ISSN XXXX XXXX © 2017 IJESC

Research Article Volume 7 Issue No.6

Coagulation/Flocculation Process for Cationic and Anionic Dye Removal using Water Treatment Residuals

Siddharth Butani[1], Sachin Mane[2]
ME Student[1], Assistant Professor[2]
Department of Civil Engineering
D.Y. Patil College of Engineering, Akurdi, Pune, India

Abstract:
In this research, the potential of aluminum-based water treatment residual (WTR) discharged from the water treatment plant has been evaluated as a coagulant for color removal from cationic and anionic dye solutions. The sample of water treatment residuals (WTR) was collected from water treatment plant (Nigdi, Pune) where Poly Aluminum Chloride (PAC) is used as coagulant in the coagulation/flocculation process. The effects of initial pH, initial dye concentration and WTR dosage were studied. The results have shown that maximum color removal of 81.08, 77.88 and 72% for anionic dye and 94.54, 91.77 and 84.53% for cationic dye were obtained at initial dye concentrations of 25, 50 and 75mg/L, respectively, at pH 3.0 and WTR dose of 120mg/L. Although lower amount of WTR were required for the removal of dyes from wastewater, the reuse of WTR as a low cost material can offer several advantages such as higher efficiency of cationic an anionic dye color removal and economic savings on overall wastewater treatment plant operation costs. The study thus indicates that the reuse of water treatment residual would be an attractive option as a coagulant for the color removal.

Keywords: Anionic dye, Cationic dye, Coagulation/flocculation process, Color removal, Water Treatment Residuals

I. INTRODUCTION

A dye is a colored substance that has an affinity to the substrate to which it is being applied. Industries such as textile, leather, paper, plastics, etc., are some of the sources for dye effluents. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Textile dyes are classified under the categories of anionic, cationic and non-ionic dyes. Anionic dyes mostly include the direct, acid and reactive dyes. Acid dyes are water- soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Basic dyes are only the class of cationic dyes used in the textile industry. Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Basic dyes are also used in the coloration of paper. Non-ionic dyes refer to disperse dyes, which do not ionize in aqueous medium. It is estimated that about 15% of the total world production of colorants are lost in the synthesis and processing of colorant. Rapid developments of textile industries which use different type of dyes have resulted in severe water pollution. Wet processing operation during textile processing, i.e. desizing, scouring, bleaching, dyeing, printing, and finishing generate considerable amount of colored effluent due to consumption of large quantities of water at its different steps [1]. The discharge of highly colored untreated effluents from these industries is a major environmental problem especially in developing countries. The presence of even a small fraction of dyes in water is highly visible and it affects the aesthetic merit of streams and water resources. Unless and otherwise properly treated, dyes can also affect the photosynthetic activity in aquatic life significantly due to reduced light penetration and may also be toxic to certain forms of life due to presence of metals and chlorides in them. Over 100,000 commercially available dyes exist and more than 7×10^5 tonnes per year are produced annually. Further, the possible carcinogenic, mutagenic and/or allergenic effects of dyes have been established [2]. Most of the dyes have complex aromatic structure which makes them resistant to light, biological activity, photo-degradation, ozone and other degradative environments and hence complicating the selection of suitable methods for their removal. There is a constant need for the development of effective processes that can effectively remove the dyes from wastewater as the removal of dyes from the wastewater is considered as an environment challenge and also government legislations require textile wastewater to be treated. Various methodologies for treating dye bearing effluents have been reported in the literature. These include precipitation, coagulation/flocculation, adsorption, membrane filtration, ion exchange, reverse osmosis, advanced oxidation processes, and aerobic and anaerobic biological processes. These processes have shown varying degrees of dye removal. Adsorption techniques have lots of potential in the treatment of dye-containing waters when high performance and low-cost adsorbents are available [3]. Generally, advanced oxidation processes are advantageous for the removal of most dyes, but a common problem is their relatively high cost in large-scale utilization. Moreover, the possible formation of some more toxic intermediates is of greater concern. On the other hand, biological processes for dye removal have upper hand in concern with higher dye concentration and treatment time, though these processes are largely ineffective for color removal from wastewater due to poor biodegradability of some dyes. Coagulation/flocculation is one of the most effective chemical treatment methods for dye removal from industrial wastewaters, and is not based on the partial decomposition of dye compounds and thus no potentially harmful and toxic intermediates are produced. Although the use of coagulant for dye removal is applicable, huge amounts of chemical sludge are generated by treatment plants every day. The proper disposal, regeneration, or reuse of waste sludge has become a significant environmental issue. Also, it should be noted that such chemical treatment method (Coagulation/ flocculation process) incurs higher operational cost from the use of coagulants and the treatment and disposal of a large amount of chemical sludge generated during the process. While current sludge disposal methods may still suffice for the time being, the need for environmental sustainability and fiscal responsibility coupled with population increases will continually provide the drive towards beneficial reuse. Under these circumstances the idea of using the water treatment sludge generated from the water treatment plant may be favorable. A number of research works has been done particularly in recent years to study the reuse of WTR in many constructive ways either by recycling or by direct application in building and construction materials, use in water and wastewater treatment, and land-based application for soil improvement. A few studies have also been reported on the reuse of aluminum-and iron-based WTR for treating acid textile dyes. The present study examines the potential and effectiveness of aluminum-based WTR as an alternative coagulant for the removal of a cationic dye (Basicol Green CM) and anionic dye (Colocid Red MX) from water, which is widely used in textile industries. The effect of three parameters, namely, initial pH, WTR dosage, and initial dye concentration on color removal efficiency was studied.

