



Chemical treatment of polluted waste using different coagulants

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Received 20 November 2011; Accepted 1 December 2011

ABSTRACT

Textile industry is a very diverse sector in terms of raw materials, processes, products and equipment and has a very complicated industrial chain. Wastewater treatment is one of the major problems faced by textile manufacturers. Environmental problems of the textile industry are mainly caused by discharges of wastewater. Coagulation is a widely used method for the treatment of several wastewaters industrial streams. In the present paper several types of coagulant have been used for the treatment of a certain textile effluent. Ferric chloride, lime and alum have been examined in their effectiveness of reducing chemical load of the effluent. The implementation of those coagulants decrease the COD up to 53.9% using lime, up to 65.7% using ferric chloride and up to 81.7% using alum. The results are very useful for the optimizations of several chemical treatments of waste streams from small industries.

Keywords: Coagulation; Textile wastewaters; Chemical Treatment; COD reduction

1. Introduction

Textile industry is a very diverse sector in terms of raw materials, processes, products and equipment and has a very complicated industrial chain. The textile finishing covers the bleaching, dyeing, printing and stiffening of textile products in the various processing stages (fibre, yarn, fabric, knits, finished items). The purpose of finishing is in every instance the improvement of the serviceability and adaptation of the products to meet the ever-changing demands of fashion and function. The impacts on the environment by textile industry have been recognized for some time, both in terms of the discharge of pollutants and of the consumption of water and energy [1]. Characterization of textile process

effluent streams is very important to develop strategies for water treatment and reuse. To optimize treatment and reuse possibilities, textile industry waste streams should be in principle considered separately.

Environmental problems of the textile industry are mainly caused by discharges of wastewater. The textile sector has a high water demand. Its biggest impact on the environment is related to primary water consumption (80–100 m³ t⁻¹ of finished textile) and waste water discharge (115–175 kg of COD per t of finished textile, a large range of organic chemicals, low biodegradability, colour and salinity). Therefore, reuse of the effluents represents an economic and ecological challenge for the overall sector [2]. Textile processing employs a variety of chemicals, depending on the nature of the raw material and product [3]. The effluents resulting from these processes differ greatly in composition, due to differences

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in processes, used fabrics and machinery [4]. Main pollution in textile wastewater came from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuffs, which generally are organic compounds of complex structure. The combination of the processes and products make the wastewater from textile plant to contain many type of pollutants. It contains various waste chemical pollutants such as sizing agents, wetting agents, dyes, pigments, softening agents, stiffening agents, fluorocarbon, surfactants, oils, wax and many other additives which are used throughout the processes. These pollutants contribute to high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, color, acidity, basicity and other soluble substances, [5,6].

Textile dyes are structurally different molecules themselves with low or no biodegradability. The removal of color is associated with breakup of the conjugated unsaturated bonds in molecules. For this reason, many chemical treatment processes have been used extensively to treat textile wastewaters. The best combination of methods differs from plant to plant depending on the size, type of waste and degree of treatment needed. Generally, the treatment options can be divided into three main categories namely biological, chemical and physical methods. Among the chemical methods are coagulation or flocculation and oxidation. One of the main advantages of the conventional coagulation and flocculation is the removal of the waste stream due to the removal of dye molecules from the dye bath effluent and not due to partial decomposition of dyes which can lead to an even more potentially harmful and toxic aromatic compound [7]. Chemical treatment techniques are effective for colour removal but use more energy and chemicals than biological processes. They also concentrate the pollution into solid or liquid side streams requiring additional treatment of disposal while the major disadvantage is the production of sludge [7]. In coagulation process large amount of sludge is created which may become a pollutant itself and increase the treatment cost. However, that sludge's can be promoted to incineration plants or to cement industries.

