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Combined Coagulation-Microfiltration Process for Dye Wastewater Treatment

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Abstract: The performance of combined coagulation-microfiltration process for the removal of dyes in a binary mixture of dye wastewater of varied concentrations and fruit drink wastewater at three different strengths; low (10ppm), medium (50ppm) and high (100ppm) was investigated. Synthetic dye wastewater was prepared in the laboratory while fruit drink wastewater was purchased from the grocery store. Color removal efficiency was also investigated for the three coagulants; Ferric Chloride, Aluminum Sulfate and Ferrous Sulfate. Transmittance and Absorbance values were used as indices to measure the efficacy of the combined coagulation- microfiltration process. Transmittance and absorbance values of 99.8% and 0.001 respectively were achieved post treatment. Ferric Chloride and Aluminum Sulfate gave better results than Ferrous Sulfate, which gave the poorest results in terms of color removal efficiency. The results of this study revealed the viability of combined coagulation-microfiltration as an inexpensive and effective method of treating dye wastewater and showed the empirical relationship between coagulant dosage, dye strength and removal efficiency on the effluent quality of combined wastewater samples.

***Keywords*: Dye, coagulation, microfiltration, wastewater, transmittance, absorbance**

I. INTRODUCTION

Wastewater is liquid discharged by domestic residences, commercial properties, industry, agricultural processes that contain some contaminants that result from the mixing of wastewater from different sources[1]. Industries particularly textile, food, paper and pulp manufacturing are known to consume large volumes of water during their daily operations. They therefore contribute a pro-rata amount of wastewater as effluent that is characteristic of their raw material properties. The use of synthetic chemical dyes in various industrial processes, including paper and pulp manufacturing, plastics, dyeing of cloth, leather treatment and printing has increased considerably over the last few years, resulting in the release of dye-containing industrial effluents into the soil and aquatic ecosystems[2,3]. This has led to the pollution of the environment with dyes that are not easily degradable. In some cases, the dye solution can also undergo anaerobic degradation to form potentially carcinogenic compounds that can end up in the food chain[3]. Moreover, highly colored wastewaters can block the penetration of sunlight and oxygen, essential for the survival of various aquatic forms[3].

Dyes are colored substances that have an affinity to the substrate to which they are applied. They are generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber[4]. Dyes are unique chemical compounds that react with a substrate in different ways depending on their structure. While some react forming chemical bonds, others react physically and are as such easier to remove from their substrate. They can be classified based on the source from which they are made, their chemical structure, nuclear structure and based on their industrial use. Other important classes based on application have also been established. These include but are not limited to leather dyes, fuel dyes, smoke dyes, solvent dyes, sublimation dyes.

Dye wastewater can be defined as wastewater or effluents discharged by industries, particularly the textile industry which are contaminated with a dye or a mixture of dyes depending on the particular operation. Color is the most prominent characteristic of dye wastewater even at low concentrations and needs to be removed before wastewater can be discharged[5,6]. The removal of color from wastewaters is often more important than the removal of the soluble colorless organic substances, which usually contribute to the major fraction of the biochemical oxygen demand (BOD). Methods for the removal of BOD from most effluents are fairly well established; dyes, however, are more difficult to treat because their synthetic origin are mainly complex aromatic molecular structures, often synthesized to resist fading on exposure to sweat, soap, water, light or oxidizing agents[2,3].

In recent times, there have been stringent environmental laws regarding the treatment of effluents prior to discharge. This has necessitated the need for industries to embark on dye wastewater treatment in order to adhere strictly to the set regulations. Consequently, various methods such as coagulation, adsorption, photo-catalytic decolorization and oxidation, electrochemical method, ion exchange, membrane filtration and use of ozone have been employed to treat dye wastewater. Biological treatment processes are also used to treat dye wastewater. These processes however are generally efficient for biochemical oxygen demand (BOD) and suspended solids removal (TSS) but are largely ineffective for removing color from wastewater[7-9]. Generally, there are two decolorization methods; destruction of dye molecules and separation of dyes from water[10,11]. Conventional methods involved in the destruction or transformation of dyes such as chemical oxidation, photo-catalysis and biodegradation[11,12] have been found to be inadequate and require extensive energy to break down the dye molecules, most of which are stable to light, oxidizing agents and microbiological degradation[11,13,14,15]. Separation methods such as adsorption and membrane Adsorption of dyes on powder activated carbon is popular and effective[11]. However, the activated carbon is not cheap, and the adsorption performance is reduced sharply after regeneration or reactivation, which also results in a 10–15% loss of the sorbent[16-18]. Additionally, sorption methods are characterized by low purification efficiency, especially in terms of decolorization[19]. The use of ozone and hydrogen peroxide is very promising for environmental reasons but is very expensive when considering the quantity required to bring about the necessary wastewater treatment[19]. Consequently, the need to surmount the demerits of individual processes has necessitated the use of combined processes in order to enhance the overall treatment performance. Coagulation is widely used for dye removal due to its low capital cost and simple operation[11,18,20,21]. Additionally, to achieve water with re-usable quality, an additional treatment stage requiring the use of a membrane at the ultimate step is required[22].

