Colour Removal from Biologically Treated Textile Dyeing Wastewater with Natural and Novel Pre-Hydrolysed Coagulants

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ABSTRACT: In this paper, natural (chitosan and starch) and novel pre-hydrolysed coagulants (PACl, PAFC, PFS and PFC) were performed with coagulant aid for colour removal from a biologically treated textile wastewater including multiple dyes (indigo and reactive). According to the experimental results, optimum coagulant dosages which provide the best colour removal for PACl, PAFCl, PFS (%10) and PFCl (%10), were determined as 80 mg/L, 10 mg/L, 3 mg/L and 40 mg/L, respectively, at pH 4 and pH 6,98 (natural pH of studied wastewater, pHnww). Maximum colour removal was determined as 97% for PAFCl, minimum removal was 23% for PFCl at pH 4, while it was calculated as 75% and 52% at pHnww. COD removal was observed as 45% at pH 4 and 55% at pHnww for maximum colour removal. Sludge production rate was measured as 71 kg/d while this rate was found as 60 kg/d at pHnww. On the other hand colour removal efficiencies were determined in the range of 55-88% at pHnww and pH 3 for chitosan while it was calculated as 52% for starch at pHnww and pH 9. According to the results, PAFCl and chitosan were found as the best coagulants for colour removal of investigated textile wastewater. According to the economic analysis results, the best colour effiency were found as 97% with PAFCl and the second best colour removal were found as 88% with Chitosan. Due to lower sludge production than PAFCl and lower chemical costs; Chitosan can be considered as a reasonable alternative for this wastewater.

Keywords: Natural and Novel pre-hydrolysed coagulant, Colour removal, Textile wastewater, PAFCl, Chitosan.

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INTRODUCTION

Textile industry use huge amount of water and complex hazardous chemicals at various processing stages of the textile materials. The unused parts of these chemicals are discharged as wastewater that is high in temperature, biochemical oxygen demand (BOD), chemical oxygen demand (COD), colour, pH, turbidity and toxic chemicals. Conventional chemical and biological treatment methods are widely applied in the textile and other coloured wastewater. Although these systems are succesfull to remove the conventional parameters, textile influents containing especially different types of dyes which have high molecular weight and complex structures, show very low biodegradability in terms of colour removal and so, they are insufficient to provide the discharge standarts for receiving bodies (1). In this context, it is very important to decide which approach is the most suitable for colour removal from textile wastewater in terms of environment. Generally, wastewater containing dyes is difficult to treat due to the nature of the dye. Most of the dyes are stable against to light and oxidizing agents and are resistant to biologic degradation. The most used technologies to treat wastewater containing dyes are based on physical–chemical and/or biological processes. Coagulation and sedimentation processes are known to be effective in eliminating the colours of insoluble dyes such as disperse ones. However, these are not conditions for soluble dyes including reactive dyes (2). The well-known conventional coagulants such as alum, polyaluminum chloride, iron(II) sulfate and lime are widely used in textile wastewater treatment. More than 90% of colour removal from acid dyes could be achieved by activated carbon. However, it is not effective coagulant for basic and direct dyes (3). Chemical coagulation has a complex structure involving various interacted parameters, therefore it must be defined how well coagulant will function under given conditions. On the basis of colour removal, chemical coagulants can be categorised as hydrolysing metallic salts, pre-hydrolysing metallic salts and synthetic cationic polymers, respectively (4). Recently, the usage of natural (chitosan, starch derivatives, guar gum, tannins, alginates exct.) and novel hydrolysed polymers (polyaluminium chloride (PACl), polyaluminium ferric chloride (PAFCl), polyferrous sulphate (PFS) and polyferric chloride (PFCl)) in wastewater treatment application have increased rapidly (1,5,6). It is reported in the literature that these polymers are more efficient than conventional inorganic coagulants for especially colour removal due to the synergistic effect of two different coagulant substances in a single substance (6). The literature studies have reported that novel pre-hydrolysed coagulants such as polyaluminium chloride (PACl), polyaluminium ferric chloride (PAFCl), polyferrous sulphate (PFS) and polyferric chloride (PFCl) have an advantage that good colour removal even at low temperature. Another advantage of these coagulant is to produce lower volume of sludge compared to conventional coagulants. In this context, the effectiveness of various novel pre-hydrolysing coagulants for the treatment of textile wastewater have been studied in the literature recently. These studies mostly reported that both they don't need pH correction, additional coagulant aid etc. (1,4,7). When the literature studies done with PACL are examined; it has been found that PACl provides stronger and rapidly settleable floc formation, which causes faster flocculation than that of alum at the same dose (7,8). Studies, run in textile wastewaters with PAFCl are very limited in the literature. In the study performed by Gao et al. in 2001, it was found that PAFCl is more effective in colour and turbidity removal than PACl and PFS for the wastewater of the petrochemical industry at pH 7.0-8.4. It is shown that floc formation occured faster than the other coagulants. The coexistence of aluminum and iron ions in PAFCl has been found to result in faster floc formation, sedimentation and hence more efficient colour removal (8). In a study conducted by Wang *et al*. (2008) on textile wastewater with PFS; in the case of 150 mg/L PFS applied to wastewater at pH 9, it was found that 71% COD, 56% BOD, 62% AKM and >50% colour removal were achieved (9). When literature studies done with PFCl are examined; in studies published by Wang *et al*. in 2010, ferric chloride ($FeCl_3$), PFCl and polydimethyldiallylammonium chloride (PDMDAAC) flocculants in textile wastewaters were compared for colour removal. It has been found that the combined use of the flocculants in the study gives more successful results. It has been reported that the combination of $FeCl_3$ - PDMDAAC and PFCl - PDMDAAC is more effective in colour removal than conventional use (10). A study done by Chen et al. for a synthetic dyed textile wastewaters in 2010, PFCl and polyamine (EPI-DMA) were investigated for colour removal and flocking performance at different concentrations. Colour removal for direct yellow 201 and remazol red 24 were obtained as 98%and 19% with PFCl at pH 7.5. It was found that in the combination of PFCl / EPI-DMA, the colour removal were found 97.5% for remazol red 24 and direct yellow 201 at pH 6.0 and flock formation has been found to give better results (11). In the study conducted by Wei et al., the effects of different dosages of PFCl/PDMDAAC combinations on the colour removal and flocculation dynamics of reactive and disperse dyeing textile wastewaters were investigated. 60% of reactive dyes, 95.5% of colour removal in disperse dyes and the highest rate of floc formation were determined with 30 mg/L PFCl/PDADMAAC application (12).

