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Reduction dye in paint and construction chemicals wastewater by improved coagulation–flocculation process

T. Ennil Bektaş

ABSTRACT

A coagulation–flocculation process was applied to wastewater of paint and construction chemicals producing factory in Turkey. Ferric chloride was used as coagulant and several natural based materials, namely limestone, pumice, sepiolite, bentonite and mussel shell were used as flocculant aids. The effects of dosage of flocculant aids on the pH, color and electrical conductivity of wastewater were studied. The experimental results showed that the treatment with all substances was very effective. The pHs of treated wastewater were obtained in the range of 5–7 without needing pH adjustment process. Fifteen Pt-Co color values were obtained on average, which is similar to pure water clarity. The amount of solute in the wastewater was evaluated by the electrical conductivity values. According to the results, under the optimum treatment conditions, chemical oxygen demands were determined. As a result of the work, the cost of chemicals for the wastewater treatment processes has been reduced by about 90%.

Key words | coagulation, dye, flocculation, natural materials, wastewater

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INTRODUCTION

The wastewater discharged from paint and construction chemicals producing factory is generally highly concentrated with organic and inorganic pollutants (Nasr *et al.* 2007). The discharge of dyes into receiving waters is one major cause of water pollution. The direct discharge of this wastewater into the environment affects its ecological status by causing various undesirable changes (Robinson *et al.* 2002; Verma *et al.* 2012). The treatment of wastewater containing dye is not effective with traditional processes due to the stable nature of dye that are associated with a large degree of aromatic structure (Zhang *et al.* 2016). Color can be removed from wastewater by chemical and physical methods including adsorption, ion exchange, coagulation–flocculation, oxidation and electrochemical methods. Coagulation flocculation is the most common use for wastewaters containing dye and suspended solids (Gürtekin 2011; Birjandi *et al.* 2013; Köse & Çalışkan 2016). Suspended solids in water have a negative charge and since they have the same type of surface charge, they repel each other when they come close together. Therefore, suspended solids will remain in suspension and will not clump together and settle out of the water, unless proper coagulation and flocculation are used. The coagulation–flocculation process, generally using inorganic coagulants such as aluminum sulphate (alum), ferric chloride ($FeCl_3$), ferrous sulphate ($FeSO_4$) has been applied to this type of wastewater to reduce dye and suspended solids (Lofrona *et al.* 2006). Coagulation is the destabilization of colloids by addition of chemicals that neutralize the negative charges. The destabilization can be achieved by one or more of the following mechanisms, after the addition of a coagulant agent (Crittenden *et al.* 2005):

(1) Compression of the electrical double layer.
(2) Adsorption and charge neutralization.
(3) Adsorption and interparticle bridging.
(4) Enmeshment in precipitate (by using of excess coagulant dose, 'sweep flocculation').

After the destabilization, flocculation promotes the aggregation and flocs formation, usually after the addition of an appropriate flocculant agent (Zahrim *et al.* 2011). Two general types of flocculation can be identified: micro-flocculation (or perikinetic flocculation), in which particles aggregation is brought about by the thermal motion of fluid molecules (Brownian motion) and macro-flocculation (orthokinetic flocculation), in which particle aggregation is

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brought about by inducing velocity gradients and mixing in the suspension (Crittenden *et al.* 2005).

Many studies have been conducted regarding the reclamation of dye wastewater by using coagulation/flocculation (Tan *et al.* 2000; Zahrim *et al.* 2010; Khayet *et al.* 2011). Recently, some natural based materials such Achatinoidea shells (Menkiti & Ejimofor 2016), banana pith (Kakoi *et al.* 2016), chitosan (Özacar Sengli 2002), peach kernel and beans (Jahn 2001) and rice starch (Teh *et al.* 2014) were utilized in coagulation–flocculation processes.

The wastewater containing dye and construction chemicals of the factory was applied to the pre-treatment by coagulation flocculation method and then was sent to the wastewater treatment plant of Eskişehir organized industrial zone. In this study, it was aimed to reduce costs by using environmentally friendly, degradable and cheap materials instead of the chemicals used for the treatment method of the factory. The factory manufactures interior and exterior paints, fillers, acrylic pastes and fluids, adhesives and joint fillers, primers and binders, waterproofing materials. Therefore, these substances are also present in wastewaters. The wastewater contains so many organic materials with high values of chemical oxygen demand (COD) and total suspended solids which lead to pollution problems.

