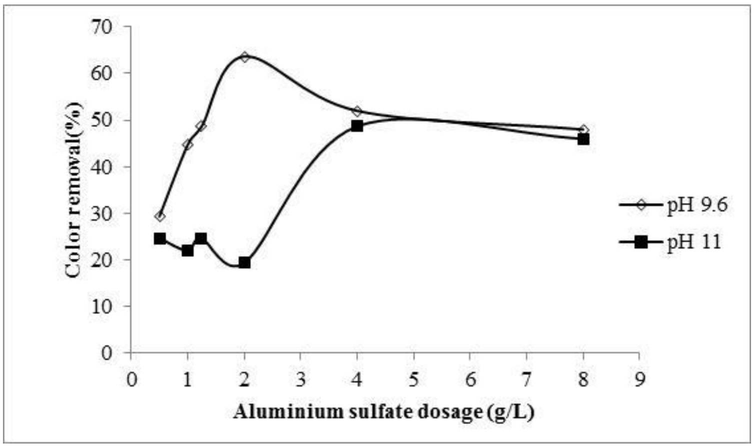
3. RESULTS AND DISCUSSION

3. 1. The effect of the initial pH and coagulant dosage

The color removal was highly dependent on the pH and coagulant dosage. Figs. 1a and 1b show the removal of color from sample 1 during coagulation with various aluminum sulfate doses using initially acidic and alkaline pH values, respectively. Figs. 2a and 2b show the removal of color from sample 2 during coagulation with various doses of ferric sulfate at initially acidic and alkaline pH values, respectively. To study the effects of pH on color removal, the initial pH of the wastewater was adjusted from 4 to 11 using nitric acid and sodium hydroxide.

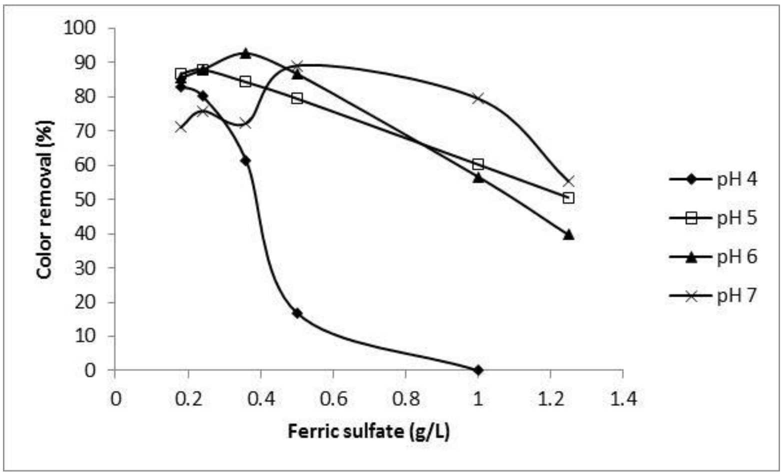


(a)

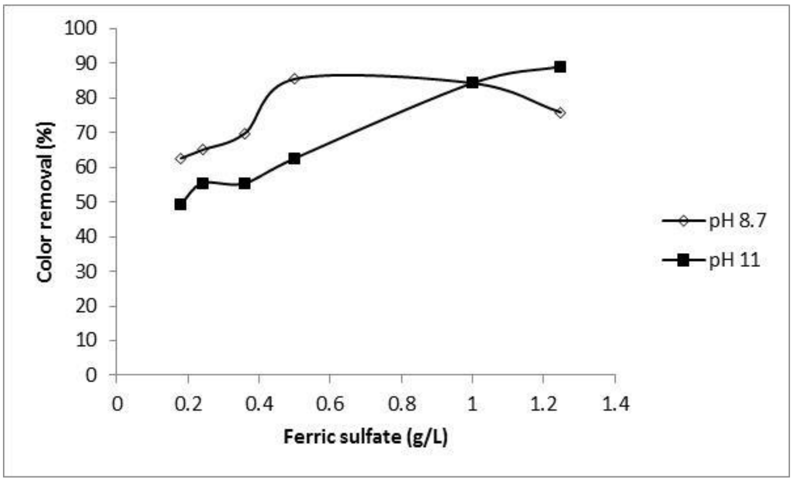


(b)

Figure 1. a) Removal of dye from sample 1 during coagulation with various doses of aluminum sulfate at an initial pH in the acidic region. b) initial pH in the basic region.



(a)



(b)

Figure 2. a) Removal of dye from sample 2 during coagulation with various doses of ferric sulfate at an initial pH in the acidic region. b) initial pH in the basic region.