Coagulation is a well-known process in wastewater treatment [8]. Mineral salts of polyvalent cations have been widely used as coagulant since the end of last century. Aluminum salts are often used as coagulants for wastewaters of different chemical and biological characteristics [9]. The use of iron salts has also been reported [10]. In addition, lime is a very popular coagulant due to its attractive cost. For a coagulation process it is very important to find out efficient coagulating agents for the flocculation/precipitation process. This method has been also used for the removal of different organic substances from drinking water [11].

This paper focus on the treatment of wastewaters from textiles using lime, ferric chloride, alum as an economical and easy applicable methods for small industries which produce limited quantities of those waste.

2. Materials and methods

2.1. Materials

The wastewater used in this study has been collected from a very small textile plant based in Cyprus. There is no any information available pertaining to the type of dyestuffs and other chemicals used in the industrial process. The wastewater was first filtered using a screen filter (5 mm) to remove large suspended solids before it was used for the subsequent studies.

For the experiments three deferent coagulants have been used: Aluminum sulfate (alum) [$Al_2(SO_4)_3 \cdot 18H_2O$ with Molecular weight of 666.7 g], Ferric Chloride [$FeCl_3$ with Molecular weight of 162.1 g] and Lime [$Ca(OH)_2$ with Molecular weight of 74.1].

2.2. Methodology

A conventional jar test apparatus was used in the experiments to coagulate sample of textile wastewater in order to carrying the chemical precipitation. Variable dosages of the used coagulants have been applied. The range of dosage that has been utilized to the initial wastewater was between 100 and 1000 mg l⁻¹ of coagulant with an increasing step of 100 mg l⁻¹. The optimum experimental conditions for COD and color reduction have been found.

Those experiments were carried out without any initial pH adjustment. Then, for the best dosage of the each coagulant the influence of pH for COD removal has been studied. The examined pH range was between 5.0 and 8.0 for alum and lime and between 2.0 and 5.0 for ferric chloride with an increasing step of 0.5. In order to adjust the pH, 0.1 N HCl and 0.1 N NaOH were used.

All the experiments have been carried out in stable conditions of $25 \pm 1^\circ C$. The different amounts of the coagulant were added to dye solution and were mixed using a magnetic stirrer with a rotation speed of 650 min⁻¹. After 15 min the stirring rotation speed was lowered to 400 min⁻¹ for another 30 min and then the speed was fixed up to 50 min⁻¹ for the next 75 min (total mixing time of 2 h). The precipitate was filtered after 22 h through cellulose filter paper (0.150 μm) and the filtrate were analysed for several parameters as indicated below.

2.3. Methods of analysis

pH, Electronic conductivity (EC), COD, BOD₅, COD/BOD₅, Total Organic Carbon (TOC), Colour, Total

Dissolved Solids (TDS), Total Suspended Solids (TSS), Total Kjeldahl Nitrogen (TKN), Total Phosphorus (TP), Nitrates (NO_3^-), Sulfates (SO_4^-), Chlorium (Cl^- Carbanates (HOC_3^-), Turbidity, Cd, Cu, Cr, Zn, Pb, Fe and sampling Temperature (T) were determined according to the Standard Methods for Examination of Water and Wastewater [12]. Statistical analysis was carried out using 2011 Microsoft Excel.

3. Results and discussions

Characterization of textile process effluent streams is very important to develop strategies for water treatment and reuse. The physicochemical characteristics of the examined textile wastewater are presented in Table 1. Also, the same table presents the physicochemical characteristics of the textile waste water from other researches. Also the water's quality plays a significant role in the characterization of the final waste due to the presents of natural salts.

