

Article Info

Received: 15 Oct 2016 | Revised Submission: 24 Oct 2016 | Accepted: 02 Nov 2016 | Available Online: 15 Nov 2016

Reduction of Toxic Parameters in Effluents Through Coagulation and Flocculation Using Natural Plant Fibers

*V. Pon. Panneerselvam**

ABSTRACT

The present study deals with the determination of physical and chemical parameters in the treatment process of waste water by flocculation and coagulation processes using natural coagulants and assessing their feasibility for water treatment by comparing the performance with each other and with a synthetic coagulant. Initial studies were done on the synthetic waste water to determine the optimal pH and dosage, the activity of natural coagulant, followed by the real effluent from tannery waste. The raw tannery effluent was bluish-black in colour, mildly basic in nature, with high COD 4000mg/l and turbidity in the range 700NTU, was diluted and dosed with organic coagulants, AloeVera, MoringaOleifera and Cactus (O.ficus-indica).. The study observed that coagulant Moringa Oleifera of 15 mg/L dose at 6 pH gave the best reduction efficiencies for major physicochemical parameters followed by Aloe Vera and Cactus under identical conditions. The study reveals that the untreated tannery effluents can be treated with environmental confirmative naturally occurring coagulants.

Keywords: *Coagulation; Flocculation.*

1.0 Introduction

The ubiquitous use of water in tanneries has caused a serious problem of drainage and disposal of industrial waste water.

Effluents from industries are degrading the underground and surface water quality through seepage and discharge into rivers, due to toxic and undesirable chemical constituents present in them and thus, being a major cause of water pollution throughout the Palar River's drainage basin. The constituents of tannery waste water are of inorganic, organic and toxic nature and require extensive treatment before discharge to prevent physical, chemical and biological pollution of the scarce water resources.

The leather industries in Vellore are mainly concentrated in Ranipet area around the Northern bank of Palar River in to which the water is discarded. Many tanning industries are located in Ranipet area, and the majority of these tanneries are engaged in chrome tanning process.

Daily, discharged wastes from all the tanneries in Ranipet industrial zone is disposed into the Palar River. Thus, the effective treatment of tannery effluents is a matter of concern for the preservation of the water resources in the area. A huge amount of research has already been carried out on effluent treatment using different technologies, such as flotation, electrochemical treatment, sedimentation, coagulation, filtration, ultrafiltration and reverse osmosis process. Several researchers have used different natural coagulating agents for treating the effluents.

Coagulation has been known to us for effluent treatment since the 19th century in England where lime along with combination with calcium chloride or magnesium was used for this purpose.

Coagulation and flocculation are usually followed by sedimentation, filtration, and disinfection, in the primary stage, succeeded by chlorination. This method is used worldwide for water treatment before it is finally distributed to the consumers.

*HOD(ug)/Civil Engineering Pattukkottai Polytechnic College Pattukkottai-614601 (E-mail: vppselva@yahoo.co.in)

Various types of coagulants are used in typical water treatment processes for making the water fit for use by the consumers. These can be classified into inorganic coagulants, synthetic polymers, and biological coagulants.

A part of the existing problem is that the operational procedures at many treatment plants in developing countries are based on arbitrary guidelines, specifically in relation to the dosage of chemicals. Another problem that plagues the developing nations is of a shortage of skilled workers and insufficient laboratory facilities to monitor process parameters required to run the plant.

The authors aim to tackle this problem by providing a viable alternative to the current method of wastewater treatment by inorganic salts by using organic coagulants which don't cause harm to the environment in addition to being cost effective and easy to use by the unskilled labourers.

Natural coagulants originating from vegetables and seeds were in use for the purpose of water treatment before the wide scale use of chemical salts, but they have not been able to displace the use of chemical salts as the scientific grasp of their effectiveness and mechanism of action was lacking.

The usage of biological coagulants has not picked up so far because of the lack of clarity in the method to use them commercially.

They have given way to inorganic salts progressively under modernization and survived only in some parts of some developing countries. However, there has been a renewed interest in understanding the activity of natural coagulants for water treatment in most countries.