At an aluminum sulfate concentration of 0.5 g/L, the color removal values for the initial pH values of 4, 5, 6, 7, 9.6 and 11 were approximately 41%, 41%, 81%, 38%, 29% and 25%, respectively. At a ferric sulfate concentration of 0.36 g/L, the color removal values for initial pH values of 4, 5, 6, 7, 8.7 and 11 were approximately 61%, 84%, 93%, 72%, 70% and 55%, respectively. The effective initial pH for aluminum sulfate and ferric sulfate was 6. Previous studies have reported that pH values of 5-6 are optimum for the coagulation of reactive dyes [5, 9, 18, 20].

Over the usual neutral pH (5-9) range of water, particles generally carry a negative surface charge. Due to their surface charge, aquatic particles are often stable as colloids and resistant to aggregation. Thus, coagulants are needed to destabilize the particles. Aluminum and iron salts provide cationic hydrolysis products that are strongly adsorbed on negative particles and can give effective destabilization [20]. However, the dye solution is more ionized at pH 6, thus enhanced the coagulation.

Variations in color removal can occur as a function of coagulant dosage at different initial pH values, as shown in Fig. 1 and Fig. 2. The obtained results, indicated that using 0.5 g/L aluminum sulfate and 0.36 g/L ferric sulfate at an initial pH of 6 would result in maximum color removal. Color removal efficiency tended to decrease when the dosage of coagulant was above 0,5 g/L aluminum sulfate and 0.36 g/L ferric sulfate in the coagulation of sample 1 and 2. This decrease could be probably due to re-stabilization phenomenon.

As shown in Fig. 3, the COD reduction efficiency in sample 1 was high (70%) when the initial pH was between 4 and 7 and decreased to 61% when the initial pH was between 9.6 and 11 and when the optimum aluminum sulfate dosage was used at all pH values. The production of precipitation during the coagulation is helpful to the reduction of COD. In Fig. 4, the COD reduction efficiency (47%) in sample 2 did not significantly change the coagulation at any of the initial pH values.

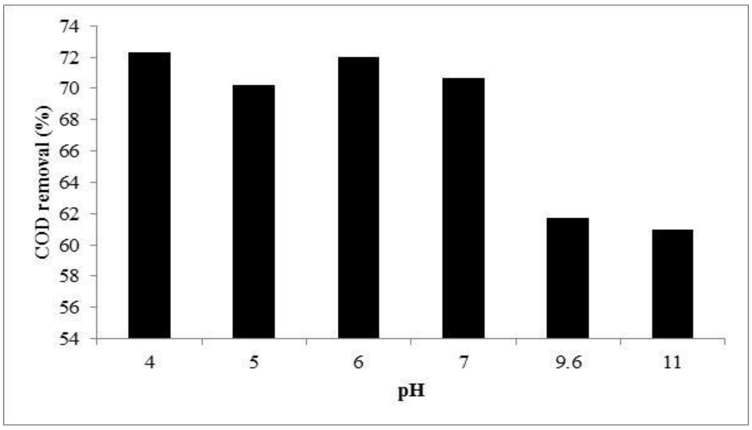


Figure 3. Effect of initial pH on COD reduction for sample 1.

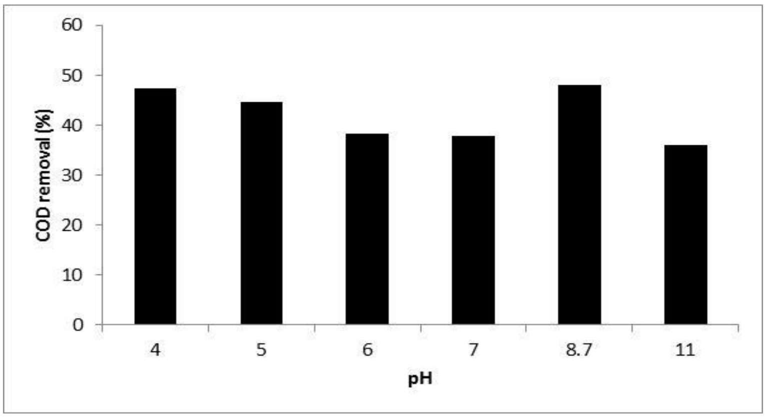


Figure 4. Effect of initial pH on COD reduction for sample 2.

3. 2. Effects of the flocculant aids

To improve the performance of the different coagulants, limestone, magnesite, kaoline and cationic polyelectrolyte (sedipür) were used as flocculant aids with aluminum sulfate.

The impacts of adding different doses of flocculant aids varied from 0.0025 to 2.5 g/L in combination with a constant aluminum sulfate dose (0.5 g/L) at an initial pH value of 6. The results presented in Fig. 5 indicate that the optimum doses of the flocculant aids were 0.02, 0.02, 0.08, and 0.015 g/L for limestone, magnesite, kaoline and sedipür, respectively. Color removal (Fig. 5) and COD reduction both aided the aluminum sulfate (Fig. 6) and reached 89, 81, 79, and 69% and 72, 81, 79, and 78%, respectively.