Comparing the results with those that are presented in the international literature it is obvious that our results

are similar. pH are vary from 5 to 11, EC from 2800 to 4300 $\mu\text{S cm}^{-1}$, COD from 1000 to 3500 ppm, BOD from 160 to 800 ppm, Colors vary from 612 to 4500 ADMI units. Also the waste water from textile presented with high concentration of Cr, Cu, Fe, sulfates and chlorine. Due to the high pollutants the wastewater produced from textiles, cannot be disposed in any treatment plants before a pre-treatment stage. If untreated wastewater would be discharged in aquatic environment, some effects could take place, like: (1) Effect of BOD: depletes dissolved oxygen from streams, lakes and oceans; may cause death of aerobic organisms (fish kills etc.); increases anaerobic properties of water, (2) Effect of TSS: increases turbidity (less light—reduced photosynthesis, causes fish's gills to get plugged up); increases silting (reduces lifetime of lakes, changes benthic ecology), (3) Effect of pH: organisms are very susceptible to acids and bases.

3.1. COD Reduction relating to dosage of coagulant

Figs. 1a–c presents the efficiency of the dosage of lime, ferric chloride and alum respectively in reducing

Table 1
Physicochemical characteristics of the collected samples

Characteristics	Mean value of 20 samples	[13]	[14] ^a	[14] ^b	[15]	[16]	[17]
pH	8.31 ± 0.46	6.95	5.51	10.9	8	10.21–11.53	8.2–11.4
Electronic conductivity $\mu\text{S cm}^{-1}$	2875 ± 236	3990	–	–	–	–	3652–4380
COD, ppm	1420 ± 267	3422	3491.3	2788.2	1300	1067–2430	1634–2020
BOD ₅ , ppm	339 ± 121	–	800	300	790	163–645	547–687
COD/BOD ₅	4.18 ± 1.06	–	–	–	–	–	0.33–0.34
TOC, ppm	692 ± 109	900	–	–	–	–	–
ADMI colour units	4053 ± 225	–	–	–	–	612–4637	–
Total Dissolved Solids (TDS), ppm	1115 ± 130	–	–	–	1300	250–2200	–
Total Suspended Solids (TSS), ppm	205 ± 11	1112	432.8	105.2	835	35–1200	306–442
Total Kjeldahl Nitrogen (TKN), ppm	176 ± 46	–	–	–	–	–	45.6–50.4
Total Phosphorous (TP), ppm	3.15 ± 0.87	–	–	–	35	0.09–3.42	2.54–9.42
Nitrates, ppm	24.3 ± 11.4	–	2.5	9.4	–	0.8–7.97	–
Sulfates, ppm	553 ± 109	–	–	–	800	0.1–1.94	184–1070
Chlorium, ppm	570 ± 27	–	–	–	–	–	69–136
Iron (Fe), ppm	4.160 ± 1.681	–	–	–	–	0.45–2.14	4–6
Zinc (Zn), ppm	0.754 ± 0.198	–	–	–	–	–	–
Chromium (Cr), ppm	2.204 ± 0.487	–	–	–	–	0.5	–
Cadmium (Cd), ppm	0.203 ± 0.098	–	–	–	–	–	–
Cooper (Cu) ppm	0.523 ± 0.176	–	–	–	–	1.16–5.14	–
Turbidity, NTU	4520 ± 875	5700	–	–	–	–	–
Temperature, °C	49 ± 5	–	–	–	–	26.7–35.7	–

^aWastewater characteristics for Section 1, corresponding to Burning Sector.

^bWastewater characteristics for Section 4, corresponding to Mercerizing Sector.