II. MATERIALS AND METHODS

A. *Dyes*

Two commercially available dyes were selected to examine the color removal performance using PACS. The selected cationic dye was Basicol Green CM, having maximum absorption wavelength of 616 nm and anionic dye was Colocid Red MX, having maximum absorption wavelength of 453 nm. The anionic dye contains hydrazone group (=N-N-) in its molecules while cationic dye contains amide group (-N=) in its molecules.

B. *Synthetic dye solution*

Synthetic dye solution was prepared by dissolving cationic dye (Basicol Green CM) and anionic dye (Colocid Red MX) which are widely used in the textile industries. A stock dye solution of 1,000 mg/L was prepared in distilled water and it was diluted to the required concentrations.

C. *Water treatment residuals*

The WTR was collected from the coagulation/flocculation unit of a water treatment plant in Nigdi, Pune, India, where Poly Aluminum Chloride (PAC) is used as a coagulant. The collected sludge was stored at room temperature (27–30°C) in its original form and was used in its raw state. Elemental analyses of the dried PAC-based WTR were carried out by ICP (Element XR, Thermo Fisher Scientific, and Germany).

D. *Experimental Procedure*

A six-beaker jar test was used to simulate the coagulation/flocculation process. Each beaker contained 500 mL of the synthetic dye solution. WTR in its raw form was added as the coagulant. The WTR dosages were calculated based on dry weight. The standard coagulation procedure involved 2-min rapid mixing at 150 rpm, followed by 30-min slow mixing at 25 rpm, and 20-min settling. The three important parameters that affect coagulation process, namely, initial pH, WTR dosage, and initial dye concentration were varied in different experiments in specified ranges. The ranges for these parameters were selected based on the values reported in the literature and on the preliminary tests conducted. Initial pH of the samples was adjusted to a desired value by adding 0.1 N H_2SO_4 or NaOH using a pH meter (HACH HQ40D). The ranges of the three parameters used in the study are shown in Table 1. Color was measured using a VIS spectrophotometer (HACH DR3900) at a wavelength corresponding to the maximum absorbance as reported earlier in the paper for the cationic dye anionic dye used. Percentage of dye removal was calculated by the following equation (Eq. (1)):

$$\text{Colour removal (\%)} = (C_r - C_t) / C_r * 100 \quad (1)$$

where Cr and Ct are color concentration of raw and treated solutions, respectively.

Table.1. Ranges of Different Parameters Used In Study

Sr. No.	Parameter	Range
1.	Initial pH	3-11
2.	WTR dosage (mg/L)	20-120
3.	Dye concentration	25-75

