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Valorization of the Apatitic Calcium Phosphate in the Treatment of Textile Waste Effluent

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Abstract

Due to its unquestionable properties and besides its natural abundance, apatitic calcium phosphate is used, in the present work, to discolor the textile waste effluents using the method of coagulation-flocculation. The characterization of effluents, before and after treatment, was realized by the UV Spectrophotometer and the dosage of the chemical oxygen demand (COD). Results show that the color of textile waste effluents before and after coagulation flocculation has shown that after an operation of liming, the color reduction was 70 % and the organic load reduction was of 75 % using a dose of 4 $g.L^{-1}$ of apatite during 90 minutes as maximal time of treatment in optimal operating conditions (pH, current density, reaction time, etc). The reproducibility of the results proves the satisfactory and encouraging properties of apatitic calcium phosphate as coagulant for the discoloration of the studied textile waste effluents.

Keywords

Valorization, Apatitic Calcium Phosphate, Textile Waste Effluent, Coagulation Flocculation

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1. Introduction

The textile dyeing process generates a significant flow of aqueous effluents of very different characteristics [1], which depend mainly on the type of particles to be dyed, the nature of dyes, dyeing auxiliaries and substances added to treat the tissue. Textile wastewater is characterized by high chemical oxygen demand (COD), low biodegradability, high-salt content and is the source of aesthetic pollution related to color [2]. Several treatment techniques are applied to discolor these effluents full of organic matter. A wide range of wastewater treatment techniques have been tested based on biological and physico-chemical processes [3-8]. One of those treatments is the adsorption on apatitic calcium phosphate after settling of the effluent and adjusting its pH [9]. However, as the retention of dyes and organic matter was incomplete, we executed a pre-treatment of the effluent by coagulation flocculation, using the apatitic calcium phosphate as a coagulant because of its physical properties (compactness, porosity, active surface area and fineness of grind).

This work aims to test the capabilities of the apatitic calcium phosphate to destabilize colloidal materials from textile waste effluents and their effects on discoloration and reduction of organic matter. After a physicochemical characterization of the effluent to be treated, a decanting process is carried out followed by a coagulation flocculation process by aluminum sulphate, lime or apatite. The resulted filtrate is neutralized by lime after an optimization of the coagulation pH and the dose of coagulant.

2. Materials and Methods

2.1. Material

The material used is the apatitic calcium phosphate, which is composed of very small particles. It has a particular and very

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stable structure allowing a large number of substitutions [10, 11].

The chemical composition was determined by X-ray fluorescence and the calcium carbonate content by Bernard calcimeter (Table 1) according to the methods of Rodier analysis standardized by AFNOR [12, 13]. The specific surface is determined at 77 K by the Brunauer, Emmett and Teller (BET) method, and the zeta potential is measured at pH = 7,5. Porosity, density and loss on ignition (LOI) are also measured (Table 2).

Table 1. Chemical composition of apatite in % of weight.

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	P_2O_5	$CaCO_3$
Weight (%)	6.8	0.9	0.25	53.15	0.99	0	0.51	31.63	0.35

Table 2. Physical characterization of natural apatite.

Parameter	Real density	Porosity	Specific surface ($m^2.g^{-1}$)	Zeta potential (mV) at pH = 7.5	LOI* (%)
Value	3.1723	0.542	14	-27.8	7.62

*LOI: Perte au feu

Table 3. Chemical composition of decanted textile waste effluents

Parameter	Calcium Title (°F)	COD ($mgO_2.L^{-1}$)	SO_4^{2-}	PO_4^{3-}	NO_3^-	Cl^-	P_t	N_t
Composition ($mg.L^{-1}$)	95	1404	208	0.16	0.452	37.44	0.72	2.88

Table 4. Physical Parametersof decanted textile waste effluents.

Parameter	pH	Tre(°C)	χ ($\mu S.cm^{-1}$)	Turbidity (FTU)	MES ($mg.L^{-1}$)	λ_{max}*(nm)	A_{max*}
Measured value	9.2	24	1433.80	100.64	330	340	1.5

*λ_{max}: Maximum Wavelength corresponding to the maximum absorption
*A_{max} : maximum absorption

2.2. Waste Effluent

The waste effluent used in this study is from a textile industry located in Fez city, Morocco. First, the effluent was decanted for an hour then filtered using a membrane of 45 microns of porosity. The physico-chemical parameters (Tables 3 and 4) are determined by the methods of Rodier analysis standardized by AFNOR [5, 6]. The absorbance is measured by UV-Visible Spectroscopy and the calcium title by acid-base assay.

2.3. Coagulants

The used coagulants are:

- Aluminum sulphate (Al.S) ($Al_2(SO_4)_3, 18H_2O$) with a concentration of 2% at a dose ranging from 50 to 300 $g.m^{-3}$;
- Ferric chloride (F.Cl) ($FeCl_36H_2O$) with a concentration of 2% at a dose ranging from 50 to 300 $g.m^{-3}$;
- Lime (Li): Ca $(OH)_2$ at a dose between 1and 18 gL^{-1};
- Apatite (Ap) at a dose between 1 and 6 $g.L^{-1}$.