Over the normal range of water pH (5–9) particles nearly always carry a negative surface charge and because of this, are colloiddally stable and resistant to aggregation. Coagulants are then needed to destabilise the particles which are done by adsorbing counter ions to neutralise the charge on particles.

It is well known that biological flocculants can play these roles because they have particular bio macromolecular structures with a large number of functional groups which can interact with contaminants. The coagulants discussed in this paper are promising bio flocculants for the preservation of environment as well as purification purposes, as reported in recent patents.

Numerous mechanisms such as polymer bridging, polymer adsorption and charge neutralization (including electrostatic patch effects), depletion flocculation, displacement flocculation, etc. have been proposed to explain the destabilisation of colloids and suspensions by polymers.

Patch flocculation happens when huge molecules with a high charge density adsorb to particles to form positively and negatively charged areas on the particle surface (this results in strong electrical attraction between particles).

Polymer bridging happens when long chain polymers adsorb onto the surface of more than one particle, thereby forming strong aggregates of large flocs.

For the case where the polymer and the adsorption site are of opposite signs, it is hypothesized that charge neutralization is the mechanism in action.

Mechanisms of coagulation/flocculation involved in the removal of dissolved and particulate contaminants using naturally occurring coagulants often cited are charge neutralization, adsorption, precipitative coagulation, bridge formation (related to the high molecular weight of biomolecules) and electrostatic patch.

From the literature it is known that efficiency of the coagulation/flocculation process depends on the following factors.

The origin and the nature of the naturally occurring coagulant like its molecular weight; the process variables such as the type of equipment used, the type of reagent used in conjunction with it, the dosage of the coagulant, the residence time in the jar test apparatus and the rate of rotation; the chemical and physical properties of the pollutants present (such as polarity) and finally the solution like temperature, pH, the zeta potential, the colour, the concentration of the colloidal particles, the presence or absence of impurities (i.e., dissolved salts or trace elements such as ions and chemicals). The objective of the study to determine the activity of natural coagulants on the treatment of real effluents comparable with synthetic wastewater.

This study aims to extend the previous work and find a viable way to use the naturally occurring coagulants such as Aloe Vera, Moringa Oleifera seeds and Cactus.

1.1 Preparation of coagulant

The Moringa Oleifera seeds were sourced locally from a vendor. They were air-dried at 45°C for 48 hours. The chaff surrounding the seed kernel was removed and the kernels were ground finely using a blender into powder. This was the coagulant prepared from Moringa Oleifera.

The cactus pads were washed thoroughly and the outer covering along with the thorns was removed to extract the mucilage. The mucilage obtained was then air dried in an oven at 65°C for 24 hours. The dried mucilage was then ground into the powdered form and coagulant was thus prepared.

The Aloe Vera leaves were washed thoroughly followed by draining of aloin by keeping the leaves in the horizontal position and the gel was scooped out from within. This gel was used for the coagulation purpose. The aluminum sulphate (alum) which was used for comparison was also sourced locally.

1.2. Experimental run

Variables that are affected by temperature such as pH, viscosity, density and floc volume concentration, which makes it important to maintain and control the temperature for an accurate result.

The temperature of the wastewater is kept constant at room temperature for the duration of the experiment. Sample solution of the coagulants, synthetic wastewater, tannery effluent, sodium hydroxide and hydrochloric acid were prepared at suitable concentration to ensure that the experiment would run smoothly and the results can be measured with an acceptable degree of precision. In this jar testing experiment, 0.1 M of NaOH and 0.1 M of HCl were used to adjust the pH level to desired pH value of the wastewater.

1.3 Preparation of effluents

In order to carry out the preliminary studies to determine the efficiency of coagulants, we used 30gm of clay which was sourced from a nearby nursery and mixed in 700ml of water and mixed rapidly at 250(RPM) for 15 minutes and prepared the synthetic effluent. The suspension was then allowed to settle for 16 hours and the supernatant was transferred into the jar test apparatus to carry out the experiment. Thus the synthetic water was prepared.

During our preliminary studies using synthetic water it was noted that the highly turbid water (>800NTU) cannot be treated without using a high dosage of the natural coagulants which invariably increases the biological and chemical load on water. From the literature it is known that efficiency of the coagulation/flocculation process depends on the following factors.

