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INDUSTRIAL WASTE Fe-Al COAGULATION AGENT UTILIZATION FOR WASTEWATER TREATMENT

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Abstract

This study shows the wastewater efficient treatment process resulted with Fe-Al complex coagulation agent obtained from industrial waste. Coagulation agent prezented 24.5 - 28.0 $g \cdot L^{-1}$ Fe and 16.0 - 17.5 $g \cdot L^{-1}$ Al content. pH coagulation agent is in the range pH=1-2. The wastewater with high degree *i.e.* chemical oxygen demand (COD) = 25,000-30,000 mg $O_2 \cdot L^{-1}$, Total organic carbon (TOC) = 3,600 - 4,000mg $C \cdot L^{-1}$, dry matter = 9.55 - 10.45 $g \cdot L^{-1}$, etc. is resulted from printing house. Treated water samples with the optimal dose of coagulation agent based on iron-aluminium salts obtained from industrial waste prezented similar TOC and dry matter reduction efficiencies with samples treated with the optimal dose of ferric chloride. COD reduction efficiency in treated water samples with the optimal dose of coagulation agent based on iron-aluminium salts it was 10% greater *vs*. reduction efficiency obtained from samples water treated with classic coagulation agent, $FeCl_3$. The advantage of the complex Fe-Al coagulation agent obtained from industrial waste was that it can be used for some wastewater of printing house in lower optimal dose, by 30%, *vs.* ferric chloride, coagulation agent. The complex Fe-Al coagulation agent obtained from industrial waste cost is much less than that of classical coagulation agents.

Keywords: *COD and TOC reduction efficiencies, Fe-Al complex coagulation agent, wastewater of printing house*

Introduction

The main pollutants in wastewater resulting from the production of printing agents and their use in packaging, textiles etc. are fine suspension and colloidal systems *i.e.* acrylic soluble compounds, compounds with chromospheres groups, alcohols, etc. Printing agents also contain dozens of additives, such as stabilizers, anti-foaming agents, blocking agents, surfactants, preservatives, etc. Coagulation of this type of wastewater involves processes of destabilization of fine particles and colloidal systems. In first step with subsequent union in large aggregates, mass transfer processes, adsorption processes of some organic/inorganic chemical species on the aggregates formed, etc. (Wu et al. 2002; Zhao et al. 2005; Ding et al. 2011). The coagulation process relates at increases effect of removing soluble substances by co precipitation and/or sweep coagulation (O'Melia 1980; Amirtharajah & O'Melia 1990; Letterman et al. 1999). Sweep flock is achieved by adding an excess of coagulant to the water that becomes saturated and the coagulant precipitates. The importance of the coagulation stage in a wastewater purification process results in the water cleaning effect, respectively, of the amount of pollutant removed from this water. Process efficiency is determined through conventional global parameters by characterization of raw and treated water: colour, turbidity, suspensions, organic matter expressed by demand chemical oxygen demand COD and / or total organic carbon TOC etc. and by specific parameters, *i.e.* a pollutant or class of pollutants. Chemical coagulation is considered as the optimal potential method for treating wastewater from print shop (Metes et al. 2000). Fast coagulation results are a waiting for the advanced reduction of turbidity, the formation of a coagulating sludge as compact as possible, which later are complemented by other specific analyzes of the process. Coagulation is largely rivalling with more expensive treatments such as adsorption on adsorbent materials *i.e.* activated charcoal or oxidation by ozone (Fissinger & Bersillon 1977). Aluminium or iron salts such as chlorides or sulphates are used as coagulating agents. This type of coagulant determines the aggregation of the matter present in the wastewaters in the form of a fine suspension or in a colloidal state with the formation of large heavy flocks which deposit at the bottom of the vessel. Replacement of classical coagulation agents with coagulation agents from industrial waste which containing trivalent metal ions present a feasible option in terms of both sustainable waste management and of course, the much lower cost price. The purpose of the paper was to replace classical coagulating agents, *i.e.* iron chloride in the coagulation step of highly polluted water resulting from cardboard packaging units with a coagulating agent with high content of Fe and Al originated from industrial waste.

Materials and Methods

Wastewaters from a printing unit with characteristics listed in Table 1 have been studied. Wastewater is in the form of a fine dispersion of print agent of apparently black ink. The fine black suspension of the wastewater passed into the filtrate completely through filtering on the filter paper Sartorius filter papers FT 2-206. Waters have sweet smell. The pH of the water was between pH = 7.05 ± 0.34.The wastewater shows high pollution, *i.e.* chemical oxygen demand (COD) = 25,000 - 30,000 mg $O_2 \cdot L^{-1}$, Total organic carbon (TOC) = 3,600 - 4,000 mg $C \cdot L^{-1}$, dry matter = 9.55 - 10.45 $g \cdot L^{-1}$.

