Pol. J. Environ. Stud. Vol. 29, No. 6 (2020), 4131-4137
DOI: *10.15244/pjoes/120770* ONLINE PUBLICATION DATE: 2020-07-13

Original Research

A Comparative Treatability Study for Textile Wastewater: Agricultural Waste Adsorbent Versus Activated Carbon

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Received: 6 February 2020
Accepted: 18 April 2020

Abstract

This study aimed to remove color from textile wastewater taken from a common effluent channel in Bursa, western Turkey. For this purpose, chemical coagulation with various coagulants including $Al_2(SO_4)_3{\cdot}18H_2O$, $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}7H_2O$ was applied, followed by adsorption processes. In the coagulation experiments, the maximum color removal efficiency (48%) was obtained at pH 6.5 with a 300 mg/L dose of $Al_2(SO_4)_3{\cdot}18H_2O$. The adsorption experiments were conducted using 5 g each of agricultural waste adsorbent (corncob) particles with dimensions of 0.25 mm, 0.50 mm, 0.85 mm and 1.25 mm on the chemically treated wastewater samples, and color removal efficiencies of up to 100% were obtained. In addition, adsorption columns were designed according to the experimental data. As a result of the design calculations, 84 tons of the corncob are required to effectively remove color from 10,000 m^3 of textile wastewater. In addition to the color removal efficiencies of the applied processes, the associated operating costs were also calculated.

Keywords: activated carbon, adsorption, agricultural waste adsorbent, textile wastewater

Introduction

The textile sector uses high amount of water, and various chemicals, such as inorganic compounds, elements, polymers and organic products are used in this sector [1, 2].

The textile wastewater is characterized by high pH and alkalinity, and contains highly organic matter and dyes [3]. Color in textile wastewater is an important parameter that must be removed due to the resulting reduction in light penetration, which precludes photosynthesis and is aesthetically undesirable in receiving media [4].

Although the dyes that are the source of the color are at low concentrations in the wastewater, they form undesired visual pollution [5]. There are more than 100000 commercial dyestuffs, and over 7.10^5 tons of dyes are produced each year [6].

Removing the color of dyes from wastewater is difficult because of their chemical structure and synthetic origin. The methods most commonly used for color removal from textile wastewater are the coagulation/flocculation process [7, 8], coagulation, Fenton and adsorption processes [9], coagulation-

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flocculation and advanced oxidation processes [10], biological and chemical treatments [11, 12], aerobic biological treatment [13], anaerobic biological treatment [14], microfiltration [15], electrocoagulation [16, 17], solar photocatalysis [18], ozonation, adsorption and biological treatment [19], reverse osmosis and nanofiltration [20, 21], adsorption and ultrafiltration [22], electrocoagulation/nanofiltration [23], and advanced oxidation processes [24, 25].

In the literature, color removal from textile wastewater by different treatment methods was investigated and higher removal efficiencies were obtained. Ilhan et al. [26] studied the Fenton process on acrylic yarn dye-house wastewater and achieved 82.8% COD, 96.2% color, 75.6% TOC removal. Yadav et al. [9] applied coagulation, Fenton oxidation and adsorption on textile wastewater and 100% color and over 83% COD removal efficiencies were obtained at optimum conditions. The UASB reactor was evaluated for color and COD removal from real textile wastewater, and 30% color and 96% COD removal efficiency due to biodegradation was achieved by Amaral et al. [27], while Buthelezi et al. [28] obtained 97% color removal efficiency from textile wastewater by indigenous bacteria. Dhaouefi et al. [29] obtained 78% of TOC, 47% of nitrogen and 26% of phosphorus removal from synthetic textile wastewater using anaerobic/aerobic treatment process.

Color removal by coagulation and adsorption methods was studied by different researchers in the literature. Coagulation with $FeSO_4$ followed by adsorption processes was applied and 99% of the color was removed [9]. Sadaf et al. [30] investigated dye removal by adsorption using bagasse, an agricultural waste. The results showed that a maximum dye removal was obtained, and Langmuir isotherm is appropriate. According to the results, the bagasse is an efficient biosorbent for the removal of Indosol Turquoise FBL. In another study conducted by Baseri et al. [31], basic dyes from synthetic textile effluent were removed by activated carbon prepared from wood, and color removal efficiencies up to 98% were obtained.