Pressure-driven membranes techniques such as ultrafiltration (UF), microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO) have been found to be effective in the removal of dyes from wastewater. While reverse osmosis and nanofiltration have been used for efficient dye removal, the high energy requirement and operational costs associated have made them less attractive. Ultrafiltration, which has been successfully used for separating high molecular weight and insoluble dyes from water[11], however, is not able to remove those water-soluble dyes with low molecular weights[13,23]. Therefore, microfiltration is considered as a relatively cost-effective low-pressure membrane process especially as recent advances in membrane technology have led to the reduction in cost of membranes and studies indicate that low-pressure membrane process appears to be a cost effective option[22,24].

Against this background, a coagulation-microfiltration hybrid technology is used to treat and evaluate the extent of dye removal from textile wastewater singly and a binary mixture of textile wastewater and fruit drink wastewater.

II. Materials & Method

Acid Red 88 dye was used to prepare dye wastewater in the laboratory. The following coagulants were used to study the color removal using coagulation with the dye; Aluminum Sulfate, Anhydrous Ferric Chloride and Ferrous Sulfate. Equipment used were; weighing balance (Mettler Toledo), Spectrophotometer (Genesis 20), shaker, 115V 60CV AC and TOC analyzer (Shimadzu 5050).

Batch mode analysis was used wherein each sample of 50 ml each was prepared from diluting the dye stock solutions and coagulant stock solutions both in aqueous form, to ensure proper mixing and no loss of particles of the elements. Fruit drink wastewater was prepared similarly and combined in equal ratio (1:1) with synthetic dye wastewater. After getting the desired concentrations from the stock solution and preparation of the samples, the samples were mixed vigorously for 1 minute at 100rev/min (fast shake) followed by 30 minutes of slow shaking at 30rev/min and then allowed to settle overnight. The supernatant then obtained from these samples were analyzed and transmittance and absorbance readings were taken.

Acid Red 88

Acid red is an azo dye, which has a characteristic red color that tends to appear black in relatively high concentration solutions. Azo dyes are dyes that have the functional group R−N=N−R′, in which R and R′ are usually aryl. They are a commercially important family of azo compounds. Azo dyes are used to treat textiles, leather articles, and some food substances.

Azo dyes are solids. Most are salts, the colored component being the anion usually, although some cationic azo dyes are known. Most proteins are cationic, thus dying of leather and wool corresponds to an ion exchange reaction. The anionic dye adheres to these articles through electrostatic forces. Cationic azo dyes typically contain quaternary ammonium centers. Chemically related to azo dyes are azo pigments, which are insoluble in water and other solvents[25,26]. Acid Red 88 had been described by[27] as a mono-azo textile dye, widely used in the textile and food industry. It has a chemical formula of $C_{20}H_{13}N_2NaO_4S$ and a molar mass of 400.38 $gmol^{-1}$.

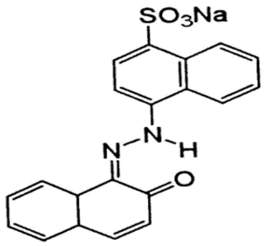

Figure 1 The Chemical Structure of Acid Red 88[28]

Fruit Drink

Fruit drinks are generally concentrated natural fruit pulps which are then flavored and are therefore reconstituted with water to make a drink. They originate from natural fruit but are usually dehydrated to reduce their moisture content to less than 3%. The main aim of dehydration is to extend the storage life of the fruit content. Fruit juice concentrates are usually prepared from fruit juices by evaporating water therefrom at atmospheric pressure or under vacuum. In addition, various fruit juice concentrates have been prepared by freezing and removing the water as ice from the concentrated juice[29]. An empirical relationship exists between the absorbance and concentration of a solution through the Beer-Lambert's law[30].

III. Result And Discussion

The observations and results have been compared and tabulated to depict the behavior and performance of three coagulants with coagulant dosages (0,20,40,60,80,100 ppm) on dye concentrations (50,100,150 and 200 ppm) in the presence of fruit drink concentrations of (10,50,100 ppm). The dye concentrations were compared singly, then in the presence of the fruit drink solutions. Binary mixtures were subsequently described as combined wastewater low strength, combined wastewater medium strength and combined wastewater high strength.