Many natural plant and non-plant derived polymers such as chitosan, starch, guar gum, arabic gum, moringa, tannin, cactus etc. are known as natural coagulants. There are limited studies carried out with starch for coagulation of industrial wastewater. In a study conducted by Hasçakır in 2003 with starch coagulation; 85-90% and 20%

COD removal have been achieved for paper industry wastewater and domestic wastewater, respectively. In the same study, 70-75% COD removal and 30-35% COD removal in domestic wastewater were detected when starch was used as a flocculant together with alum, lime and ferric chloride, but no study was made on the formation and amount of sludge (13). Chitosan is obtained from the fleece material based on the shells of red-crusted crabs and shrimps and proved an adsorbent and/or coagulant characteristics. Chitosan has high cationic charge density with long polymer chains leading to bridging of aggregation and precipitation behave as a biological cationic polymer. Numerous works have demonstrated that chitosan can be a potential alternative to conventional coagulation/flocculation application for waste water treatment to remove both particulate and dissolved substances. However, more studies are required to optimize the process. Sanghi and Bhattacharya (2005) showed that chitosan is very effective as a coagulant aid to remove acidic and direct dyes. They also reported that reactive dyes with anthraquinone groups were the most difficult to remove with chitosan and PAC (14). Gandjidoust *et al.* (1997) reported that chitosan resulted in the higher removal in both colour and TOC than synthetic polymers (poly(acrylmide) or PAM, poly(ethyleneimine) or PEI) and a chemical coagulant (alum) (15). Similar results were reported by Rodrigues et al. (2008) and Wang *et al.* (2007) for the treatment of pulp and paper mill wastewater. These groups have also proposed modified chitosan-based biopolymers as adsorbents and/or coagulants for the removal of SS, COD and colour from pulp and paper mill effluent (16, 17). In addition, these coagulants, which will not interfere with biological treatment due to the fact that the coagulant residue can serve as a nutrient for microorganisms and novel properties of natural coagulants having the biodegradable nature of non-toxic biodegradable properties, can be regarded as promising coagulant and coagulant aid for the treatment of textile wastewater, especially for the first stage.