Color removal by adsorption is one of the most effective of the physico-chemical treatment methods. The activated carbon is an adsorbent commonly used for color removal; however, its cost is quite high. Therefore, cheaper and newer adsorbents are required for use in the adsorption process [32]. Different adsorbents, such as tree crumbs, volatile ash-cool mixtures, silica gels, natural clays, and corncobs could be used for color removal from wastewater. The cheap prices and ease of supply of these adsorbents make them favourable [33].

The aim of this study is to investigate color removal from textile industry by coagulation and adsorption methods. For this purpose, corncobs of different sizes were used as an agricultural waste adsorbent. In addition, the operating costs of coagulation and asdsorption processes were calculated.

Materials and Methods

Wastewater Samples

The samples were obtained from the common effluent of a textile dyeing factory in Bursa (western Turkey) and analyzed according to Standard Methods [34]. The color was measured using a UV-vis spectrophotometer (Hach Lange, DR5000) according to Method 2120 C defined in Standard Methods [34]. The wastewater samples were composite samples taken during a 24 hour period at three different times. The flow rate of the wastewater originating from the textile factory was determined to be 1200 m^3/day. The characterization of the wastewater is shown in Table 1.

Chemical Coagulation Experiments

Chemical coagulation were performed using a Jar test (Velp Scientifica FC6S model, Italy) at room temperature (20±1ºC) with the reagents $Al_2(SO_4)_3 \cdot 18H_2O$, $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ (Merck, Germany) used at variable dosages between 250 and 600 mg/L and optimum pH values determined at constant coagulant dosages (250 mg/L) (pH = 6.5 for $Al_2(SO_4)_3 \cdot 18H_2O$, pH = 8.0 for $FeCl_3 \cdot 6H_2O$ and pH = 8.0 for $FeSO_4 \cdot 7H_2O$). For each chemical, the optimum reagent dosages were determined. The pH was adjusted with the addition of 1 M H_2SO_4 and NaOH. One liter samples of the wastewater were added with each chemical at different dosages. One and a half hours of sedimentation was carried out after a coagulation period of 30 min (20 rpm) and flash mixing of 1-2 minutes (120 rpm).

Table 1. Characterization of textile dyeing process wastewater.

Parameter	Unit	Results of analysis of raw wastewater
pH	mg/L	8.1±0.55
COD	mg/L	1100±85
BOD_5	mg/L	440±32
TKN	mg/L	48±2.7
Total P	mg/L	11±0.85
Oil-grease	mg/L	74±5.5
SS	mg/L	110±8.6
Total Cr	mg/L	<0.1
Pb	mg/L	0.22±0.05
Cd	mg/L	0.12±0.02
Cu	mg/L	1.8±0.2
Zn	mg/L	2.9±0.2
Total CN	mg/L	-
Color (Absorbance)	abs-585 nm	0.492±0.032

Adsorption Experiments

Adsorption experiments using different sizes of corncob were carried out. For this purpose, the corncobs which were obtained from a local agricultural field in Bursa city were ground to sizes of 0.25, 0.50, 0.85, and 1.25 mm, and then 5 g of corncob from each size class were weighed and added to the Jar Test apparatus with 1 L of effluent from the chemical coagulation. The length, diameter, and grain size of corncob were 21 cm, 4 cm, 0.8 cm, respectively. Flash mixing (400 rpm) was applied for five days, and the color removal efficiencies of each size of corncob particles were determined as absorbance removal efficiencies. The experiments were also conducted with granular activated carbon (GAC; Jacobi; 0.5-1.0 mm) to compare the results with corncob. For this purpose, 10 g GAC per liter was added to the chemically treated effluent having varying dilution ratios, and flash mixing was applied for 24 h. After the 24 h reaction time, the color was analysed.

Results and Discussion

Chemical Coagulation Experiments

The chemical coagulation process has been extensively applied to textile wastewater for removing organic compounds and color [35]. Gilpavas et al. [36] reported 48% COD and 98% of turbidity removal was achieved using 700 mg/L of $Al_2(SO_4)_3$ as a coagulant at pH 9.96 by the coagulation-flocculation process. In another study conducted by Sher et al. [37], $Al_2(SO_4)_3 \cdot 18H_2O$ and anionic polyacrylamide were used as coagulant and flocculant, respectively and 91% COD removal was obtained. Rodrigues et al. [4] carried out treatability studies on cotton, acrylic and polyester dyeing wastewaters using $FeSO_4.7H_2O$ and examined the color and dissolved organic carbon (DOC) removal. At the end of the study, a significant amount of color (91% for cotton, 94% for acrylic effluents and 100% for polyester effluent) and insufficient DOC removal were observed (33% for polyester, 45% for cotton and 28% for acrylic effluents).