The treated effluents, under optimal pH conditions, by Al.S, F.Cl and Ap are acidic. The compensation of the acidification is achieved by the powdered lime at $1g.L^{-1}$.

2.4. Coagulation-Flocculation

The coagulation is carried out for three minutes at a fast stirring speed of 250 rpm, while the flocculation is carried out for twelve minutes at a speed of 30 rpm for a sample of 500 mL. Then, the mixture is decanted for thirty minutes. Finally, the supernatant was centrifuged at 5000 rpm for fifteen minutes, for a subsequent analysis.

The experiments are carried out in three steps by a Jar-test bench:

- Detecting, after coagulation, the optimum pH of the treated effluent corresponding to the maximum removal of color and turbidity. The pH is adjusted by adding sulfuric acid (0,1 $mol.L^{-1}$) or sodium hydroxide (0.1 $mol.L^{-1}$).
- Identifying the optimal dose of coagulant, to treat the maximum amount of effluent by fixing the pH at its optimum and varying the concentrations of the six solutions of Jar-test.
- Neutralizing the pH by liming (adding a maximum mass of $1g.L^{-1}$ of lime) the effluent treated by apatite according to the Moroccan waste water standards [14-15]. After a new measurement of parameters, the most effective coagulant, and the optimum concentration for the optimum pH were also determined.

3. Results and Discussions

The pH values corresponding to the best coagulation of the treated effluent by the 4 studied coagulants are shown in Figure 1. The removal of organic matter and color is maximum for pH values near to 4.3 for Al.S, 4.6 for F.Cl, 11 for the lime and 5.25 for Ap. It is noteworthy that the ferric chloride tones the effluent with a yellow color, which makes it difficult to study the effect of the pH on the bleaching effluent.

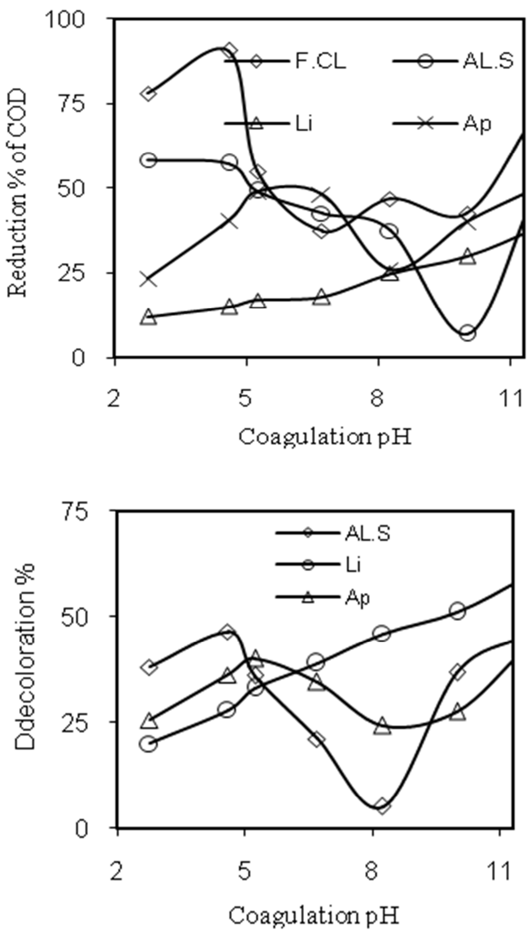
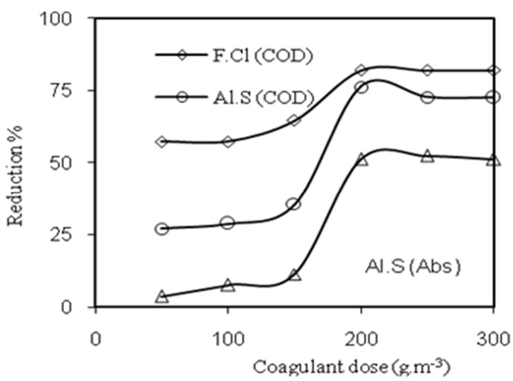


Figure 1. Effect of the coagulation pH on the reduction of COD and the absorbance.



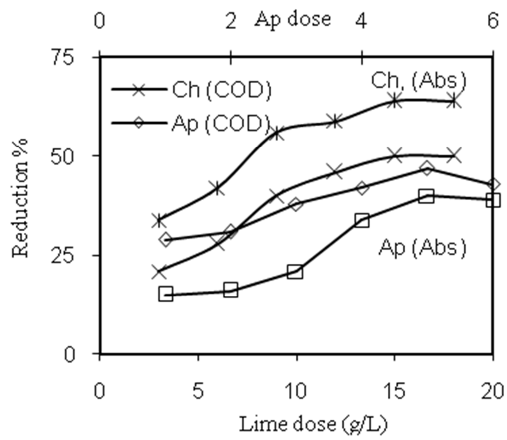


Figure 2. Effect of the coagulant dose on the reduction of COD and the absorbance