This study was conducted using paint and construction chemicals producing factory wastewaters to evaluate the efficacies of ferric chloride coagulation and flocculation. Natural materials as flocculant aids were evaluated. The cost of the chemical substances used in the conditions of the factory and the cost of the recommended quantity of substances to be used according to the results obtained from the experimental studies were compared.

METHODS

Wastewater used in experiments that consisted of dye was collected from a paint and construction chemicals producing factory in Eskişehir, Turkey. Table 1 and Figure 1 show the characteristics of samples. In this case, it appeared that the wastewater had very high color and COD values. The samples were refrigerated at 4 °C prior to performing subsequent experiments. The chemicals used in this study were analytical grade Merck product.

Table 1 | Characterization of wastewater sample

Parameter	Value
COD (mg/L)	3,540
Color (Pt-Co)	>500
Conductivity (mS/cm)	0.68
pH	7.9

Figure 1 | Wastewater sample image.

Conductivity and pH were measured using a CMD630 digital model conductivity meter and a Thermo Orion model pH meter, respectively. 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 ferric chloride ($FeCl_3.6H_2O$, 40% by weight) as coagulant for wastewater. To improve the performance of the coagulants, limestone, pumice, sepiolite, bentonite and mussel shell were used as flocculant aids. Limestone, as used by the minerals industry, is any rock composed mostly of calcium carbonate ($CaCO_3$). Raw limestone was obtained from Eskişehir Cement Factory. Pumice is a natural pozzolan produced by release of gases during cooling and solidification of lava. Pumice is primarily silicon dioxide (amorphous aluminum silicate), some aluminum oxide, and trace amounts of other oxides. Pumice was obtained from Nevşehir area. Sepiolite is an inexpensive material and most of the world reserves are found in Turkey. Sepiolite, which is a kind of fibrous silicate clay mineral, is formed of tetrahedral and octahedral sheets. Sepiolite was obtained from hand-carving waste from Eskişehir Margı area. Bentonite is defined as a clay mineral, mainly containing montmorillonite with layered crystal structure. Bentonite consists of alumina sandwiched between two silica tetrahedral layers. Bentonite was obtained from Balıkesir area. Mussel shells are composed of 95% calcium carbonate, and the remainder is organic matter and other compounds. The mussel shells are

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Table 2 | Experimental results for limestone, pumice and sepiolite

		Limestone			Pumice			Sepiolite		
$FeCl_3$ (mL/L)	Floc. aids Dose (g/L)	pH	Pt-Co	Elec. cond. (ms/cm)	pH	Pt-Co	Elec. cond. (ms/cm)	pH	Pt-Co	Elec. cond. (ms/cm)
0.7	0.2	3.9	0	1.5	5.34	0	1.28	5.29	5	1.1
	0.4	4.2	12	1.67	4.8	24	1.3	5.52	4	1.1
	0.6	4.6	11	1.67	4.95	11	1.3	5.16	4	1.1
	0.8	4.2	12	1.63	4.92	17	1.3	5.39	28	1.1
	1	4.7	9	1.60	5.42	13	1.3	5.72	13	1.1

discarded into the environment. Mussel shells were obtained from Mudanya fish restaurants. All materials were used in powder form.

The experiments were performed at room temperature (20 ± 2 °C) using 500 mL of the wastewater sample by adding 0.35 mL coagulant dose. A period of fast agitation for 2 min at 220 rpm was followed by a period of slow agitation for 60 min at 80 rpm. The flocculant aid was added to the sample during the slow mixing step. After allowing settling to occur (24 h), the sample was filtered. The supernatant was collected for analysis.

RESULTS AND DISCUSSION

To improve the performance of the coagulant, limestone, pumice, sepiolite, bentonite and mussel shell were used as flocculant aids with ferric chloride. It was observed that no dye was removed in experiments made with only natural materials that did not use iron chloride. The impacts of adding different doses of flocculant aids varied from 0.2 to 1 g/L in combination with a constant ferric chloride dose (0.7 mL/L) at an initial pH value of 7.9. The results presented in Tables 2 and 3 indicate that the optimum doses of the flocculant aids were 1, 0.2, 0.4, 1 and 0.8 g/L for limestone, pumice, sepiolite, bentonite and mussel shell, respectively. The color removal was decreased effectively for all flocculant aids. Ca^{+2}, Mg^{+2} and Al^{+3} helped to neutralize the negative charge on the particles, which led to an increase in the amounts of flocs or may chemically interact with dissolved components in the raw wastewater. Therefore, it is considered that the coagulation flocculation process in the treatment process is accompanied by adsorption and chemical precipitation. Since organic compounds do not conduct electricity well, they are low conductivity in wastewater. The increase in the electrical conductivity values of the treated wastewater indicates that most of the suspended solids have been removed. COD reduction reached 1,480, 800, 720, 1,080 and 1,480 mg/L, respectively. The results presented in Figure 2. For the optimum flocculant aid dosage, sepiolite recorded the highest reduction of COD. Figure 3 shows the state of raw wastewater and wastewater that has undergone the treatment process. For the 500 mL wastewater, 1.65 g of sludge was produced by the method of the factory and 1.09 g of sludge was obtained for all the materials we used, especially for bentonite. A reduction of about 34% was achieved in the resulting sludge. Sludges with lower chemical content can lead to more efficient results in sectors such as refractory, concrete and cement.