In this study, two different experiments were carried out. The first one is chemical coagulation with various coagulants and the second one is adsorption with different sizes of corncob. During chemical coagulation, the optimum pH values were determined to be 6.5, 8.0 and 8.0 for $Al_2(SO_4)_3 \cdot 18H_2O$, $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$, respectively. The best COD and color removal was obtained with $Al_2(SO_4)_3 \cdot 18H_2O$ in chemical coagulation of the textile wastewater effluent. COD removal at an $Al_2(SO_4)_3 \cdot 18H_2O$ dose of 300 mg/L resulted in an effluent COD of 300 mg/L (62%) and color of 0.256 (48%) (at pH 6.5). COD of 440 mg/L (60%) and color of 0.28 (43%) removal were obtained in coagulation using $FeCl_3 \cdot 6H_2O$ with a dose of 350 mg/L (at pH 8.0), while COD removal at a $FeSO_4 \cdot 7H_2O$ dose of 400 mg/L resulted in an effluent COD of 440 mg/L (60%) and color of 0.271 (45%) (at pH 8.0). The coagulant dosage effects on the removal of COD and color are shown in Fig. 1 and 2.

Adsorption Experiments

Corn is the third one after wheat and rice from the point of cultivation area and the first one in terms of production area in the world. In Turkey, corn has the largest acreage of grain after wheat and barley. Corn planting area in our country is 6.82 million decar and 6.3 million tons of corn is produced in 2016 [38]. Corncob, an agricultural waste is abundantly available and low-cost adsorbent for organic compounds removal from wastewater due to its good adsorption capacity and chemical stability [39]. Corncobs can also be dried and burnt after the adsorption process to obtain energy. The adsorption experiments were executed at acidic pH values due to the cellulosic structure of corncobs, which is known to increase in adsorption capacity under acidic conditions [40].

There are some studies in the literature related to the removal of color by adsorption using corncob. The corncob was used for dye removal in a study conducted by El-Geundi [41] and high adsorption capacity (160 mg dye/g maize cob for Astrazon Blue) was observed. Robinson et al. [42] used 10 gram/L of

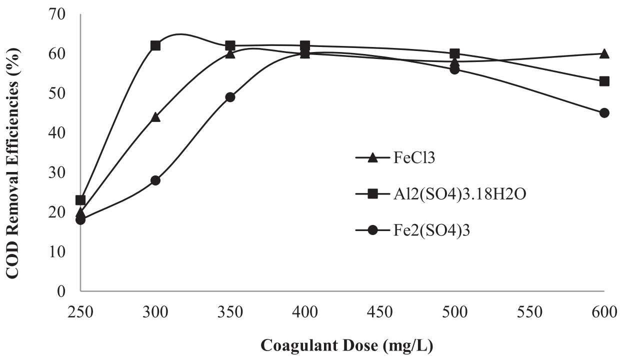

Fig. 1. Effects of coagulant dosage on COD removal during chemical coagulation experiments.

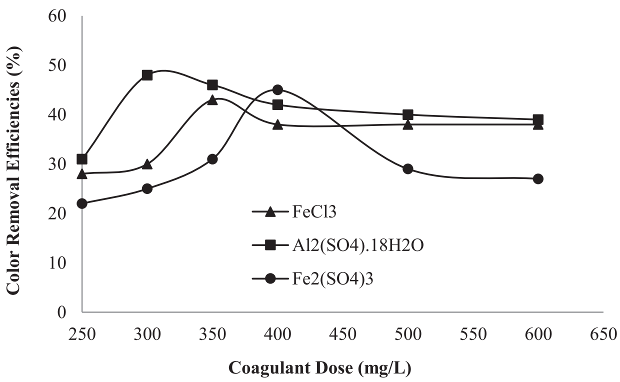

Fig. 2. Effects of coagulant dosage on color removal during chemical coagulation experiments.

600 mm corncob and obtained 92% dyes removal in 48 h, while the adsorption capacity for methylene blue was obtained 163.93 mg/g on the magnetic carbonaceous adsorbent derived from corncob [43]. Safranin basic dye from aqueous solutions was removed by adsorption using corncob by Preethi et al. [44], and the results indicated that corncob, an agricultural waste biomass, proved to be an excellent low-cost sorbent. All these experimental results show that corncob is effective adsorbent concerning the removal of color from textile wastewater.