The origin and the nature of the naturally occurring coagulant like its molecular weight; the process variables such as the type of equipment used, the type of reagent used in conjunction with it, the dosage of the coagulant, the residence time in the jar test apparatus and the rate of rotation; the chemical and physical properties of the pollutants present (such as polarity) and finally the solution like temperature, pH, the zeta potential, the colour, the concentration of the colloidal particles, the presence or absence of impurities (i.e., dissolved salts or trace elements such as ions and chemicals).

2.0 Methodology

The objective of the study to determine the activity of natural coagulants on the treatment of real effluents comparable with synthetic wastewater. This study aims to extend the previous work and find a viable way to use the naturally occurring coagulants such as Aloe Vera, Moringa Oleifera seeds and Cactus.

The increase in the concentration (over dosage) decreased the turbidity removal. Some studies show the dosage of coagulants used for the experiment is relatively much higher in comparison with concentrations of commonly used chemical coagulants used for water treatment, and using these higher dosages might make using natural coagulants economically and chemically unfeasible for the reasons stated above. Since the tannery water has very high NTU (>900), it is not feasible to treat the water directly by the application of natural coagulants while doing the experiment. So the tannery waste water was diluted in 1:10 ratio for the purpose of the experiment. The coagulation activity is studied using 4 parameters: pH, dosage, COD and turbidity and the effect of variation of dosage and pH were studied on turbidity and COD.

The optimal dosage of each coagulant was determined in the beginning and this dosage was further used to find optimal pH.

Turbidity and COD of all samples were studied and the efficiency of all the coagulants was recorded.

Table 1 Initial Parameters of Synthetic Water and Tannery Waste Water

Parameters	Initial values	Tannery Waste Water
pH	7.4	7.8
Turbidity	55.0NTU	74.43 NTU
COD	376.23mg/l	502.6 mg/l

2.1. Jar-test experiments

The most commonly used method for evaluating and optimizing the coagulation-flocculation processes is the jar test. This study consists of a series of simultaneous batch experiments involving three stages, namely, rapid mixing, slow mixing, and sedimentation. Beakers of 1 litre were filled with 500ml of the model turbid water and the tannery effluent, both of which were already prepared beforehand, and one blank was also kept as a control beaker.

The apparatus allowed six beakers to be stirred simultaneously, and the rotational speed could be varied between 0 and 400 rotations per minute (RPM), thus allowing simulation of different mixing intensities at the same time.

In a typical run, beakers were filled with one liter of the turbid water and were agitated at the preselected intensity of rapid mixing. The coagulant doses were put into each beaker using pipettes of the desired capacity, while the rapid mixing phase was in progress. The duration of rapid mixing was controlled with the inbuilt timer.

After rapid mixing, slow mixing was quickly established. After slow mixing, the beakers were removed from the setup. In this study, the intensity and duration of both rapid mixing and slow mixing were fixed respectively at 150 RPM for 2 minutes in the case of rapid mixing and 35 RPM for 20 minutes in the case of slow mixing.

The sedimentation process was carried out over a period of 30 minutes, remaining constant for

all samples. Various dosages of different coagulants were prepared as follows: Various dosages of different coagulants were prepared as follows:

- Moringa Oleifera dosage: The 500 ml volume of synthetic waste water samples were used at different Moringa Oleifera dosage of 5, 10, 15 and 20mg/l.
- Aloe Vera dosage: The 500 ml volume of Synthetic waste water samples were taken with different aloe Vera dosages (V/v) of 100 % (pure), 1%, 2% and 5% Aloe Vera.
- Cactus Dosage: The 500 ml volume of effluent samples were used at a different cactus dosage of 20, 40, 60 and 80mg/l.

2.2 Calibration of equipment

Turbidity measurements were conducted using a DeepVision turbidimeter. Turbidimeter was calibrated using distilled water and 40 NTU standard solution was prepared using 1g hydrazine and 10gm hexamethylene tetramine solution. The pH was varied using concentrated sulphuric acid 0.1M and sodium hydroxide 0.1M solution. The pH was measured using a LaMotte pH meter. Conductivity was measured using a LaMotte conductivity meter. For determination of COD, the effluents were digested in Spectra Lab digester and the titration was carried out using the standard reagents and procedure.