III. RESULTS AND DISCUSSIONS

A. *Characteristics of WTR*

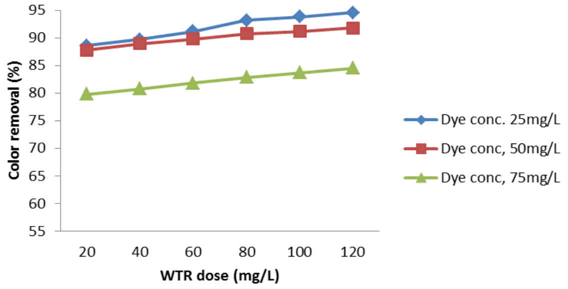
Important physicochemical characteristics of WTR collected are presented in Table 2. The WTR consists of 14.56 mg Al/g of dry mass and 21.20 mg Fe/g of dry mass. Other elements such as calcium, magnesium, and potassium were also present. WTR was slightly acidic (pH 6.75) with a solid content of 12.24%. Typical aluminum content in the range of 17.09–171.77 mg/g dry mass has been reported in the literature [4]-[6]. However, most of the values reported are for alum-based WTR while PACl-based WTR was used in the present study. In addition to aluminum, iron present in WTR also contributes to the coagulation process. The elemental composition of WTR will depend on the type of the coagulant used, raw water quality, and the dose of the coagulant.

Table.2. Physiochemical Characteristics of WTR

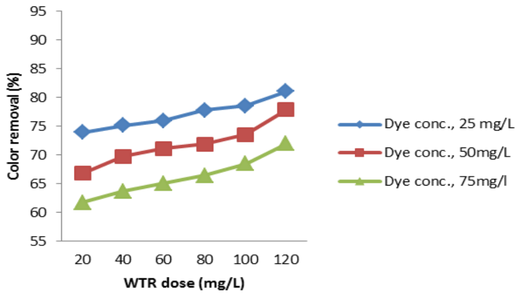
Sr. No.	Parameters	Result
1.	pH	6.75
2.	Solid Content(%)	12.24
3.	Calcium(mg/g of dry WTR)	5.20
4.	Magnesium(mg/g of dry WTR)	4.26
5.	Iron(mg/g of dry WTR)	21.20
6.	Aluminium(mg/g of dry WTR)	17.56
7.	Potassium(mg/g of dry WTR)	1.69

B. *Effect of water treatment residual dose*

Fig. 1 shows the effect of WTR dose on color removal at different initial dye concentrations. These tests were conducted at an initial pH of 3.0. It can be seen that the color removal increased with the increase in WTR dose and the highest color removal was obtained at a dose of 120 mg/L. The maximum color removal of 94.54, 91.77, and 84.53% for cationic dye and 81.08, 77.88 and 72.00 for anionic were obtained for initial dye concentrations 25, 50 and 75 mg/L, respectively. Similar trends of increase in color removal with the increase in coagulant dose were obtained using WTR as a coagulant on acidic and basic dyes, and a dye removal of 94.2% for basic dye and 86% for acidic dye was reported at a dose of 4.55 g/L with PACl-based WTR[7]. Further, previous studies on cationic and anionic dyes employing alum as coagulant reported color removal in the range of 80–90% at doses of 40–200 mg/L[8, 9], whereas with ferric salt as coagulant gave 75% color removal at a dose of 60 mg/L[9].



(a)



(b)

Figure. 1 Effect of WTR dose on color removal on different dye concentration (initial pH 3.0) (a) for cationic dye (b) for anionic dye

