## Coagulation-Adsorption Hybrid Process for the Treatment of Dyes and Pigments Wastewater

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## ABSTRACT

The study aimed to improve the effectiveness of dyes and pigments wastewater treatment. Hybrid system of adsorption and coagulation was applied for the reduction of COD, color, turbidity and TSS. Activated carbon adsorbent was prepared from a waste of sugar industry boiler. It was processed through physicochemical treatment with sulfuric acid following grinding, sieving, washing and drying unit operations. Combined wastewater of dyes and pigments manufacturing plant was treated with a hybrid process of coagulation and adsorption.  $FeCl_3$ ,  $FeSO_4$  and Alum coagulants were tested individually and found them less effective. It was revealed that  $FeCl_3$  coagulation, adsorption and hybrid process reduced COD (41, 51 and 54%), Color (67, 70 and 89%), turbidity (69, 71 and 90%) and TSS (82, 93 and 97%) respectively. Combination of  $FeCl_3$ -SBFA (Sugarcane Bagasse Fly Ash) proved 90% efficient in removal than coagulation as an individual process. 4g adsorbent dose was optimized for this hybrid process.

Key Words: Dyes Wastewater, Adsorption, Coagulation, Sugarcane Bagasse Fly Ash, Coagulants.

#### 1. INTRODUCTION

yes and pigments wastewater is one of the problematic groups. They are released in river water from various industries, especially in the production of dyes and textile finishing [1]. Apart from dyes wastewater contains high range of color, BOD, COD, turbidity, pH, temperature, alkaline substances, acids, heavy metals and toxic substances [2]. Dyes wastewater exhibit wide range of pH from 2-14, COD from 50mg/L to approximately 18000 mg/L, TDS from 50-6000mg/L and very strong color. The characteristic of wastewater varies according to each dye product manufacturing [3]. Discharge of dyes effluents in rivers causes environmental

pollution and produces allergic diseases [4]. Standard commercial activated carbon is used as an adsorbent for the removal of color and organic pollutants, but is expensive in use and regeneration. Many researchers have focused on developing low cost adsorbent materials from chitin [5], chitosan [6], perlite [7], natural clay [8-9], bagasse pith [10], coal fly ash [11], boiler bottom ash [12] and rice husks [13].

Pakistan is the fifth largest sugarcane producer in the world with production of 47,800 million tons. It produces 13,384 million tons of sugarcane bagasse and about 0.5 million

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tons of sugarcane bagasse fly ash in 2009 [14]. 2000 MW power can be generated by using sugarcane bagasse as a fuel [15]. Sugarcane bagasse fly ash is used as filler in building materials, concrete and cement manufacturing [16]. Several investigators have studied about adsorption for removing phenolic compounds [17-18], heavy metals [19-20] and dyes [21]. In this study attempts have been made to develop low cost adsorbent using sugarcane bagasse fly ash [22] for the treatment of complex nature dyes wastewater for the removal of color, COD [23], turbidity and suspended solids. Treatment efficiency for wastewater was enhanced through coupling of chemical coagulation-adsorption process using various coagulants and SBFA.

#### 2. MATERIALS AND METHOD

## 2.1 Collection of Dyes and Pigments Wastewater

Dyes and pigments wastewater was multiple mixtures of dyes, binder emulsion, textile chemicals and pigments processing plant products and washing water. This effluent was collected from waste water pit of Clariant Pakistan Limited, Jamshoro for analysis and the treatment study. The effluent quality parameters such as pH, TDS, Color, COD, turbidity and TSS were analyzed according to the standard laboratory protocols.

## 2.2 Analysis of Dyes and Pigments Wastewater

The pH and TDS of effluent samples were measured through pH (Hach, USA) and conductivity meter ((Hach, USA). Effluent Color was determined by using platinum cobalt standard method 8025 at specific wavelengths and program with help of Spectrophotometer (DR-2000, Hach, USA). COD of effluent was determined by dichromate COD method by using COD vial (Potassium dichromate mercury (II) sulfate and sulfuric acid, Merck Company, Germany). It was heated in Spectroquant, COD heater (TR-320, Merck, USA) at 148°C for 2 hours, then COD reading was measured through Spectrophotometer (DR-2000, Hach, USA). Turbidity and TSS of effluent samples were determined through absorptometric method by using Spectrophotometer (DR 2000, Hach, USA).