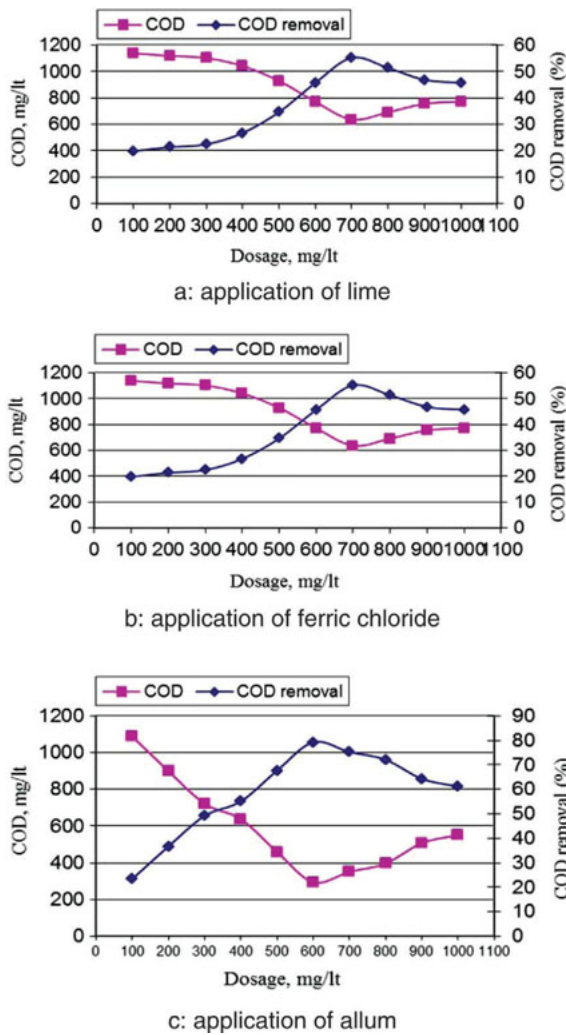


Fig. 1. Effect of coagulants dosage on COD removal (initial COD, 1420 mg l⁻¹).

the COD of the textile wastewater can be observed. The initial COD concentration was 1420 ± 267 and must be noted that the pH in this point has not be adjusted. The implementation of lime (Fig. 1a) up to 700 mg l⁻¹ that gives a maximum COD removal of 55.2 % (COD 505.06 mg l⁻¹). For Ferric Chloride the optimum dosage is 600 mg l⁻¹ that gives a maximum COD removal of 69.3 % (COD 585.26 mg l⁻¹) while for alum the optimum dosage is 600 mg l⁻¹ that gives a maximum COD removal of 79.3 % (COD 628.04 mg l⁻¹).

3.2. Color removal relating to dosage of coagulant

In Figs. 2a–c the effect of the dosage of lime, ferric chloride and alum respectively in the color reduction and % color removal of the raw effluent is presented. Generally, the color removal is increased with the addition of the coagulant. It must be also noted that for small