In this study, the adsorption experiments were conducted in two stages:

– Adsorption on raw wastewater
– Adsorption on chemically treated wastewater

The Langmuir and Freundlich Isoterherms are frequently used in adsorption process. The Langmuir isotherm can be indicated in Eq. (1).

$$\frac{C_e}{q_e} = \frac{1}{q_o.b} + \frac{C_e}{q_o} \quad (1)$$

In Eq. (1), Ce is the equilibrium concentration (mg/L), q_e is the adsorbed amount at equilibrium (mg/g), q_o is the adsorption capacity (mg/g), and b is the adsorption energy (l/mg) [45].

In Eq. (2), the Freundlich isotherm model is shown:

$$q_e = K_f.C_e^{1/n} \quad (2)$$

In Eq. (2), q_e is the adsorbed amount at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate and K_f and n are the Freundlich constants in which n indicates the favorability of the adsorption process and K_f (mg/g (l/mg)^n) is the adsorption capacity of the adsorbent [46].

The adsorption process was carried out on raw wastewater with the size of 1.25, 0.85, 0.5 and 0.25 mm corncob particles. The R^2 values were found for Langmuir and Freundlich Isotherms are 0.988 and 0.72, respectively. Fig. 3 shows that the plots of Ce/qe versus Ce for corncob for Langmuir Isotherm Graph on raw wastewater. As it can be seen from Fig. 3, sufficient

Table 2. Color removal efficiencies depending on the sizes of the corncob particles.

	Absorbance Values (585 nm)	Color Removal Efficiency (%)
Raw wastewater	0.492	-
Effluent of chemical treatment	0.256	48
Sizes of corncob particles (mm)		
1.25	0.046	82
0.85	0.033	87
0.5	0.028	89
0.25	0.0256	90

amounts of color could not be removed by adsorption on raw wastewater. The Q° is calculated as 0.036 Abs unit/g corncob according to Fig. 3. Parallel to these results, amount (weight/volume) of corncob for color/COD removal from studied wastewater samples will be increased without the application of physico-chemical pre-treatment. Therefore, the physico-chemical pretreatment step after these results is necessary to reduce the excessive usage of corncob for the reduction of waste adsorbent disposal. The absorbance values of the chemically treated wastewater were measured as 0.023, 0.013, 0.0051 and 0.00255 Abs (Table 2) at the end of the mixing period.

Determination of the most appropriate correlation for the equilibrium data is necessary to optimize the system. Both the Langmuir and Freundlich isotherm models were examined in this study.

The value of q_o was calculated from plots given in Table 3. The correlation coefficient values for corncob and GAC were calculated as 0.9995 and 0.998, respectively. These values show that the adsorption of color onto the corncob or GAC was a well fit with the Langmuir model (Fig. 4).

The value of K_f was obtained from the intercept is given in Table 3. The R^2 values for corncob and GAC

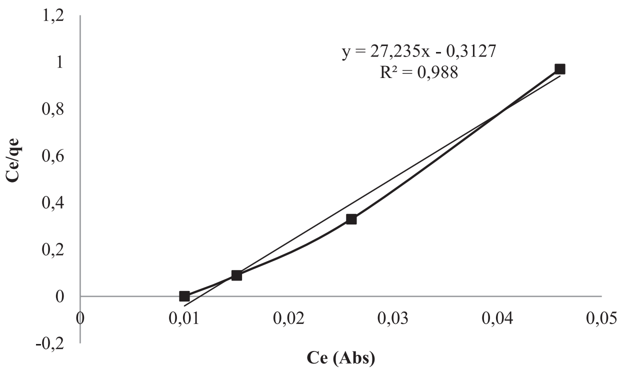

Fig. 3. Langmuir Isotherm Graph on raw wastewater.

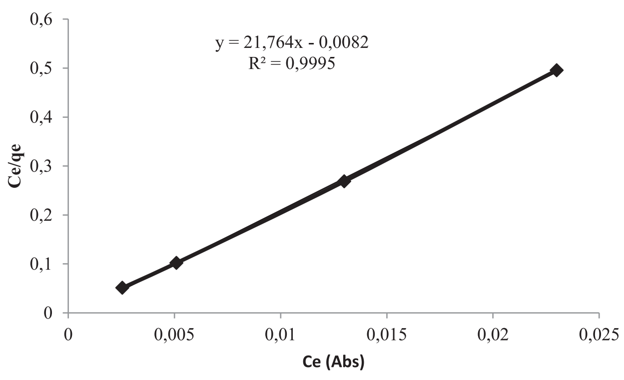

Fig. 4. Langmuir Isotherm Graph on chemically treated wastewater.