Effect of Dye Concentration

A general trend was observed whereby an increase in dye concentration lead to a pro-rata decrease in transmittance values and increase in absorbance values indicating a reduction in the efficacy of the coagulation – microfiltration hybrid treatment process and consequently, reduction in color removal efficiency. The best transmittance and absorbance values were seen at low dye concentration (usually 50 - 100 ppm) while reduced values were observed to be from dye at high concentration (150 – 200ppm) as shown in Table 1 below;

TABLE 1
Dye Concentration Values for Acid Red 88 at 100mg/L Coagulant Treatment

	$FeCl_3$		$Al_2(SO4)_3$		$FeSO_4$	
Dye Conc. (mg/L)	Absorbance	Transmittance (%)	Absorbance	Transmittance (%)	Absorbance	Transmittance (%)
0	0	100	0	100	0	100
50	0.023	94.8	0.001	99.8	0.099	79.7
100	0.031	93.3	0.001	99.8	0.118	76.2
150	0.036	92.2	0.019	95.7	0.195	63.9
200	0.039	91.3	0.053	88.5	0.595	25.4

TABLE 2
Effect of Coagulant Dose on 50 mg/L SDW

	$FeCl_3$		$Al_2(SO4)_3$		$FeSO_4$	
Coagulant Dose (mg/L)	Absorbance	Transmittance (%)	Absorbance	Transmittance (%)	Absorbance	Transmittance (%)
0	1.041	9.1	1.041	9.1	1.041	9.1
20	0.38	41.8	0.133	73.5	0.623	23.8
40	0.129	74.4	0.017	96.2	0.589	25.8
60	0.11	77.7	0.004	99.1	0.218	60.6
80	0.031	93.1	0.002	99.6	0.123	75.4
100	0.023	94.8	0.001	99.8	0.099	79.7

Transmittance value of 94.8%, 99.8% and 79.7% were observed for $FeCl_3$, $Al_2(SO4)_3$ and $FeSO_4$ respectively at dye concentrations of 50 mg/L. As dye concentration increased to 200 mg/L however, transmittance values reduced to 91.3%, 88.5% and 25.4% accordingly, indicating a reduction in color removal efficiency. Similar trends have been reported by [31-33]. The trend observed is because at low dye concentrations, the coagulant is easily able to spread through the solution and bring about effective charge neutralization and subsequent settling as opposed to the ease of operation with concentrated solutions.

Effect of Coagulant Dosage on Wastewater

Five different coagulant dosages were used (0, 20,40,60,80,100 ppm). It was observed that with increased coagulant dosage came an increase of charge neutralization and settling and a disappearance of color, evident by the increasing transmittance values and reducing absorbance values. Table 2 below shows the effect of coagulant dose on 50mg/L single dye wastewater (SDW). Evidently, at coagulant dose of 40 mg/L, transmittance values reported for all 3 coagulants were 74.4%, 96.2% and 25.8% for $FeCl_3$,

$Al_2(SO4)_3$ and $FeSO_4$ respectively. Absorbance values were 0.129, 0.017 and 0.589. These values are consistent with Beer-Lambert Law[30]. As coagulant dose increased to 100 mg/L however, higher transmittance values; 94.8%, 99.8% and 79.7% were obtained (with their corresponding absorbance values depicted below). The higher transmittance values indicated an increased color removal efficiency. Earlier study reported that at 40 mg/L coagulant treatment, $Al_2(SO4)_3$ gave good results above 90%[33] . This is in agreement with the results shown below;

Effect of Dye Strength on Combined Wastewater

The best values for absorbance and transmittance of 0.002 and 99.6% were observed respectively for low concentration dye – low strength fruit indicating that the coagulants were able to effect charge neutralization and subsequent settling relatively easily owing to the combined low dye strength. The dilution effect, (causing increased surface area) of the low strength fruit drink wastewater also contributed to the increased transmittance and reduced absorbance values accordingly. During the microfiltration stage, it was much easier to hold back the suspended solids and organics owing to the relatively low dye –fruit drink concentration[32].

Medium concentration dye – medium strength fruit drink gave comparatively lower transmittance and corresponding higher absorbance values than its low concentration-low strength fruit drink counterpart. Transmittance and absorbance values were seen to be 99.1% and 0.004 respectively. The least values of 95.9% and 0.019 were observed for high dye concentration-high strength fruit drink as summarized in Table 3.