# 2.3 Collection and Elemental Analysis of SBFA

Samples of SBFA were collected from Habib Sugar Mills Limited, Nawabshah, Pakistan for dyes effluent treatment. The elemental composition of SBFA was analyzed at Fuel Research Laboratory, PCSIR, Karachi. Elemental composition of SBFA was determined as SiO<sub>2</sub> (87.87%), Al<sub>2</sub>O<sub>3</sub> (2.47%), CaO (2.86%), Fe<sub>2</sub>O<sub>3</sub> (4.05%), MgO (1.10%), Na<sub>2</sub>O (0.17%), K<sub>2</sub>O (0.44%), SO<sub>3</sub> (0.16%), Density (1.01g/ cm<sup>3</sup>) and Loss of ignition (13.45%).

#### 2.4 Preparation of Adsorbent from SBFA

SBFA adsorbent was prepared through screening, pretreatment, washing and drying steps. Fly ash was grinded and sieved into fine porous size (200 mesh) through RO-Tap Type Sieve shaker (Model- A-871205, Heiko Seisakusho Tokyo Japan) at 290 rpm speed. This fine porous fly ash was treated through washing with warm distilled water (60°C) and 10%  $H_2SO_4$  solution five times. Pre-treated ash sample was dried in a laboratory oven (L-201C, Grieve Corporation, USA) at 110°C temperatures for 12 hours for activation of ash adsorbent, and then cooled at room temperature [24].

## 2.5 Determination of Structure Morphology of SBFA

The structure morphology of SBFA was determined through SEM (Scanning Electron Microscope), (Model JSM-6380, JEOL Ltd, Tokyo, Japan) [25] at Advance Research Laboratory, Mehran University of Engineering & Technology, Jamshoro, Pakistan (Fig. 1).

#### 2.6 Treatment of Wastewater through Adsorption Process by the use of SBFA

Raw effluent samples were treated through adsorption process by use of SBFA adsorbent at different doses in Jar test system by maintaining process parameters as agitation time 30 minutes, 27°C temperature, agitation speed 250 rpm and settling time 1 hour. After adsorption process, treated samples were filtered by use of filter paper 42 (125mm, Whatman Manufacturing Company, UK) through vacuum filtration system. These treated effluent samples were analyzed according to the standard laboratory protocols.

## 2.7 Treatment of Effluents Through Chemical Coagulation-Adsorption Process

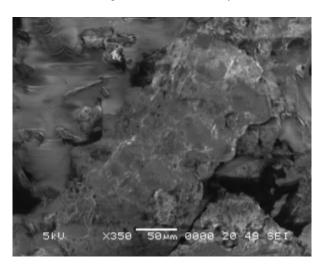
Commercial coagulants such as Ferric Chloride, Ferrous Sulfate, Alum and lime were purchased from Al-Mehran Chemicals Limited, Karachi and applied for effluents treatment. Effluent samples were treated through coagulation process by using FeCl<sub>3</sub>-lime, FeSO<sub>4</sub>-lime and Alum-lime coagulants (1.2-0.80g/l) in Jar test system by maintaining process parameters as agitation speed 250 rpm, agitation time 1 hour, temperature 27°C and settling time 1 hour. After settling of flakes, coagulated samples were filtered through vacuum filtration system and were

analyzed. Again coagulated effluent samples were treated through adsorption process by use of SBFA at different doses. This treatment was conducted in Jar test system by maintaining parameters such as agitation time 30 minutes, 27°C temperature, agitation speed 250 rpm and settling time 1 hour. After adsorption process, treated samples were filtered through vacuum filtration system. The treatment efficiency of single and coupled processes was compared from effluent analysis.

#### 3. **RESULTS AND DISCUSSION**

## 3.1 Treatment of Dyes and Pigments Wastewater through Adsorption Process

Fly ash has porosity (0.36%), pore volume (0.1067 cm<sup>3</sup>/g), surface area (168.39 m<sup>2</sup>/g) [24]. In single adsorption process good treatment performance was observed at 4g adsorbent dose of SBFA. It showed good performance in the reduction of COD (51%), color (70%), turbidity (71%) and TSS (93%). In Adsorption process, rates of TDS and EC (Electrical Conductivity) increased by 40% and 38%. pH of effluent declined on increasing SBFA dose. SBFA has high porosity and adsorption capacity for adsorption of wastewater pollutants. The components of SBFA are mostly in acidic nature and result in reduction of pH. The adsorption capacity for wastewater increases at maximum time contact. SBFA always increase the concentration of