Table 3. Comparison of the Langmuir and Freundlich adsorption constants.

Adsorbent	Parameter	Langmuir constants		Freundlich constants	
		R^2	Q^o	R^2	Kf
Corncob	Color	0.9995	0.046 Abs unit/ g corncob	0.9212	0.041 Abs unit/ g corncob
GAC	Color	0.998	0.124 Abs unit/g GAC	0.878	0.086 Abs unit/g GAC

are 0.92 and 0.878, respectively. This means that the adsorption of color onto the corncob or GAC was not favorable with the Freundlich isotherm model.

When compared adsorption by corncob and GAC, it is shown that R^2 value in adsorption by GAC is a bit higher than adsorption by corncob. Moreover, adsorption capacity in GAC is five times higher than corncob.

In addition to the calculations, adsorption columns incorporating corncobs were designed to investigate the usage of corncob for the removal of color from the chemically treated textile wastewater, which had a flow rate of 10000 m^3/day. The density of corncob was assumed to be 0.28 ton/m^3 [47] and the filtration rate was taken to be 10 m/h [48]. An adsorption unit including 12 columns was designed according to the experimental data. The amount of corncobs necessary to effectively remove color from the textile wastewater was determined to be 84 tons.

Cost Evaluation

The capital and operating costs and maintenance are the cost of treatment plants. The operating costs (reagents costs and electricity consumption) of the applied processes were considered (Table 4) in this study. The price of reagents [49] and electricity [50] was taken from market prices. The labor and sludge disposal costs were excluded.

According to Table 4, the treatment cost of coagulation with $Al_2(SO_4)_3 \cdot 18H_2O$ was the lowest when compared the treatment cost of coagulation with $FeSO_4 \cdot 7H_2O$ and coagulation with $FeCl_3 \cdot 6H_2O$. The adsorption with corncob resulted in 90% color removal while the adsorption with GAC resulted in 99% color removal (Table 4). On the other hand, the treatment cost of adsorption with corncob is five times cheaper than adsorption with GAC.

Conclusions

Color removal by chemical coagulation and adsorption processes in textile wastewater was studied. The wastewater contained colorful material and organic substances. The conclusions of this study can be given as:

– The maximum removal efficiencies obtained from the chemical coagulation experiments were 62% and 48% for COD and color, respectively.
– The adsorption capacity was calculated as 0.046 Abs unit/g corncob.
– The operating cost of adsorption with corncob was calculated as 175.53 €/ton.
– The optimal treatment cost was calculated as 0.008 €/m^3 in coagulation with $Al_2(SO_4)_3 \cdot 18H_2O$.
– Adsorption by corncob is an efficient and economical solution for chemically treated textile wastewater when compared to GAC.

While the adsorption capacity of GAC is higher than corncob in this study, the operating cost of adsorption with corncob is lower than GAC. Consequently, the

Table 4. Reagents costs and the operating costs.

Reagents	Basis	Cost (€)	Process	Treatment Cost
$Al_2(SO_4)_3 \cdot 18H_2O$	ton	95.75	Coagulation with $Al_2(SO_4)_3.18H_2O$	0.008 €/m^3
$FeSO_4 \cdot 7H_2O$	ton	63.83	Coagulation with $FeSO_4.7H_2O$	0.009 €/m^3
$FeCl_3 \cdot 6H_2O$	ton	95.75	Coagulation with $FeCl_3.6H_2O$	0.01 €/m^3
Electricity	kWh	0.11	Color removal with corncob (Following chemical precipitation)	0.04 €/m^3
Sulphuric acid	ton	85.11	Color removal with corncob (On raw wastewater)	0.1 €/m^3
			Color removal with GAC (Following chemical precipitation)	0.2 €/m^3
Sodium Hydroxide	ton	95.75	Color removal efficiency (%)	
Corncob	ton	175.53	Corncob	90
GAC	ton	1514.89	GAC	99

application of adsorption by corncob following chemical coagulation is an economical and applicable choice for color removal from textile wastewater.

Acknowledgements

The author acknowledges Prof. Taner Yonar for his endless help and Bursa Uludag University for the editing support of this study.

Conflict of Interest

The author declare no conflict of interest.

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