The aim of this study is to evaluate the colour removal efficiency of biologically treated textile dyeing wastewater, including multiple dyes (indigo and reactive), with natural and novel pre-hydrolysed coagulants and to describe optimum conditions (pH, coagulant dosage, sludge volume etc.) based on the economically achievable best removal efficiency.

MATERIAL AND METHODS

Materials

This study was carried out in the wastewater treatment system treating denim washing (70%) and reactive dyeing (30%) wastewater located in Çorlu town of Tekirdağ. Treatment system has a 1500 m^3/d capacity composed of physical and biological treatment units including conventional activated sludge processes. Treated wastewater has been discharged in a receiving body called Sinanlı stream. Experimental studies were carried out on treated wastewater samples to characterize wastewater for one year. For wastewater characterisation; between 2013/ November-December and 2014/January, daily composite samples were taken from the biological treatment effluent, which were called 'raw wastewater' in chemical experimental study results.

Coagulants and Coagulation/ Floculation test procedure (Jar Test)

All natural and novel pre-hydrolysed coagulants were supplied as analytical grade. Only PFCl was prepared according to the method used by Jincheng Wei *et.al*. (18). All coagulation/ flocculation experiments were conducted in one liter glass beakers using a conventional Jar–test apparatus (VELP Scientifica, FC6S) equipped with four beakers. 1000 mL stock solutions of each polymer were prepared 10 % w/w. 1 mL (2 mg/L) anionic polyelectolite was used as coagulant aids for each coagulant. The sollutions were stirred rapidly at 200 rpm for 2 min during the addition of coagulants, followed by slow stirring at 45 rpm for 15 min and settling for 30 min. After settling, supernatant samples were collected and filtered using coarse filter for further analysis. Optimum conditions were assessed for colour and COD removal before treatability experiments were started. Jar test trials were made at efficient pH intervals (acidic, basic and real ww), mixing rate and flocculant dosage which is determined in treatability pre-studies for each coagulant. The pH of the samples were adjusted to acidic and basic conditions by adding 1N HCl or NaOH solutions for all coagulants. After then, supernatant and sludge characterisation were carried out on the samples for the determination of best options.

Analytical Methods

All analyses were performed according to the standard methods [Standart Methods, 1998] except COD and colour parameters. The COD and colour were measured according to ISO 6060 Method [ISO 6060, 1986] and ISO 7887 method [ISO 7887, 1987], respectively. The adjustment of pH was carried out using a (WTW pH315i) pH meter. The colour of the supernatant after jar test was determined by the spectral absorption coefficient (SAC) method. Percentage of SAC removal was calculated based on absorbance measurements by the spectrophotometer at three different wavelengths (λ = 436, 525 and 620).

RESULTS AND DISCUSSION

Effluent Characterisation

Wastewater characterisation is given at Table 1. It shows that colour parameter as a pollution parameter does not achieve the discharge criteria defined in the European Standard EN ISO 7887 for receiving environment although organic content and pH values are enough low for receiving body. So, it needs to further chemical treatment to achive the discharge standarts determined in Turkey.

Table 1: Wastewater characterisation of investigated treatment plant.

Parameters	Unit	Raw	Effluent	Discharge Criteria**
Total COD	mg/L	495	106	300
Soluble COD (0,45μ)	mg/L	450	80	-
Suspended Solid (SS)	mg/L	85	6	100
Conductivy	μmho/cm	-	2843	-
Colour 436 nm	CN*	-	26,2	7
525 nm	CN*	-	23,3	5
620 nm	CN*	-	23,7	3
pH	-	6,3	6,98	6-9

*CN: Colour number, (m^{-1}) **WPCR: Water Pollution Control Regulation, *** discharge criteria defined in the European Standard EN ISO 7887 for receiving environment.

Jar Test results

Optimum conditions were determined for colour and COD removal, and sludge production were evaluated under these optimum conditions. Comperative results of jar tests were given at Table 2. According to the jar test results, carried out at the determined optimum dosages, maximum colour removal was calculated as 97% for PAFCl, while minimum removal determined as 23% at pH4 with. For maximum colour removal, sludge production rate was measured as 71 kg/d while this rate was found as 60 kg/d at pHnww. On the other hand, COD removal was measured as 55 % at this maximum colour removal. Maximum colour removal was calculated almost close together at pHnww as ≈75% for PAFCL and PACl. Tun et all. (2007) studied at pH:7.5 and similar colour removal efficiencies (75%) have been obtained with the dose of PACl as high as 800 mg/L (19).