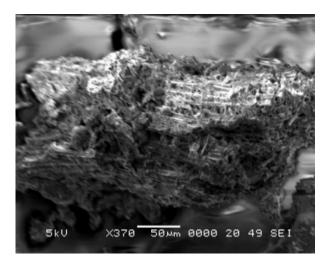


FIG. 1. SEM PHOTOS OF RAW AND PREPARED ADSORBENT OF SBFA

TDS and EC in increasing dose for wastewater treatment. On increasing dose, good removal efficiency could not be observed (Fig. 2). Rao, et. al. reduced color of low contaminated textile dyeing wastewater up to (96%) at 12g fly ash adsorbent dose [25]. In this treatment, maximum color removal rate was achieved at low adsorbent dose for dyes and pigment wastewater.

#### 3.2 **Treatment of Dyes and Pigments** Wastewater through Chemical **Coagulation-Adsorption Process**

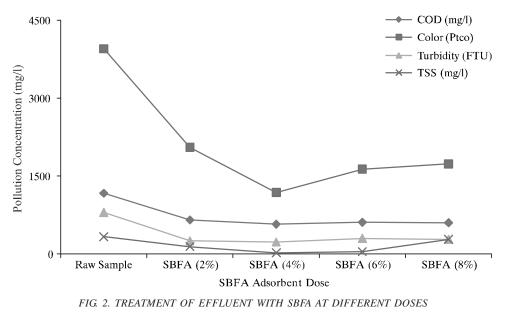
#### 3.2.1 Treatment of Wastewater with FeCl<sub>3</sub>-Lime and SBFA

In simple coagulation process though FeCl<sub>2</sub>-lime showed good results for reduction of COD (41%), color (67%), turbidity (69%) and TSS (83%). The rates of TDS, salinity and EC were increased by 38, 42 and 37%. pH of effluent also declined. Further treated through adsorption process with SBFA. At 4g SBFA adsorbent dose, it showed good performance in the reduction of COD (54%), color (89%), turbidity (90%) and TSS (98%). The TDS, salinity and EC rates were increased by 70, 75 and 66%. pH of effluent declined in both process up to 32%. Maximum doses did not give more effective results than 4% dose (Fig. 3). Ferric

Chloride coagulant is effective for treatment, but it creates the problems of severe corrosion in piping system due to increase concentration of iron in wastewater. Chloride coagulants are most effective than inorganic sulfate coagulants due to their treatment behavior. Wastewater treatment efficiency was enhanced due to high adsorption capacity and porosity of SBFA. Joo, et. al. reduced the concentration of turbidity (80.5%) and COD (86%) of textile wastewater at FeCl,-PAC dose (40-1-20mg/l) respectively [26]. Dyes and pigments wastewater is complex and highly contaminated. The treatment efficiency varies due to high concentration of orgainc pollutants and dyes present in wastewater.

#### 3.2.2 Treatment of Wastewater with FeSO<sub>4</sub>-Lime and SBFA

FeSO<sub>4</sub> coagulation process showed ineffective performance for dyes effluent treatment. It reduced the concentration of COD (16%), color (5%), turbidity (10%) and TSS (22%). TDS, salinity and EC rates were increased by 9, 13 and 9%. The sulfate coagulants are effective in low contaminated wastewater. Their treatment efficiency improves on increasing coagulant dose, contact time and agitation speed. When treated



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with SBFA at different doses, effective treatment was observed at all doses. Good removal efficiency was recorded at 6% dose. Coupled process enhanced treatment efficiency and reduced the concentration of COD (54%), color (83%), turbidity (84%) and TSS (96%). The overall rates of TDS, salinity and EC in coupled processes were increased by 40, 58 and 51%. pH of effluent declined in both processes up to 30% (Fig. 4). The porosity and adsorption capacity was improved by physic-chemical treatment. All organic pollutants and coloring agents were captured in pore structure of SBFA. The pH of wastewater decreased due to SBFA elements acidic nature in effluent. The TDS and EC rates were increased due to high dose of SBFA.