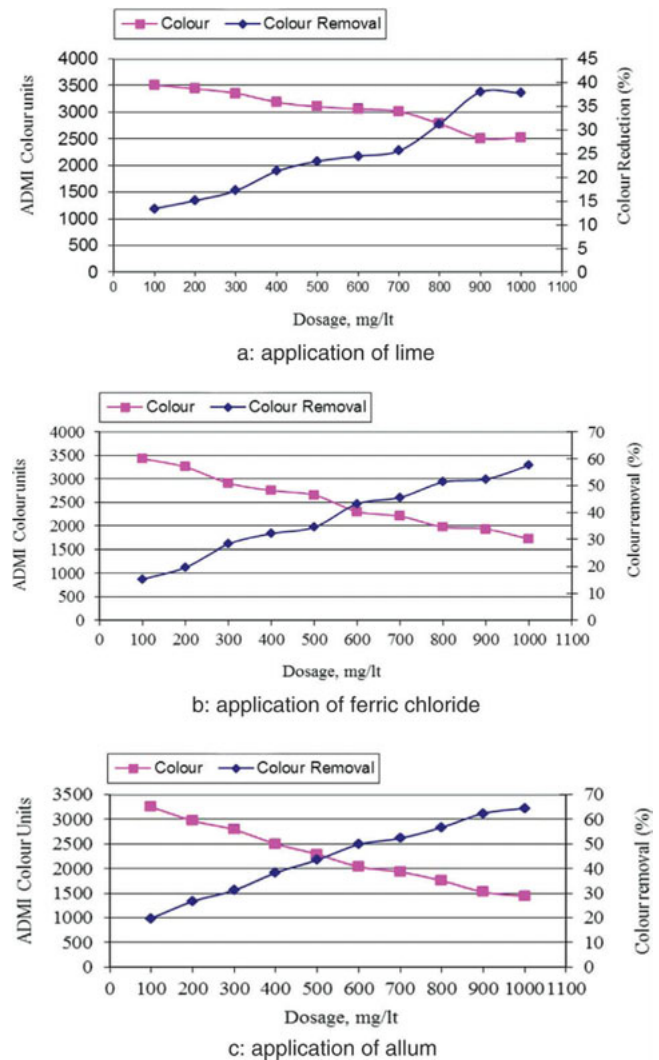


Fig. 2. Effect of coagulants dosage on color removal (initial color 4053 ADMI units).

dosages of the coagulants (especially below 500 mg l⁻¹) color removal is rather low. Also, color decreased in lower percentage than COD. The removal color using lime were limited and up to 38% using 900 mg l⁻¹ of coagulant. 64.5 % were the removal of color using alum in the highest while for the same dosage the removal efficiency of color using ferric chloride were up to 57.6%.

3.3. Influence of pH on COD removal

Figs. 3a–c presents the effect of pH for the COD reduction and % removal for the usage of lime, ferric chloride and alum. The optimum pH for the maximum COD removal was 7.5 for lime and with final COD 391.2 mg l⁻¹ (72.45%) (Fig. 3a), while the dosage was at 700 mg l⁻¹. The optimum pH for the maximum COD removal was 4.5 for ferric chloride and with final COD 238.56 mg l⁻¹

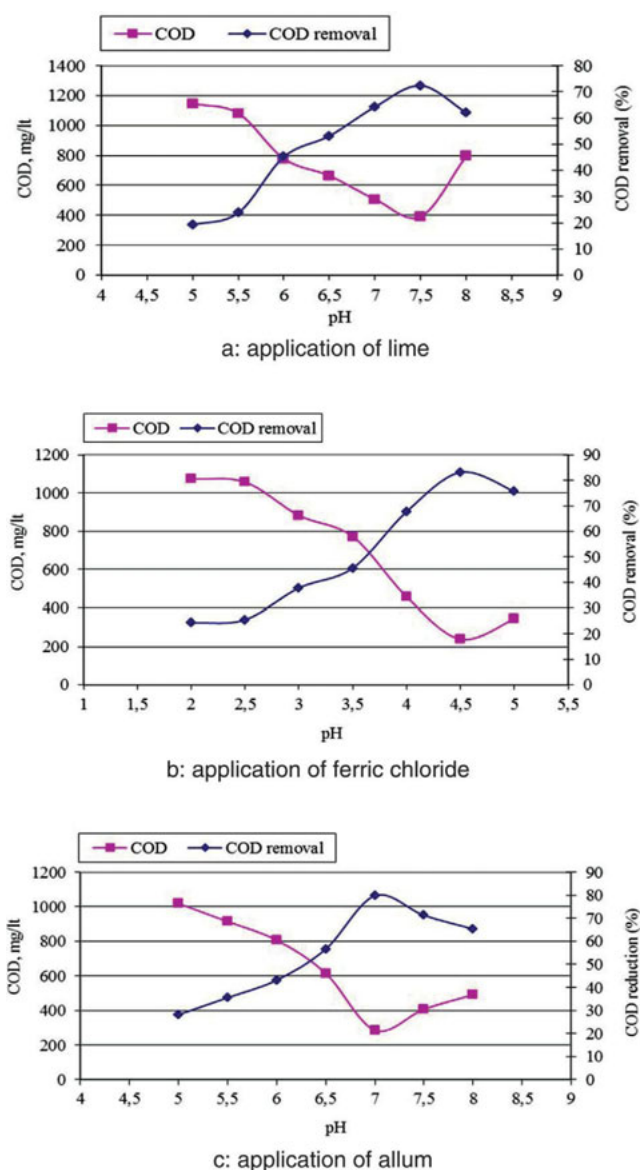


Fig. 3. Effect of pH on COD removal for the best dosage of coagulants (initial COD 1420 mg l⁻¹).