Table 2: Comperative removal efficiencies and sludge production.

<table>
<tr><td colspan="12">COLOUR REMOVAL</td></tr>
<tr><td colspan="2">80 mg/L PACl (10%)+ 1 ml (1/500) A.P.E</td><td colspan="2">10 mg/L PAFCl (10%) + 1 ml (1/500) A.P.E</td><td colspan="2">3 mg/L (10%) PFS+ 2 ml 1/500 A.P.E</td><td colspan="2">40 mg/L PFCl+ 1 ml 1/500 A.P.E</td><td colspan="2">600 mg/L Starch + 0.3 ml 1/500 A.P.E</td><td colspan="2">4.5 mg/L chitosan+ 0.1 ml 1/500 A.P.E</td></tr>
<tr><td>pH4</td><td>pHnww</td><td>pH4</td><td>pHnww</td><td>pH4</td><td>pHnww</td><td>pH4</td><td>pHnww</td><td>pHnww</td><td>pH9</td><td>pHnww</td><td>pH3</td></tr>
<tr><td>76%</td><td>74%</td><td>97%</td><td>75%</td><td>79%</td><td>48%</td><td>23%</td><td>52%</td><td>52%</td><td>52%</td><td>55%</td><td>88%</td></tr>
<tr><td colspan="12">COD REMOVAL</td></tr>
<tr><td colspan="2">80 mg/L PACl (10%)+ 1 ml (1/500) A.P.E</td><td colspan="2">10 mg/L PAFCl (10%) + 1 ml (1/500) A.P.E</td><td colspan="2">3 mg/L (10%) PFS+ 2 ml 1/500 A.P.E</td><td colspan="2">40 mg/L PFCl+ 1 ml 1/500 A.P.E</td><td colspan="2">600 mg/L Starch + 0.3 ml 1/500 A.P.E</td><td colspan="2">4.5 mg/L chitosan+ 0.1 ml 1/500 A.P.E</td></tr>
<tr><td colspan="2">pHnww</td><td>pH4</td><td>pHnww</td><td>pH4</td><td>pHnww</td><td>pH4</td><td>pHnww</td><td>pHnww</td><td>pH9</td><td colspan="2">pH3</td></tr>
<tr><td colspan="2">53%</td><td>55%</td><td>45%</td><td>47%</td><td>67%</td><td>67%</td><td>63%</td><td>60%</td><td>65%</td><td colspan="2">56%</td></tr>
<tr><td colspan="12">SLUDGE PRODUCTION (kg/day)</td></tr>
<tr><td colspan="2">80 mg/L PACl (10%)+ 1 ml (1/500) A.P.E</td><td colspan="2">10 mg/L PAFCl (10%) + 1 ml (1/500) A.P.E</td><td colspan="2">3 mg/L (10%) PFS+ 2 ml 1/500 A.P.E</td><td colspan="2">40 mg/L PFCl+ 1 ml 1/500 A.P.E</td><td colspan="2">600 mg/L Starch + 0.3 ml 1/500 A.P.E</td><td colspan="2">4.5 mg/L chitosan+ 0.1 ml 1/500 A.P.E</td></tr>
<tr><td>pH4</td><td>pHnww</td><td>pH4</td><td>pHnww</td><td>pH4</td><td>pHnww</td><td>pH4</td><td>pHnww</td><td>pHnww</td><td>pH9</td><td>pHnww</td><td>pH3</td></tr>
<tr><td>56</td><td>79</td><td>71</td><td>60</td><td>31</td><td>14</td><td>123</td><td>148</td><td>509</td><td>560</td><td>123</td><td>24</td></tr>
</table>

Maximum COD removal efficiencies were obtained at pHnww with PFS and PFCl as 67% and 63%, respectively. Minimum COD removal was determined as 45% at the same pH. Wang et al. (2008) obtained similar results with high dose of PFS (150 mg/L) at pH 9. Wang et al. (2008) studied with denim washing wastewater and obtained 71% COD, 56% BOD and 50 % colour. In our study, similar colour removal results were obtained at pHnww, while relatively higher colour removal (79%) has been obtained with as low as 3 mg/L of PFS dose at pH 4 (9).