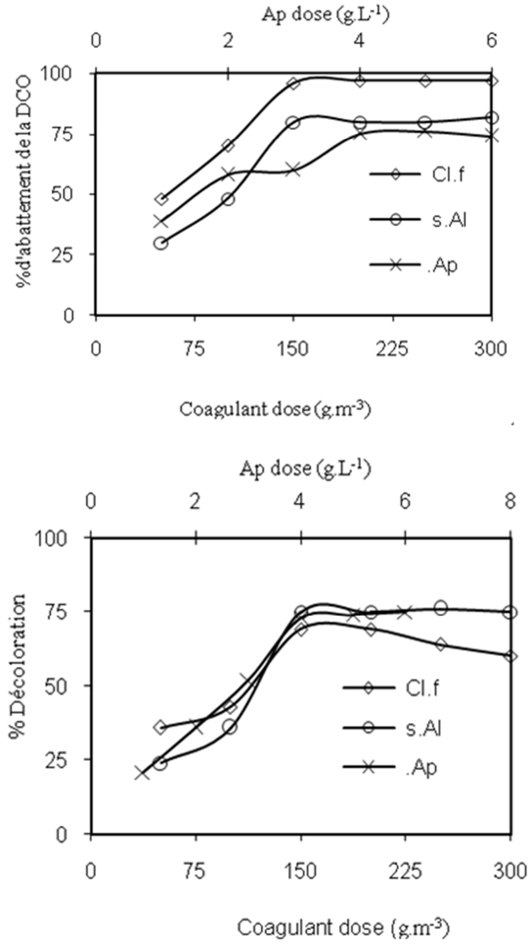


Figure 3. Effect of liming on the reduction of COD, the absorbance and the coagulant dose.

Ferric chloride >Aluminum sulphate > Apatite > Lime

The optimum coagulant doses are approximately 0.2 $g.L^{-1}$ for both commercial coagulants and 15 $g.L^{-1}$ or 5 $g.L^{-1}$ for lime and Apatite respectively (Figure 2). The reductions of the organic matter are important, about 80, 70 and 50% respectively for F.Cl, Al.S, Ap and Li. The color diminish is about 51, 40 and 64% respectively for Al.S, Ap and Li.

Under optimal pH conditions, the colorless effluent is acid, except the one obtained by coagulation with Li. A neutralization operation almost doubled the removal efficiencies of COD and reduced the amount of Ap to 4 $g.L^{-1}$ (Figure 3). Certainly, the reduction of COD and color is about 75%. Moreover, the addition of the liming operation for treatment with Al.S or F.Cl has considerably weakened the COD and the absorbance to the concentration of 0,15 $g.L^{-1}$. The reduction of COD and color reached 97% for the F.Cl and 81% for the Al.S.

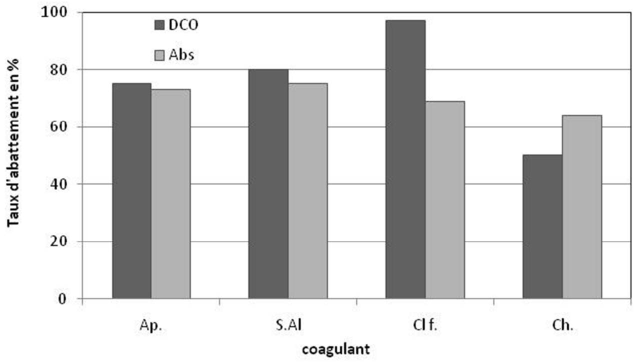


Figure 4. Comparison of the efficiency of the different coagulants.

The results of the treatment of the effluent decanted by coagulation-flocculation using Ap followed by the liming operation are comparable to those obtained by F.Cl and Al.S. Sure enough, 7.2 mg of apatite would be required to eliminate 1mg of O_2 of COD against 35.5 mg of Li, 1.2 mg of F.Cl and 0.3 mg of Al.S. Despite the low concentrations of commercial coagulants, Ap (Figure 4) is the most effective, the least expensive and very abundant in Morocco. However, the use of F.Cl tones the color of the effluent, and that of Al.S request its recovery after treatment because the Al^{3+} ions are toxic to fish and man, which makes the treatment expensive. Furthermore, Ap can be recovered after discoloration of decanted effluent to be reused in other fields such as building materials [16-18].

Coagulation floculation is an efficient process, for the removal of colour and total organic load in reactive dyes textile wastewater. The efficiency of the process is influenced strongly by the chemical and physical conditions and the time of the reaction.

4. Conclusion

The physicochemical characterization decanted textile waste effluents for an hour records their slightly basic, turbid and non-biodegradable organic character exceeding the quality standards of wastewater discharge into surface waters

The pre-treatment of textile waste effluents decanted by coagulation-flocculation with apatite, before treatment, recycling in dyeing or discharging into rivers reduces about 75% of the organic matter and color. Consequently, this operation is able to reduce a large proportion of the pollution load existing in effluents and facilitates the implementation of an alternative method of treatment such as adsorption, membrane filtration, oxidation or Fenton process and photo-Fenton.

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