Table 1. Characteristics of waste water from a printing house

Crt. No.	Parameters	Value min-max
1	Apparently colour	black
2	Real colour	black
3	Smell	sweet
4	Aspect	fine dispersion of ink agent, who partial pass through Sartorius filter paper FT 2-206
5	pH	7.05±0.34
6	Turbidity [°NTU]	can not be determined*
7	COD [$mgO_2 \cdot L^{-1}$]	25,000-30,000
8	Dry matter [$g/\cdot L^{-1}$l]	9.550-10.450
9	TOC [$mg\ C \cdot L^{-1}$]	3,600-4,000

*Turbidity analyzes could not be performed in the initial waters

The coagulation agents used were ferric chloride p.a *Chimopar Bucharest* and a complex coagulant containing iron and aluminium salts obtained from industrial waste. The characteristics of the complex coagulant obtained from industrial waste used in the coagulation tests are presented in Table 2.

Table 2. Characterization of complex coagulant ***(FA)*** obtained from industrial waste

No.	Characteristics	UM	Determined values	Method
1	pH		2.18	SR EN ISO 10523:2012
2	Copper	[$mg \cdot L^{-1}$]	712.2	SR ISO 8288-01
3	Cadmium	[$mg \cdot L^{-1}$]	<0.02	SR ISO 8288-01
4	Total Chromium	[$mg \cdot L^{-1}$]	1.24	SR EN 1233-03
5	Nickel	[$mg \cdot L^{-1}$]	1.13	SR ISO 8288-01
6	Zinc	[$mg \cdot L^{-1}$]	1.16	SR ISO 8288-01
7	Lead	[$mg \cdot L^{-1}$]	0.24	SR ISO 8288-01
8	Manganese	[$mg \cdot L^{-1}$]	64.6	SR 8662/2-96
9	Aluminium	[$g \cdot L^{-1}$]	17.5	SR EN ISO 11885:09
10	Iron	[$g \cdot L^{-1}$]	28.0	SR 13315-96/C91:2008

It is noted that:
• Concentrations of Al^{+3} and Fe^{+3} are 17.5 $g \cdot L^{-1}$ respectively 28.0 $g \cdot L^{-1}$; these concentrations are large enough to allow the use of the inorganic phase as coagulation agent
• Strong acidic media (pH = 2.18) keeps metal ions in soluble form, usable directly in coagulation processes;
• Heavy metal content is relatively low, compared to iron and aluminium ions; under these conditions the contribution of heavy metals introduced into the wastewater with the complex coagulant FA, is insignificant.

To perform the optimal dose determination tests for the wastewater coagulant in the printing works, has been achieved diluting the complex coagulant FA, at 1:10. The coagulation solution contains ÷ 2.8 mg $Fe \cdot ml^{-1}$ and 1.7 mg $Al \cdot ml^{-1}$. The classic coagulation agent to which coagulation results were reported with the complex coagulant FA, was iron chloride. Iron chloride having 4.6 mg $Fe \cdot ml^{-1}$ was used in coagulation tests. Methods: coagulation was performed with a stirrer equipped with variable speeds (Phipps & Bird Company, USA). The optimal dose of coagulation agents for maximum pollutant removal were done by Jar Test. The coagulation pH of the water investigated pH = 7.5, revised with acid or base. In the supernatant separated from the treated/coagulated samples conventional parameters were analyzed according to the standardized norms: pH determined by pH- meter 290A ORION RESEARCH USA type, turbidity with Micro 100 Laboratory Turbid meter, Scientific Inc. USA; COD by hot K dichromate oxidation in strongly acidic medium; TOC by TOC Analyzer with Multi N/C 2100 Analytic Jena, Germany.

Results and Discussion

In Table 3 are presented the results obtained by applying the Jar Test method in determination the optimal dose for wastewater from printing house. The coagulation agent used was ferric chloride. Analysis of the coagulated water samples was performed after filtration of coagulated samples at the optimal dose.

Table 3. Determination the optimal dose of coagulation agent ferrous chloride for wastewater from printing house by Jar Test method. Coagulation agent $FeCl_3$ (4.6 mg Fe·ml^{-1}), coagulation pH = 7.5

No	Parameters	Treated samples			
		3	4	5	6
1	Dose [mg Fe·L^{-1}]	55.2	73.8	92.0	113.6
2	Colour	The filtered samples are black. Incomplete coagulation			Light yellow
3	Turbidity [NTU]		-	-	13.0
4	Reduction efficiency [%]		-	-	-
5	Dry matter [g·L^{-1}]	7.5	6.4	3.6	1.55
6	Reduction efficiency [%]	28.0	38.5	65.5	85.5
7	COD [mg O_2·L^{-1}]	18,560	17,650	10,200	7,900
8	Reduction efficiency [%]	25.8	29.4	59.2	68.4
9	TOC [mg C·L^{-1}]	2,400	1,670	1,235	930.5
10	Reduction efficiency [%]	33.0	53.6	65.2	74.1