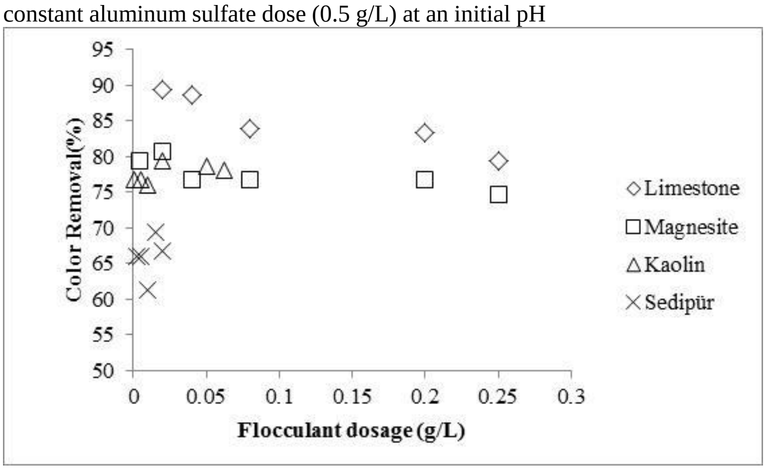


Figure 5. Removal of dye from sample 1 during coagulation with aluminum sulfate with various doses of flocculant aids.

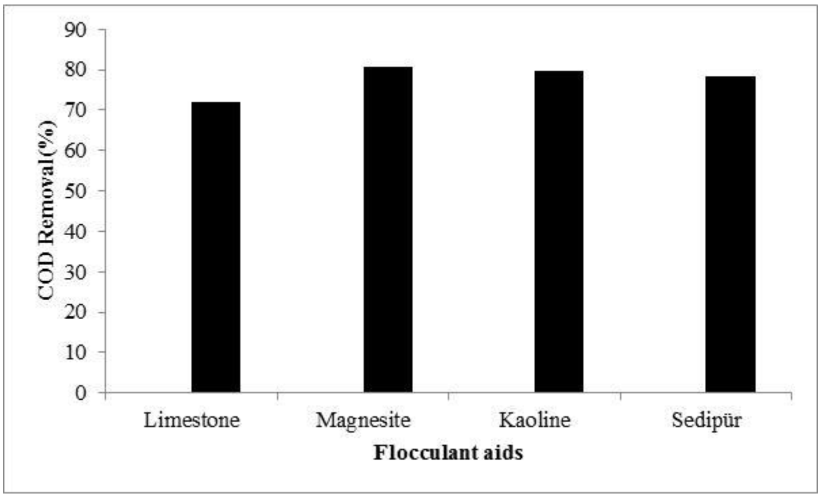


Figure 6. Effect of aluminum sulfate with various flocculant aids on COD reduction for sample 1.

The use of limestone, magnesite, pumice and sedipür as flocculant aids at different doses of 0.0025 to 0.25 g/L in combination with a constant dose of ferric sulfate (0.36 g/L) was investigated at initial pH of 6. The results of the color removal and COD reduction tests are presented in Figs. 7 and 8, respectively. The results presented in Fig. 7 indicated that the use of limestone, magnesite, pumice and sedipür doses of 0.2, 0.2, 0.25 and 0.04 g/L, respectively are very effective for color removal. The COD was reduced by 50% for all aids (Fig. 8).

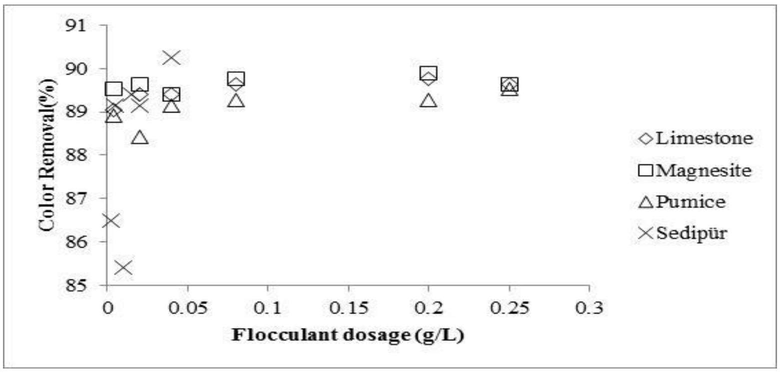


Figure 7. Removal of dye from sample 2 during coagulation with ferric sulfate with various doses of flocculant aids.