Table 3 | Experimental results for bentonite and mussel shell

		Bentonite			Mussel shell		
$FeCl_3$ (mL/L)	Floc. aids Dose (g/L)	pH	Pt-Co	Elec. cond. (ms/cm)	pH	Pt-Co	Elec. cond. (ms/cm)
0.7	0.2	5.86	17	1.2	5.77	17	1.1
	0.4	5.92	13	1	5.83	14	1.1
	0.6	6.36	23	1.1	5.57	6	1.1
	0.8	5.99	13	1.1	6.18	8	1.1
	1	6.15	19	1.2	6.01	10	1.1

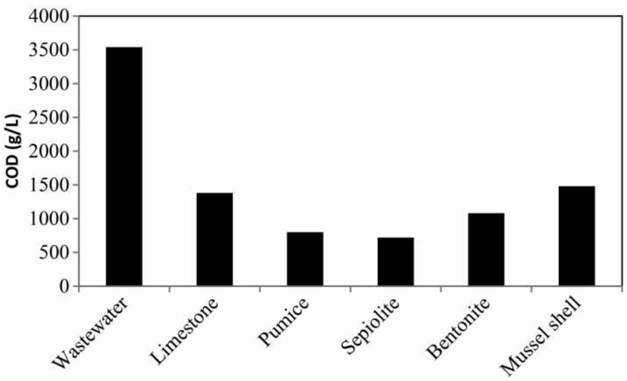

Figure 2 | Effect of ferric chloride with various flocculant aids on COD.

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Figure 3 | Wastewater and treated water image.

Effect on cost of coagulation–flocculation process

The proper determination of flocculant aids will not only improve the resulting water characteristics, but also decrease the cost of treatment. Paint and construction chemicals producing factory used ferric chloride as 7.5 L/5,000 L wastewater and NaOH as 10 L/5,000 L wastewater at the treatment system. In this study, the amount of ferric chloride used by the factory was reduced to 3.5 L/5,000 L wastewater and several natural based materials were used instead of NaOH. Figure 4 shows the cost of the different flocculant aids used. The use of all flocculant aids had an important effect on cost and improved the coagulation–flocculation process. The sludge formed in the treatment is sent to the cement plant and burned free of charge. Sludge formation was observed in fewer quantities after processing with natural materials.

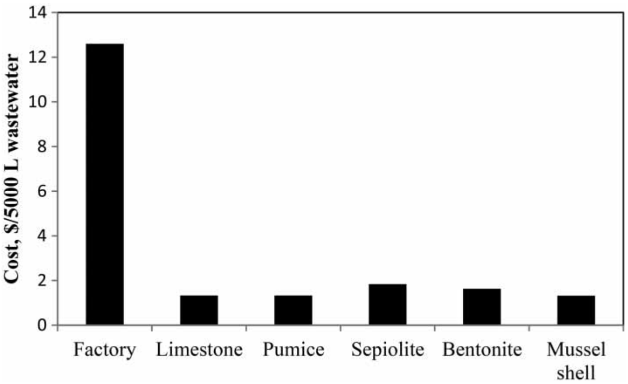

Figure 4 | Chemical cost for coagulation–flocculation process.

CONCLUSIONS

The chemical industries in Turkey face formidable environmental regulatory challenges in treating their wastewater effluents. Several physicochemical and biological wastewater treatment processes are widely utilized in the successful treatment of industrial wastewaters. The application of coagulation–flocculation was effective method for reducing color and decreasing the COD. The aim of this work is to make improvements that will reduce the cost of the treatment systems of a factory that produces paint and construction chemicals. The addition of a natural flocculant aids increase the flocculation efficiency of the coagulant, reducing the amount of coagulant required for the treatment and lowering the cost of the coagulation–flocculation process.

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