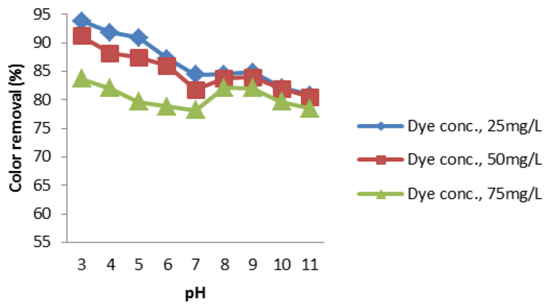
C. Effect of pH on color removal

The pH of the solution is one of the most important parameters affecting coagulation efficiency. Fig. 2 shows the color removal as a function of initial pH of the solution at a constant WTR dose of 100 mg/L. It is seen that there was a decrease in color removal with the increase in pH. Thus, maximum color removals of 93.8, 91.19 and 83.65% for cationic dye and 78.61, 73.58, and 68.46% for anionic dye were obtained at pH 3 for initial dye concentrations of 25, 50, and 75 mg/L, respectively, which were decreased to 84.37, 81.80, and 78.21 for cationic dye and 70.98, 62.78 and 62.26 for anionic dye at pH 7. However, color removal efficiency again increases marginally (nearly 1-4%) up to pH 9 and above pH 9 color efficiency decreases with increasing pH for both the dyes. Papic et al. [10] has stated that the pH should be between 3.5 and 5 for achieving higher color removal efficiency for red and green dyes. Shi et al. [11] has reported that the behavior of different aluminum species on color removal which are pH dependent, and coagulation efficiencies of poly aluminum chloride and alum tended to increase with decrease in pH and approached complete removal when pH was sufficiently lower. Lau et al. [12] reported that changes in pH during coagulation process due to the formation of Al(OH)3, which precipitate when the final pH was about 4 for alum. However, color removals were reduced at lower alum doses as pH value of 4 could not be achieved at lower doses. It was also seen that higher color removal was obtained in acidic conditions due to formation of Al^{3+} ions which were then attracted to anionic and cationic dye molecules. Several reports on utilizing aluminum salts for color removal described maximum yield of cationic and anionic dyes at lower pH range of 4–5.5, and 5.0–6.0 for poly aluminum chloride and alum, respectively. The surface charge of the coagulants (as related to the zeta potential measurements) is pH dependent, and can affect removal efficiency to some extent. Gadekar et al. [2] reported that in order to achieve color removal, the negative charges of dye molecules need to be sufficiently neutralized, thus at optimum pH dye particles retains net negative charges which facilitate the performance of cationic coagulants. Thus, charge neutralization could be considered as prerequisite condition for color removal of the dye. Structural stability of dye molecules was also affected by pH, and thus the color reduction.

D. Effect of initial dye concentration on color removal

Effect of dye concentration on color removal for cationic and anionic at different initial pH values between 3.0-11.0 at a WTR dose of 120 mg/L is presented in Fig. 3. It is seen that at each pH color removal was reduced with the increase in dye concentration. As presented in Fig. 1 maximum color removal was obtained at a lower pH of 3.0 and at this pH reduced color removal was obtained at higher initial dye concentrations. Similar results of reduced color removal with the increase in initial dye concentration at optimum pH have been reported for anionic as well as basic dyes with PACl and alum and also with WTR as coagulants [3][7]. This phenomenon may be due to the increase in dye aggregation and/or depletion of hydrolysis product of the coagulant [7].

(a)



(b)

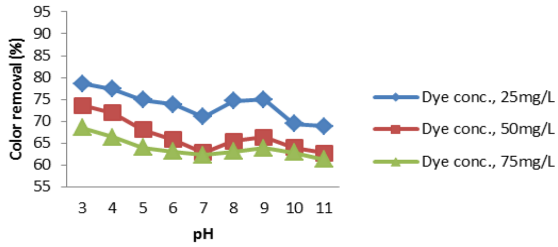
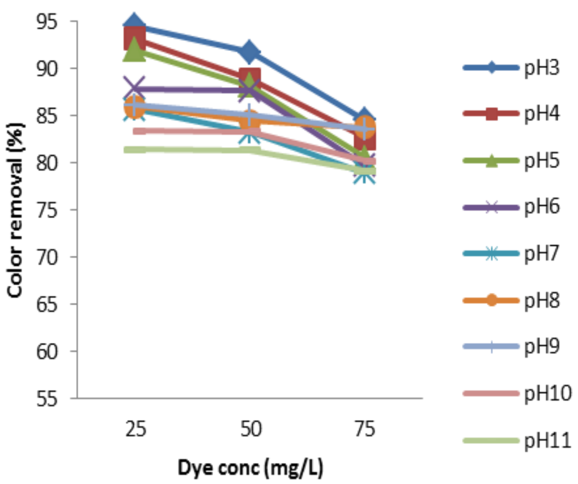


Figure.2. Effect of pH on color removal at different dye concentration (WTR dose 100mg/L) (a) for cationic dye (b) for anionic dye

(a)



(b)

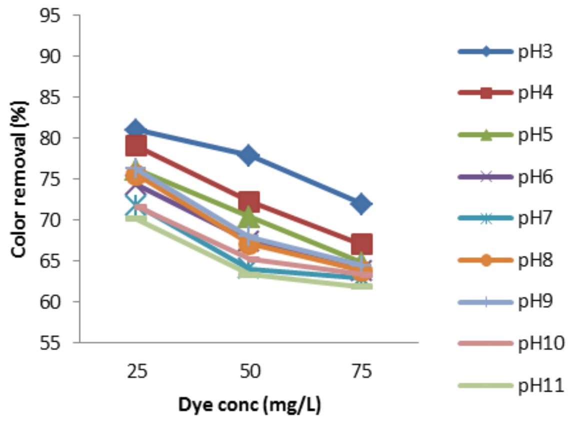


Figure.3. Effect of initial dye concentration on color removal (WTR dose 120mg/L) (a) for cationic dye (b) for anionic dye