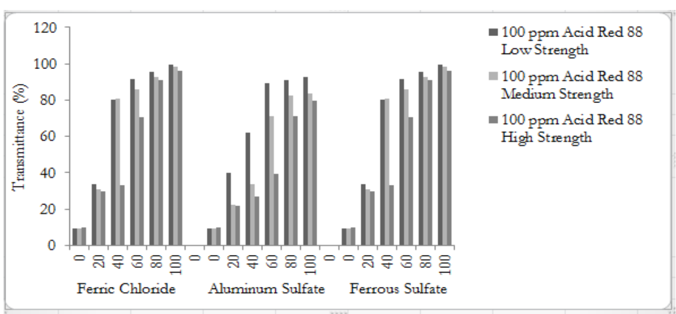

Figure 2 Relationship between different Strength of Combined Wastewater

Effect of Type and Valence of Coagulant

Just as dyes react to coagulants differently, coagulants also differ in their degrading and decolorization action on different dyes. From the results, it was observed that Ferric Chloride and Aluminum Sulfate gave better results than Ferrous Sulfate. Aluminum Sulfate gave the highest transmittance value of 99.8%. This is in agreement with results reported by[32]. Even with dye concentration of 100 mg/L, Aluminum Sulfate gave the same quality of treatment as with 50 mg/L (as shown in Table 3), lending credence to its potency. Ferric Chloride gave the next highest value of 94.8%. Ferrous Sulfate gave the least value of 79.7% as clearly depicted by Figure 3 below. This can be attributed to the reduced potency of +2 valence, exhibited by Ferrous Sulfate as compared to +3 exhibited by Ferric Chloride and Aluminum Sulfate.

The general trend observed by the effect of coagulant dosage was such that as the coagulant dosage increased, the percentage transmittance increased, indicating the efficiency of color removal.

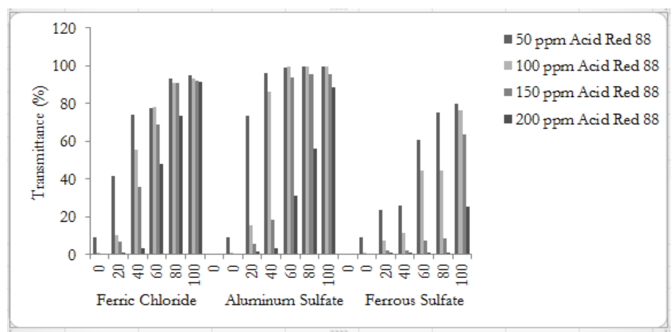

Figure 3 Acid Red 88 Single Dye at Different Coagulant Doses

TABLE 3
Highest Values of Absorbance and Transmittance for Single and Combined Wastewater

Coagulant Dose (mg/L)	Dye Concentration (mg/L)	Fruit Nectar Concentration (mg/L)	Absorbance	Transmittance (%)	Dye Strength	Coagulant
100	100	10	0.002	99.6	Low	$FeCl_3$ & $FeSO_4$
100	200	50	0.004	99.1	Medium	$FeCl_3$
100	50	100	0.019	95.9	High	$FeSO_4$
100	100	100	0.019	95.9	High	$FeCl_3$
100	50	0	0.001	99.8	Single Dye	$Al_2(SO4)_3$
100	100	0	0.001	99.8	Single Dye	$Al_2(SO4)_3$

IV. CONCLUSION

It can be concluded from the results revealed in this study that the combination of coagulation and microfiltration acts as a proper tertiary treatment process for suspended particles, organics and color removal. The treated dye wastewater (Acid Red 88) showed excellent transmittance and absorbance values and can be reused for processing or production in the textile industry. If dye wastewater is to be further treated with sophisticated technology like reverse osmosis (RO), the combined coagulation-microfiltration process can be used as a preliminary treatment to reduce energy and operational implications associated with such technology. This opportunity cost is a wise trade-off for business expansion, while maximizing the objective function of the firm, without necessarily contributing detrimental effects to the environment.

Therefore, the following conclusion can be drawn;

- As the coagulant dosage increases, the % transmittance increases, indicating higher color removal efficiency. This was generally observed for all dye concentration (50 mg/L, 100 mg/L, 150 mg/L and 200 mg/L) for both single dye wastewater and combined wastewater.
- Increase in dye concentration causes a decrease in color removal efficiency. As clearly revealed, all 50 mg/L dye wastewater samples gave higher transmittance values than their 150mg/L or 200mg/L counterpart at the same coagulant dosage.
- Coagulants with a higher valence tend to be more potent than those possessing lower valence. Ferric Chloride [$FeCl_3$] and Aluminum Sulfate [$Al_2(SO_4)_3$] showed better performance than Ferrous Sulfate [$FeSO_4$], indicating the potency of +3 valence over +2.
- In a binary mixture of dye wastewater, depending on the concentration of the species, a dilution effect occurs such that coagulants tend to perform better than if it was a single dye solution. Ferric Chloride and Ferrous Sulfate performed better in the presence of combined wastewater than they did in single wastewater.

V. ACKNOWLEDGEMENT

Authors

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