3.0 Results and Discussion

3.1 Coagulation dosage

The reduction in turbidity increases with increase dosage up to a certain value which is its optimal dosage value and after that the turbidity reduction decreases.

The reason behind high turbidity reduction at optimal dosage of coagulant is because as soon as the coagulant concentration exceeds the optimum dosage, turbidity increases because all colloids have already been neutralized and have got precipitated at the optimum dosage.

Thus if high dosage is used, the excess coagulants will simply get added and cause turbidity in water as they did not interact with oppositely charged colloidal particles as those particles have already been flocculated earlier.

The optimal performance conditions were given in Table 2.

Table 2 Optimal Performance Conditions of Different Coagulant

Coagulant	Optimal dosage	Optimal pH	Synthetic Waste		tannery effluent	
			% NTU reduction	% COD reduction	% NTU reduction	% COD reduction
Moringa Oleifera	15 g/mL	6	62.36	37.14	59.43	37.82
Cactus	40 g/mL	7	50.50	63.60	51.50	59.35
Aloe Vera	5% V/v	5	51.72	59.20	46.76	52.60

3.2 Cactus

It is hypothesized that the predominant coagulation mechanism for Opuntia is adsorption and bridging, wherein particles which cause turbidity are directly not in contact one another but are bound to a polymer-like material from Opuntia.

There is a high probability that adsorption may occur through hydrogen bonding or dipole interactions. It is likely that natural electrolytes from within the Opuntia pad, specifically the divalent cations, which are known to be important for coagulation with anionic polymers, facilitate adsorption.

3.4 Aloe Vera

The coagulation activity of aloe vera is attributed to the ionization of galacturonic acid ions in the medium which produces H⁺ ions which facilitate charge neutralization of the particles which cause turbidity.

3.5 Effect of varying pH on aloe vera

we can observe that the turbidity reduction by aloe Vera is decreasing with increasing pH and the probable reason for aloe Vera working best at this condition is that the ionization of galacturonic along with the freely available H⁺ ions in the medium are facilitating charge neutralization of the particles

which cause turbidity. And thus the charge neutralisation and flocculation are easily taking place .

3.6 Effect of varying pH on moringa oleifera

The probable reason of 6 as its optimal pH is because the amino acids present in M. Oleifera(cationic coagulant) get ionized and produce carboxylate and H⁺ charge which attract colloidal particles in the medium which get neutralized and settle down as flocs. Since this produces carboxylate ions after ionization we can observe that the water becomes more alkaline.

The reason behind high turbidity reduction at an optimal dosage of coagulant is because as soon as the M. Oleifera concentration exceeds the optimum dosage, turbidity increases because all colloids have already been neutralized and have got precipitated at the optimum dosage. Thus, if high dosage is used, the excess coagulants will simply get added and cause turbidity in water as they did not interact with oppositely charged colloidal particles as those particles have already been flocculated earlier.

3.7 Effect of varying pH on cactus

It is hypothesized that the predominant coagulation mechanism for Opuntia is adsorption and bridging, whereby particles causing turbidity are

directly not in contact one another but are bound to a polymer-like material from *Opuntia* spp.

There is a high probability that adsorption may occur through hydrogen bonding or dipole interactions.

It is likely that natural electrolytes from within the *Opuntia* spp. pad, specifically the divalent cations, which are known to be important for coagulation with anionic polymers, facilitate adsorption. It works best in a neutral pH as the polymer-like material in *Opuntia* is not denatured by the acidic and alkaline conditions in the medium.