(83.2%) (Fig. 3b), while the dosage was at 600 mg l⁻¹. The optimum pH for the maximum COD removal was 7 for alum and with final COD 286.84 mg l⁻¹ (79.8%), while the dosage was at 600 mg l⁻¹.

4. Discussion

With exception of sodium aluminate, all common iron and aluminum coagulants are acid salts and, therefore, their addition lowers the pH of the treated water. Depending on the influent's pH and alkalinity (presence of HCO₃⁻, CO₃²⁻, and OH⁻), an alkali, such as lime or caustic, may be required to neutralize the pH depression

of the coagulant. This is important because pH affects both particle surface charge and floc precipitation during coagulation. The optimum pH levels for forming aluminum and iron hydroxide flocs are those that minimize the hydroxide solubility. However, the optimum pH for coagulating suspended solids does not always coincide with the optimum pH for minimum hydroxide floc solubility.

From the above results, it is obvious that pH adjustment, play significant role, in the COD removal for all the coagulants. Furthermore, from the experimental results it can be said that the optimum results for COD removal are given by the usage of alum while the usage of lime don't presented with satisfaction result. This is because Al³⁺ and Fe³⁺ ions that are added to the effluent are more efficient and effective in charged neutralization compared with lime because of their trivalent charge. It is important to note that the coagulation process is achieved when colloidal particles are destabilized involving charge neutralization. Furthermore, coagulation takes place from the hydrolysis products of the Al³⁺ and Fe³⁺ ions which aggregate into large aluminum and iron hydroxide flocs [18]. When alum is used the higher surface area of the aluminum hydroxide flocs enables higher % COD removal efficiencies. The decrease in the COD upper an optimum dose of each coagulant can be explained in terms of the peptization of the precipitate. In reverse series the best results from our study was given from alum followed by ferric chloride and then from lime.

One of the main significant problems regarding textile waste-waters is the colored effluent. The colored effluent contains visible pollutants. The primary concern about effluent colour is not only its toxicity but also its undesirable aesthetic impact on receiving waters. The colour of the effluent discharges into receiving waters affects the aquatic flora and fauna and causes many water borne diseases. Some of the dyes are carcinogen and others after transformation or degradation yield compound such as aromatic amines, which may carcinogen or otherwise toxic. Regarding the color reduction it can be seen that there is a continuous increase in the % reduction with the increase of the coagulant dosage. Again best results are given by the usage of alum and lime seems to not be very effective in de-colourizing textile wastewaters. The color reduction of the textile wastewater with the usage of the three coagulants was rather moderate. But it can not be said that the reduction was negligible. The characterization depends on the standards and targets than must be achieved.

Generally, it is rather difficult to treat textile effluent because the industry (and/or the processing) produces multi-component wastewater. The dye contained in the effluent can vary daily and even hourly. The hot and strongly coloured wastewater contains large amount of

suspended solids, high COD concentration and greatly fluctuating pH which can be difficult to be treated. Hundreds of small scale dyeing industries are facing closure since they are not treating their effluent as it is not economical [19]. Implementation of coagulants for small industries could be an effective and economical method.

5. Conclusions

The coagulation method is an easy and relatively inexpensive method for the treatment of textile wastewaters. Generally, it provides acceptable results regarding COD (especially with pH adjustment) and colour reduction. Although, the production of sludge may be a disadvantage for this method, sludge's can proceed to incineration plant or to cement industry. Coagulation can be used as a pretreatment method in combination with some more efficient, but also more expensive treatment methods, when an extremely efficient treatment method for of such wastes is required. In such a way the overall treatment cost can be reduced so, as the method can be feasible. In any case the applicable coagulant in the optimum dose must be used, for the maximum efficiency of the coagulation process which is a very important step for the treatment of this kind of waste.