The dose of ferric chloride coagulant to which the treated sample forms heavy flocks which are retained on the filter paper was 113.6 mg Fe·L^{-1}. At this dose, the amount of dry matter was reduced with 85.5%, to 1.55 g·L^{-1}. Organic load reduction efficiencies were for COD of 68.4% and for TOC of 74.1%. In the literature, has been reported effective reduction COD up to 92.1%, after coagulation with the optimal dose of iron polychloride (Wu et al. 2002). Selection of $FeCl_3$ as a coagulant for wastewater treatment from printers caused the reduction COD with 88.75% (Zhao et al. 2005). Table 4 shows the results obtained by applying the Jar Test method in determining the optimal dose for wastewater from printing works. The coagulation agent used was a complex coagulant FA, obtained from industrial waste. The rising addition of complex coagulant FA determined the gradual reduction of the amount of printing agent in the wastewater. Although the amount of suspension is reduced, the water remains strongly loaded with coloured organic matter, which prevents determination of turbidity. In the case of FA doses between 39.1 - 86.9 mg metal·L^{-1} the treated wastewater after coagulation-filtration still strongly coloured with colloidal particles. The COD and TOC organic load reduction efficiencies were higher than for wastewater treatment with the optimal dose of classic agent, ferric chloride. In addition, these increased efficiencies of the organic load reduction were obtained at optimal doses of complex agent, 30% lower than the classic agent used, ferric chloride. The residual Al amount of the treated sample was 1.75 mg Al/L. Increasing the amount of complex coagulant FA, determined the improvement of filtration capacity, due to the fact that the flocks formed during the coagulation were larger and easier to filter. When the dose of complex coagulants increased to 90 mg metal·L^{-1}, the amount of residual Al in the treated sample was increased by a similar amount with the excess of Al from the coagulation agent.

Table 4. Determination of the optimal dose of complex coagulation agent FA, obtained from industrial wastes for wastewater from printing house, by the Jar Test method, pH-coagulation=7,5.

No.	Parameters	Treated samples				
		1	2	3	4*	5*
1	Coagulation dose [mg Fe·L^{-1}] [mg Al·L^{-1}] Total metal [mg metal·L^{-1}]	 11.2+ 6.8 18.0	 16.8+ 10.2 27.0	 33.4+ 21.0 54.4	 **47.6+** **29.8** **77.4**	 56.0+ 34.0 90.0
2	Colour	Black suspension filtered samples contains			**Low yellow**	Low yellow
3	Residual turbidity [NTU]	-	-	-	**20.9**	15.0
4	Reduction efficiency [%]	-	-	-	-	-
5	Dry matter [g·L^{-1}]	-	9.0	8.3	**1.68***	1.34
6	Reduction efficiency [%]	-	13.8	29.6	**83.9**	87.1
7	COD [mg O_2·L^{-1}]	-	23,490	21,149	**5,490**	4,992
8	Reduction efficiency [%]	-	6.0	15.4	**78.0**	80.0
9	TOC [mg C·L^{-1}]	-	2,360	2,190	**790**	830
10	Reduction efficiency TOC [%]	-	33.6	39.1	**76.9**	78.0
11	Al Residual content [mg Al·L^{-1}]				**1.75**	22.0

Coagulation agent used: 1ml of FA solution containing 2.8 mgFe·ml^{-1} and 1.7 mgAl·ml^{-1}.
Note: The coagulation process continues with more flocks formation during 5-6 hours. Increasing the coagulation dose to 77.4 mg metal/L caused the agglomeration of the printing agent particles from the treated water becoming removable by filtration. The obtained filtrate contains 1.68 g·L^{-1} of suspensions by 83.8% less than the initial wastewater. At this dose, the organic load reduction efficiencies were for COD of 78.0% and for TOC of 76.9%.

Conclusions

The complex coagulation agent behaved as an efficient coagulation agent compared to a classical coagulant such as ferric chloride. Thus, it can be used for coagulation of wastewater with high content of organic matter such as printing agents on paper, cardboard, etc in a state suspended, colloidal or dissolved. The COD and TOC organic load reduction efficiencies from samples treated with optimal coagulation agent doses were higher than for wastewater treatment with the optimal dose of classical agent, ferric chloride. In addition, the optimal dose of coagulation complex was with 30% lower than the optimal dose of classical agent used, ferric chloride. The residual Al amount of the treated sample was 1.75 mg Al/L. Not least, Fe-Al complex coagulation agent is a cheaper product than classical coagulants, being obtained from the process of recovery of industrial waste.

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