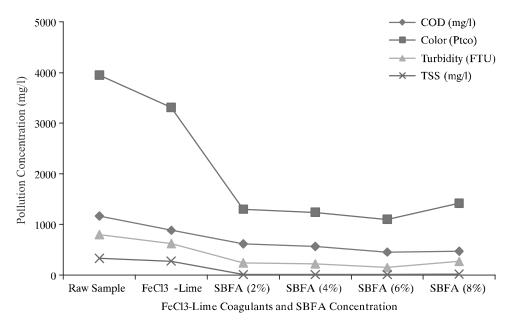


FIG. 3. TREATMENT OF EFFLUENT WITH FeCl<sub>3</sub>-LIME AND SBFA

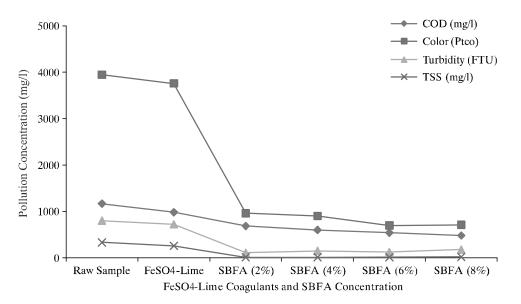


FIG. 4. TREATMENT OF WASTEWATER WITH FeSO -LIME AND SBFA

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#### 3.2.3 Treatment of Wastewater with Alum-Lime and SBFA

Complex dyes wastewater was treated through simple coagulation process by use of Alum-lime, it gave removal rates as COD (22%), color (16%), turbidity (23%) and TSS (16%). TDS, salinity and EC rates were increased by 4, 4 and 4%. Further coagulated samples were treated through adsorption process by using SBFA. Good removal efficiency was recorded at 6g adsorbent dose. It gave overall removal efficiency of coupled processes as COD (61%), color (72%), turbidity (81%) and TSS (97%). TDS, salinity and EC rates in both process increased by 49, 54, and 47%. pH of effluent declined up to 23%. Increasing dose of adsorbent did not give effective results than 6g dose. Generally it was found that absorbent doses gave average uniform results for treatment (Fig. 5). Ahmad et al. reduced 65% of TSS at 8g/l dose of alum for oily effluent [27]. Guida et al. reduced COD up to 80% on addition of alum coagulant in municipal effluent [28]. Treatment efficiency varies according to the wastewater contamination and nature. Alum coagulant slightly reduces pH of wastewater. Increasing dose of alum coagulant and contact time, maximum treatment efficiency can be achieved. Adsorption process removed all organic contaminants of wastewater effectively and improved treatment.

#### 4. CONCLUSIONS

SBFA is an effective and inexpensive adsorbent for the removal of color, COD, turbidity and TSS due to its high porosity and adsorption capacity. Simple adsorption or coagulation process is not the most effective for the treatment of dyes and pigments wastewater. Combined coagulation-adsorption processes are the most effective for dyes and pigments wastewater treatment by use of SBFA adsorbent at effective cost. Coagulation through FeCl<sub>2</sub>- lime gave the effective treatment for wastewater. Further this treatment efficiency was enhanced on the utilization of SBFA. These coupled processes gave overall removal rates as 89, 54, 90 and 98% for color, COD, turbidity and TSS respectively. FeSO, -lime and alum-lime resulted as ineffective treatment for wastewater in simple coagulation process. Dyes and pigments wastewater treatment efficiency was further enhanced on the combined use of SBFA and ferrous sulfate and reduced the color COD, turbidity and TSS by 83, 54, 84 and 96% respectively. Combined use of alum and SBFA resulted as removal of color, 72%, COD, 61%, turbidity, 81% and TSS, 97%. Environmental pollution problems can be solved by utilization of SBFA in dyes and textile industries wastewater.

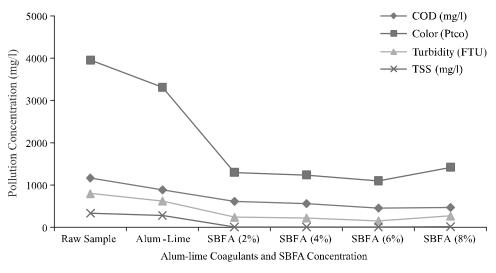


FIG. 5. TREATMENT OF WASTEWATER WITH ALUM-LIME AND SBFA

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For future trust, SBFA adsorbent bed can be developed economically at commercial scale and can be combined with coagulation process for effective treatment of complex nature wastewater of dyes and pigments.

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