4.0 Conclusion

The following conclusions were drawn from the present studies: Amongst the biomaterials undertaken for the study, *M. Oleifera* seeds gave the highest removal of turbidity and COD for the given samples of waste water. The dosage and pH were optimised to obtain the highest possible removal of turbidity. The optimal dosage of *M. Oleifera* is 15mg/l with optimal pH at 6. Cactus has optimal dosage and pH of 40mg/l and 7 respectively. Similarly, aloe Vera has the optimal dosage at 5% concentration and optimal pH as 5. Although, the performance of the coagulants were satisfactory and pilot plants have been designed, the economic feasibility analysis to design large scale treatment plants still needs to be carried out. Since the natural coagulant by itself is inefficient in treating water of very high turbidity, the authors propose that the further research can be carried out by mixing the natural occurring coagulants with synthetic ones and studying the performance of the resulting coagulant.

References

[1] J. Naumczyk and M. Rusiniak, "Physicochemical and chemical purification of tannery wastewaters," *Polish journal of environmental studies*, vol. 14, pp. 789-797, 2005.

[2] E. Ates, D. Orhon, and O. Tünay, "Characterization of tannery wastewaters for pretreatment selected case studies," *Water Science and Technology*, vol. 36, pp. 217-223, 1997.

[3] Z. Song, C. Williams, and R. Edyvean, "Treatment of tannery wastewater by chemical coagulation," *Desalination*, vol. 164, pp. 249-259, 2004.

[4] S. Krishnamoorthi, V. Sivakumar, K. Saravanan, and T. S. Prabhu, "Treatment and reuse of tannery waste water by embedded system," *Modern Applied Science*, vol. 3, p. 129, 2008.

[5] C. V. Genovese and J. F. González, "Solids removal by coagulation from fisheries waste waters," *WATER SA-PRETORIA*, vol. 24, pp. 371-372, 1998.

[6] A. Matilainen, N. Lindqvist, and T. Tuhkanen, "Comparison of the efficiency of aluminium and ferric sulphate in the removal of natural organic matter during drinking water treatment process," *Environmental technology*, vol. 26, pp. 867-876, 2005.

[7] M. Y. Wani, N. Hasan, and M. A. Malik, "Chitosan and Aloe vera: Two gifts of nature," *Journal of Dispersion Science and Technology*, vol. 31, pp. 799-811, 2010.

[8] N. F. A. binti Saharudin and R. Nithyanandam, "Wastewater Treatment by using Natural Coagulant," *2nd eureka 2014*, vol. 4, pp. 213-217, 2013.

[9] F. Renault, B. Sancey, P.-M. Badot, and G. Crini, "Chitosan for coagulation/flocculation processes—an eco-friendly approach," *European Polymer Journal*, vol. 45, pp. 1337-1348, 2009.

[10] B. Sharma, N. Dhuldhoya, and U. Merchant, "Flocculants—an ecofriendly approach," *Journal of Polymers and the Environment*, vol. 14, pp. 195-202, 2006.

[11] G. Crini, "Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment," *Progress in polymer science*, vol. 30, pp. 38-70, 2005.

- [15] V. Govindan, "Coagulation studies on natural seed extracts," *JOURNAL-INDIAN WATERWORKSASSOCIATION*, vol. 37, p. 145, 2005.
- [16] H. Hirohara, M. Takehara, A. Fukita, K. Kansai, and H. Hirohara, "Flocculant and sludge treatment method," *Japanese Patent JP2001129310*, 1999.
- [17] Q. Ren, X. Song, J. Li, R. Ma, Z. Mei, and X. Ma, "Heavy metal chelate composition containing chitosan derivatives and uses thereof," ed: Google Patents, 2003.
- [18] J. Bratby, *Coagulation and flocculation in water and wastewater treatment* vol. 2: IWA publishing, 2006.
- [19] H. Stechemesser and B. Dobiáš, *Coagulation and flocculation*: Taylor & Francis, 2005.
- [20] B. Bolto and J. Gregory, "Organic polyelectrolytes in water treatment," *Water research*, vol. 41, pp. 2301-2324, 2007.
- [21] J.-Q. Jiang, "Development of coagulation theory and new coagulants for water treatment: its past, current and future trend," *Water Science and Technology: Water Supply*, vol. 1, pp. 57-64, 2001.
- [22] C.-Y. Yin, "Emerging usage of plant-based coagulants for water and wastewater treatment," *Process Biochemistry*, vol. 45, pp. 1437-1444, 9// 2010.