References

- [1] K. Lacasse and W. Baumann, *Textile Chemicals. Environmental Data and Facts*, Springer, New York (2006).
- [2] O. Li Rosi, M. Casarci, D. Mattioli and L. De Florio, Best available technique for water reuse in textile SMEs (BATTLE LIFE Project), *Desalination*, 206 (2007) 614–619.
- [3] M.M. Aslam, M.A. Baig, I. Hassan, I.A. Qazi, M. Malik and H. Saeed, Textile wastewater characterization and reduction of its COD and BOD by oxidation, *EJEAFChe*, 3 (2004) 804–811.
- [4] I. Bisschops and H. Spanjers, Literature review on textile wastewater characterization, *Environ. Technol.*, 24 (2003) 1399–1411.
- [5] M.C. Venceslau, S. Tom and J.J. Simon, Characterization of textile wastewaters—a review, *Environ. Technol.*, 15 (1994) 917–929.
- [6] World Bank, Environmental, Health, and Safety Guidelines for Textile Manufacturing, International, Finance Corporation, World Bank Group (2007), Online at: [http://www.ifc.org/ifcext/sustainability.nsf/AttachmentsByTitle/gui_EHSGuidelines2007_TextilesMfg/\\$FILE/Final++Textiles+Manufacturing.pdf](http://www.ifc.org/ifcext/sustainability.nsf/AttachmentsByTitle/gui_EHSGuidelines2007_TextilesMfg/$FILE/Final++Textiles+Manufacturing.pdf).
- [7] V. Golob, A. Vinder and M. Simonič, Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents, *Dyes Pigments*, 67(2) (2005) 93–97.
- [8] P. Kumar, B. Prasad, I.M. Mishra and S. Chand, Treatment of composite wastewater of a cotton textile mill by thermolysis and coagulation, *J. Hazard. Mater.*, 151(2–3) (2008) 770–779.
- [9] J.E. Van Benschoten and J.K. Edzwald, Chemical aspects of coagulation using aluminum salts-I (and II), *Water Res.*, 24 (1990) 1519–1526.
- [10] N. Koprivanac, G. Bosanac, Z. Grabaric and S. Papic, Treatment of wastewaters from dye industry, *Environ. Technol.*, 14 (1993) 385–390.
- [11] E. Lefebvre and B. Legube, Iron (III) coagulation of humic substances extracted from sulfate waters: Effect of pH and humic substances concentration, *Water Res.*, 24 (1990) 591–603.
- [12] APHA, AWWA-WPCF, Standard methods for the examination of water and wastewater. 10th ed., American Public Health Association, Washington, DC (1995).
- [13] M. Kobya, O. Taner Can and M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, *J. Hazard. Mater.*, B100 (2003) 163–178.
- [14] I.-I. Savin and R. Butnaru, Wastewater characteristics in textile finishing mills, *Environ. Eng. Manage. J.*, 17(6) (2008) 859–864.
- [15] H. Seif and M. Malak, Textile wastewater treatment, Sixth International Water Technology Conference, IWTC (2001), Alexandria, Egypt, pp 608–614.
- [16] R.O. Yusuff1 and J.A. Sonibare, Characterization of textile industries' effluents in Kaduna, Nigeria and pollution implications, *Global Nest Int. J.*, 6(3), (2004) 212–221.
- [17] A. Dulov, N. Dulova and M. Trapido, Combined physicochemical treatment of textile and mixed industrial wastewater, *Ozone Sci. Eng.*, 33 (2001) 285–293.
- [18] I. Licso, Realistic coagulation mechanisms in the use of aluminum and iron (III) salts, *Water Sci. Technol.*, 36 (1997) 103–110.
- [19] Rao. B. and V.V. Rao Ram Mohan, Adsorption studies on treatment of textile dyeing industrial effluent by fly-ash, *J. Chem. Eng.*, 116(1) (2006) 77–84.