IV. CONCLUSION

In this paper, coagulation/flocculation process was studied for the removal of cationic dye (Basicol Green CM) and anionic dye (Colocid Red MX) from the solutions by using WTR as a coagulant. The result of this study indicated that up to 94.54% for cationic dye and 81.08% for anionic dye could be obtained with WTR dosage of 120 mg/L and at an initial pH of 3. Color removal is greatly affected by pH of the system, with the lower pH showing higher color removal, however color removal increases marginally beyond pH 7 but it starts decreasing after pH 9. As lower amount water treatment residual was required for anionic and cationic dye removal, the reuse of WTR as a low-cost material can offer some advantages such as higher efficiency for both the dyes removal and economic savings on overall water and wastewater treatment plant operation costs. Therefore, the use water treatment residual can be considered as an appropriate alternative for conventional costly coagulants that are widely used in waste water treatment plants.

V. ACKNOWLEDGEMENTS

The authors would like to acknowledge Colortex India Pvt. Ltd., Surat, India for providing the dyes required for research work. The authors would also like to thank Mr. Sunil Bhagwani, Deputy Engineer, Pimrpi- Chinchwad Municipal Corporation Mr. Mahesh Gadekar, Research Scholar, SVNIT and Mr. Prashant Jagtap, Chemical house in-charge, Water Treatment Plant, Nigdi, Pune for guiding, co-opreating and providing the assistance required for completion of work.

VI. REFERENCES

[1]. M. Joshi, R Bansal, R Purwar, Colour removal of textile effluents, Indian Journal of Fibre & Textile Research, Vol. 29, June 2004, pp.239-259

[2].Mahesh R. Gadekar & M. Mansoor Ahammed, Coagulation/flocculation process for dye removal using water treatment residuals: modelling through artificial neural networks, ISSN: 1944-3994 (Print) 1944-3986.

[3].S.S. Moghaddam, A.M.R. Moghaddam, M. Arami, Coagulation/flocculation process for dye removal using sludge from water treatment plant: Optimization through response surface methodology, J. Hazard.Mater. 175 (2010) 651–657.

[4].A. Babatunde, Y.Q. Zhao, Constructive approaches toward water treatment works sludge management: An international review of beneficial reuses, Crit. Rev. Environ. Sci. Technol. 37 (2007) 129–164

[5].A.T. Nair, M.M. Ahammed, Coagulant recovery from water treatment plant sludge and reuse in post-treatment of UASB reactor effluent treating municipal wastewater, Environ. Sci. Pollut. Res. 21 (2014) 10407–10418.

[6].K.B. Dassanayake, G.Y. Jayasinghe, A. Surapaneni, C. Hetherington, A review on alum sludge reuse with special reference to agricultural applications and future challenges, Waste Manage. 38 (2015) 321–335.

[7].S.S. Moghaddam, A.R.M. Moghaddam, M. Arami, Response surface optimization of acid red 119 dye from simulated wastewater using Al based waterworks sludge and polyaluminium chloride as coagulant, J. Environ. Manage. 92 (2011) 1284–1291.

[8].F. El-Gohary, A. Tawfik, Decolorization and COD reduction of disperse and reactive dyes wastewater using chemical-coagulation followed by sequential batch reactor (SBR) process, Desalination 249 (2009) 1159–1164.

[9].B. Merzouk, B. Gourich, K. Madani, C. Vial, A. Sekki, Removal of a disperse red dye from synthetic wastewater by chemical coagulation and continuous electrocoagulation. A comparative study, Desalination 272 (2011) 246–253.

[10].Sanja Papic, Natalija Koprivanac, Ana Loncaric Boz ic , Azra Metes, Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption process, Dyes and Pigments 62 (2004) 291–298

[11].B. Shi, G. Li, D. Wang, C. Feng, H. Tang, Removal of direct dyes by coagulation: The performance of preformed polymeric aluminum species, J. Hazard.Mater. 143 (2007) 567–574.

[12].Yen-Yie Lau, Yee-Shian Wong, Tjoon-Tow Teng, Norhashimah Morad, Mohd Rafatullaha and Soon-An Ong, Degradation of cationic and anionic dyes in coagulation–flocculation process using bi-functionalized silica hybrid with aluminum-ferric as auxiliary agent, RSC Adv., 2015, 5, 34206