Comperative results obtained in present study were given in Fig. 1-6.

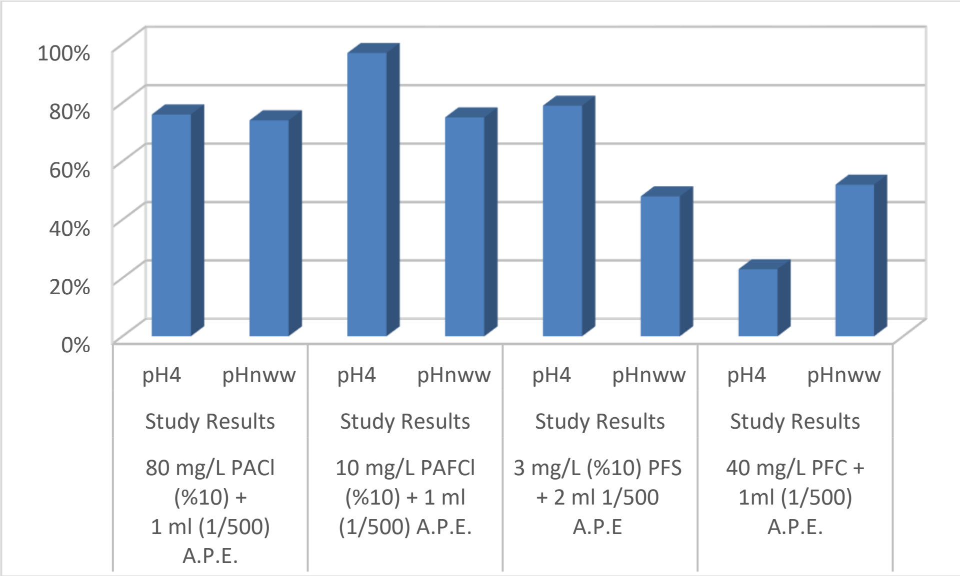

Figure 1: Comperative Colour Removal Results Obtained with Pre-hydrolized Metal Salts.

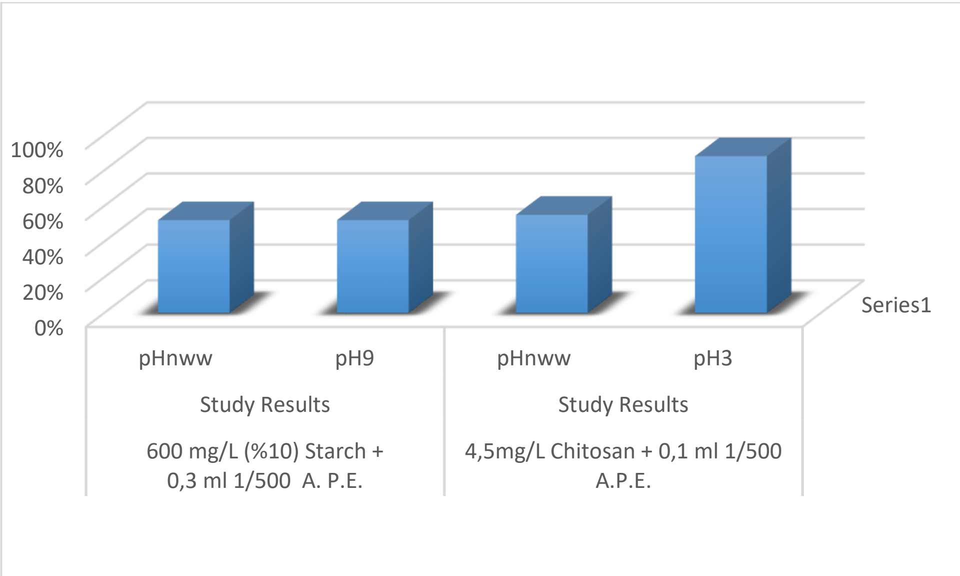

Figure 2: Comparative Colour Removal Results Obtained with Natural Coagulant.

Colour removal efficiency was determined as 52 % for PFCl at pHnww. Chen et al. (2010) evaluated yellow 201 and remazol red removal from synthetic wastewater at pH 7.5 and obtained 98% and 19% colour removal, respectively (11). Our results obtained with PFCl is relatively lower, can be attributed to usage of real wastewater. In addition, Wei et al. (2009) obtained 95.5 % of colour removal with disperse dye, while only 60% of colour removal can be achieved with reactive dye (12). Considering the reactive consistency of the given wastewater used in our study, our results are similar to the literature.