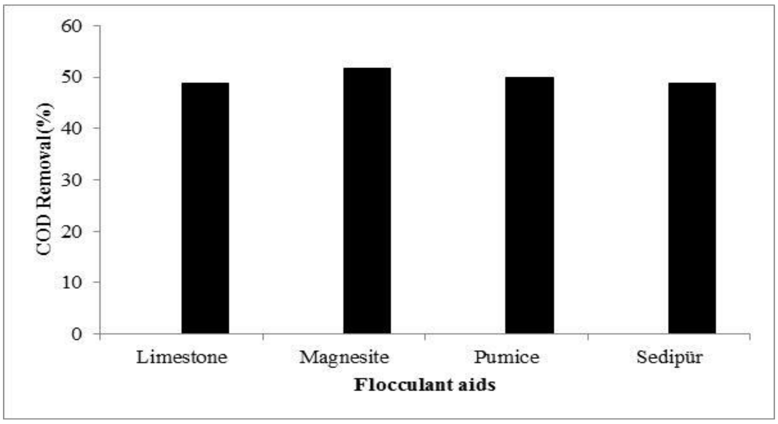
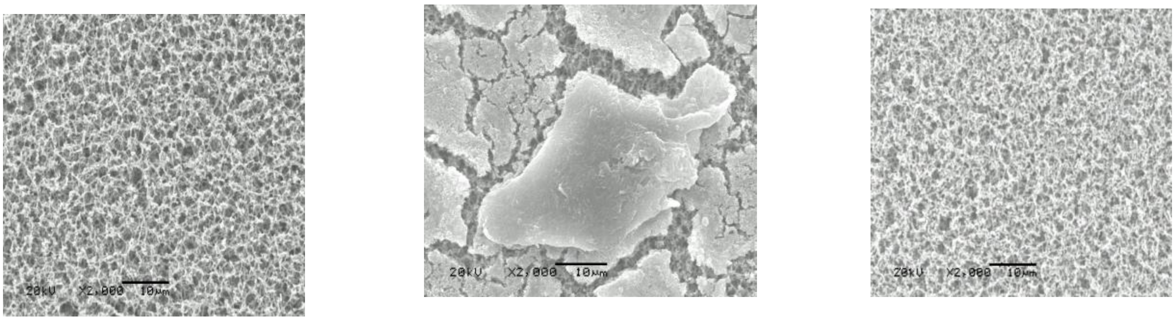


Figure 8. Effect of ferric sulfate with various flocculant aids on COD reduction for sample 2.

When used alone and with limestone, aluminum sulfate removed up to 80% and 89% of the color, respectively. Ca^{+2} helped to neutralize the negative charge on the particles, which led to an increase in the amounts of flocs. However when the limestone concentration was higher than 0,02 g/L, the color removal efficiency decreased. This decrease could be due to a change in the electrical charge on the particles surface from negative to positive in solution with a high limestone content [21]. The color removal efficiency of ferric sulfate alone and of ferric sulfate with limestone, magnesite, pumice or sedipür reached 90%. When the aluminum sulfate was used alone or with magnesite, kaoline or sedipür, up to 72%, 80%, 79.8%, and 78% of the COD was reduced, respectively. When ferric sulfate was used alone and with limestone, magnesite, pumice or sedipür up to 38%, 49%, 52%, 50%, and 49% of COD was reduced, respectively.

3. 3. Membrane cleaning procedure

Membrane fouling and scaling resulted in a loss of membrane performance due to the deposition of suspended or dissolved substances on the membrane surface and/or within the pores of the membrane. The cellulose nitrate membrane was covered by a dark brown layer after membrane filtration. Several cleaning agents were evaluated for the fouled membrane. The most effective cleaning agent for the fouled membranes was concentrated nitric acid. The SEM images of the cellulose nitrate membrane, that were taken before and after the cleaning procedure are shown in Fig. 9. These micrographs show that the structure of the cleaned membrane was similar to that of the new membrane.



(a) (b) (c)

Figure 9. SEM micrographs of the a) new membrane surface b) deposits scattered on the membrane surface c) cleaned membrane surface.

4. CONCLUSIONS

The sequential application of coagulation-flocculation and membrane filtration was superior to coagulation-flocculation process alone for reducing color and decreasing the COD. This combined treatment process offers many advantages for industrial use, such as high efficiency, lower chemical consumption, lower sludge production, and the possibility of water reuse. The addition of a natural flocculant aid helped increase the color and/or COD removal compared to using the coagulant alone. It is important to control the pH within a specific range depending on the types of wastewater and inorganic coagulants that are used. The membranes used for membrane filtration require regular periodic membrane cleaning to eliminate membrane fouling. Cellulose nitrate membranes can be cleaned easily by using concentrated nitric acid.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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