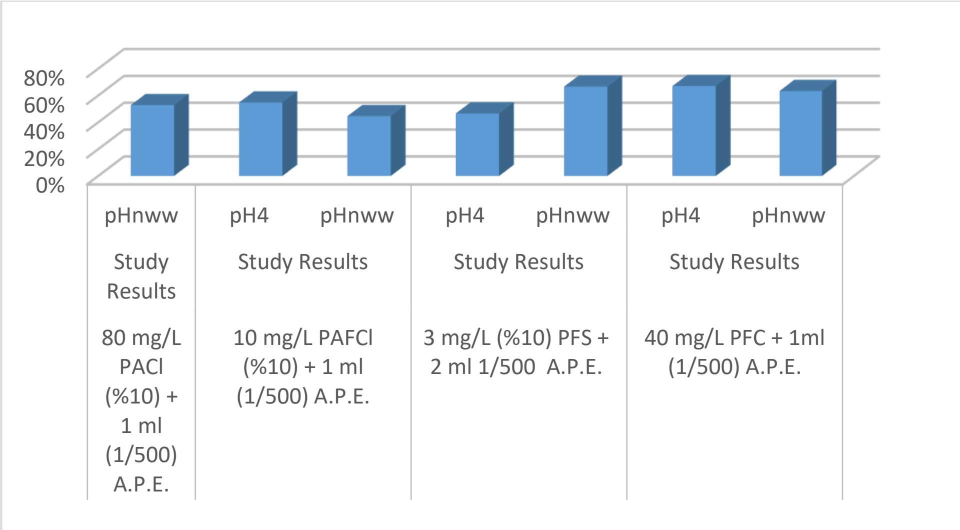

Figure 3: Comperative COD Removal Results Obtained with Pre-hydrolized Metal Salts.

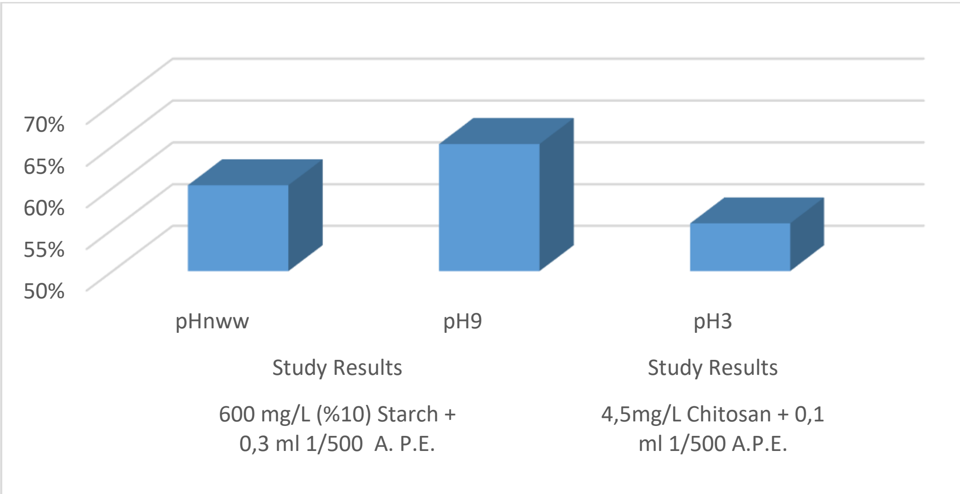

Figure 4: Comperative COD Removal Results Obtained with Natural Coagulant.

In this study 88% colour removal was obtained with 4,5 mg/L chitosan at pH 3. This removal rate obtained in accordance with the literature. Szygula et al. (2009) obtained 99% colour removal for Acid Blue 92 with 100 mg/L chitosan at pH 9 (20). Mahmoodi et al. (2011) reported 75% and 95 % colour removal for Acid Green 25 and Direct Red 23 at pH 2 (21).

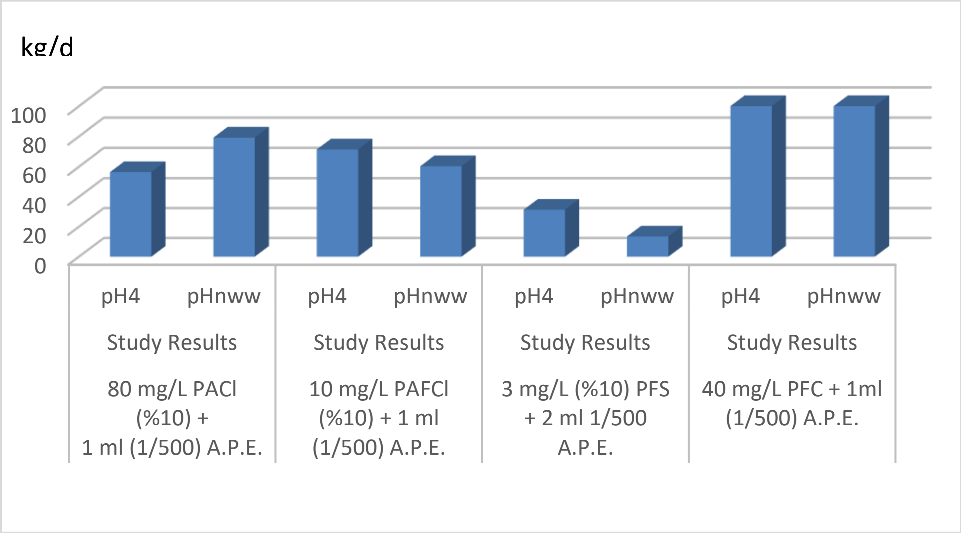

Figure 5: Comperative Sludge Production Potential Obtained with Pre-hydrolized Metal Salts.

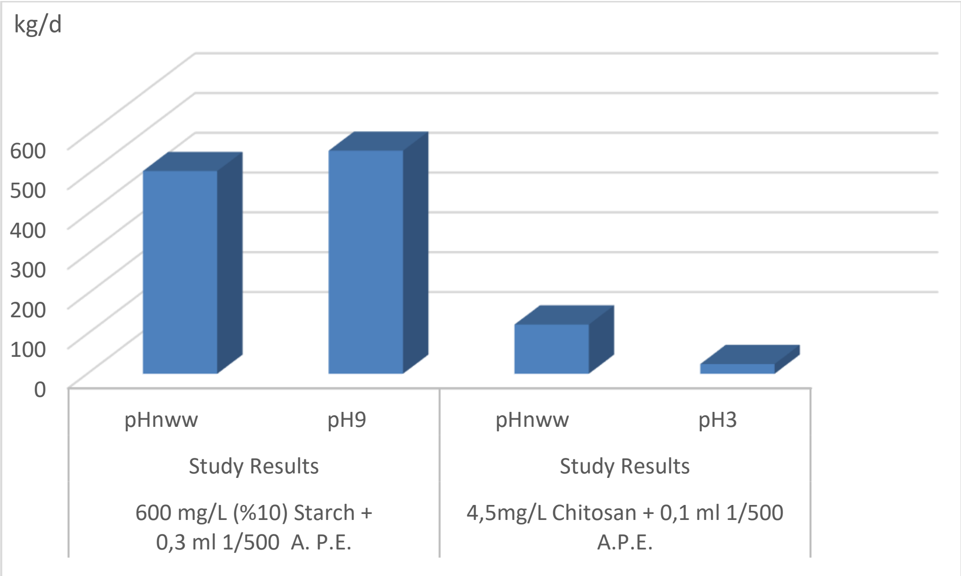

Figure 6: Comperative Sludge Production Potential Obtained with Natural Coagulants.

On the basis of daily sludge production, maximum sludge production was observed for starch at pH 9, while minimum was measured for PFS at pHnww. While colour removal efficiencies were determined as 52% for starch both at pHnww and pH9, very important difference was found for chitosan between at pHnww and pH 3. However, although pH 3 seems very efficient condition for colour removal with chitosan, this efficiency range was found to be lower than the maximum removal efficiency obtained for PAFCl as novel-prehydrolysed coagulant and also after coagulation, there is need a neutralisation. It should be considered that this results in an increase in the operating cost.

Economic Analysis

According to the economic analysis results, daily cost with PACl was determined as 81 \$/d at pHnww. Daily cost were 81 \$/d at same pH, while it increased to 27 \$/d at pH 4 for PAFCl. This difference results from the addition of pH adjustment cost. Daily cost with PFS was found as 7 \$/d and 20 \$/d for pHnww and pH 4, respectively. While daily cost with PFCl is calculated as 16 \$/d and 29 \$/d for pHnww and pH 4, respectively. Starch produce 1 \$/d as coagulant cost, similarly chitosan produce 0,01 \$/d coagulant cost for pHnww, while, 14\$/d coagulant cost was calculated for chitosan at pH 3. As it clearly shown that most of the cost is originate from the requirement of pH adjustment. Pollutant removal may be the major criteria for the selection of appropriate coagulant, pH adjustment should not be excluded. Nevertheless, sludge disposal costs were excluded in this study, therefore this situation should also be considered for total cost.

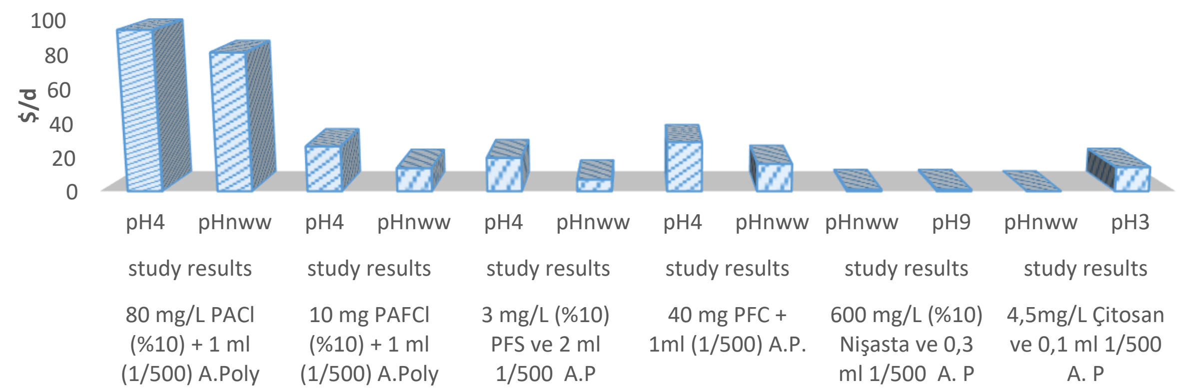

Figure 7: Comparative Coagulant Cost.

CONCLUSION

The effectiveness of various novel pre-hydrolysing coagulants (PACl, PAFCl, PFS and PFCl) for the treatment of textile wastewater have been studied in this study. Chitosan as a biological cationic polymer and as a natural coagulant, has also been investigated for textile wastewater. The results of this study may be drawn as follows:

- Maximum colour removal (97%) was obtained with PAFCl at pH 4, while PFCl gave the minimum colour removal (23%) at same pH. Chitosan yielded the second maximum colour removal as 88% at pH 3. 55% and 56 % COD removal was obtained at pH 4 and pH 3 for PAFCl and chitosan, respectively.

- Maximum COD removal (67%) was obtained with PFS and PFCl, at pHnww and pH 4, respectively.
- It was shown that PACl, PAFCl, PFS and chitosan caused considerably lower sludge production. It has been found that as novel pre-hydrolysed and natural coagulant materials, PAFCl and chitosan are the best coagulants in terms of colour removal for investigated textile wastewater. Both of these coagulant are able to provide the receiving bodies discharge standards (for colour and COD removal efficiencies determined in Turkish regulations) at both natural and adjusted pH samples, like reported in the literature for textile wastewaters. Sludge production rates were measured for these coagulants as 60 kg/d and 24 kg/d, respectively. PFS gave minimum sludge production (14 kg/d) at pHnww, while maximum sludge production was observed with starch (560 kg/d) at pH 9.
- According to the economic analysis results, the best colour effiency were found as 97% with PAFCl and the second best colour removal were found as 88% with Chitosan. Due to lower sludge production than PAFCl and lower chemical costs; Chitosan can be assessed as the optimum chemical for this wastewater.
- When the operating cost is evaluated on the basis of daily coagulant requirement, PACl gave the maximum cost at pH 4. Minimum daily coagulant cost obtained as 0,01 $/d with chitosan for pHnww. PAFCl gave 14 $/d at natural wastewater pH.
- So, in the future, it is necessary to evaluate the cost of residual sludge disposal of both coagulants in order to be able to decide the most suitable colour removal method for investigated wastewater.

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