Remediation of Spent Vegetable Tannins from Waste Tanning Liquor through Coagulation and Ultrasound Pre-Treatment: A Sustainable Approach

by

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Abstract

Vegetable tanning is one of the oldest methods of tanning. Vegetable tannins present in spent tanning liquor necessitates suitable remediation measures for sustainable solution. Vegetable tanning agent, wattle extract powder and vegetable tanning process spent liquor collected from a commercial tannery were used for the experiments. In the present approach, natural clay has been employed for the coagulation of spent vegetable tannins. Various other suitable precipitating agents such as zinc chloride ($ZnCl_2$), barium chloride ($BaCl_2$), ferric alum, lime and poly-electrolyte have also been studied for their efficacy in the treatment process and their requirement optimized. The efficacy of coagulation was monitored through settling characteristics of precipitation process and % settled volume for a given time. In the case of wattle powder, better settling of tannins was obtained due to combined use of optimized amount of clay and $ZnCl_2$. Whereas, ultrasound pre-treatment provided further enhancement. In the case of spent tannery vegetable tanning liquor, ultrasound pre-treatment of polyelectrolyte along with optimized amount of normal lime, clay and ferric alum provided rapid settling behavior, with steady state achieved in 20 minutes with settled volume of ~10 ml. Similar trend was also achieved (10 ml, 8 min.) for ultrasound pre-treated optimized clay with the use of other agents as normal. There was a significant reduction in particle size of clay (from 539 nm to 298 nm) through ultrasound pre-treatment (20 min.), leading to more surface area facilitating the coagulation process. This method could be useful for remediation of vegetable tannins present in spent vegetable tanning liquors using available natural material clay and shall also be extended to other streams. The present study has explored the ultrasound assisted coagulation science and technology for remediation of wastewater in general, whereas, spent vegetable tanning liquor in specific.

Introduction

Tanning industry is one of the oldest industries in the world.[1] Tanning process consists of three basic steps a) beam house operations b) tanning c) finishing process. Leather tanning process is classified mainly into two categories such as chrome tanning and vegetable tanning. Manufacturing of leather generates numerous by-products, solid wastes and wastewater containing different loads of pollutants and emissions.[2] Nearly 70% of the pollution loads of Bio-chemical oxygen demand (BOD), chemical oxygen demand (COD), and Total Dissolved Solids (TDS) are generated from operations such as soaking, liming, degreasing, pickling and tanning processes.[3]

Vegetable tanning is one of the oldest methods of tanning and the waste spent tanning liquor has high BOD and COD values. Physical, chemical and biological characteristics of spent tannery vegetable tanning liquor has been analyzed and reported recently.[4] Even though vegetable tannins are natural materials, one of the refractory groups of chemicals in tannery effluents are derived from tannins.[5] Study on leaching of pollutants from vegetable tanning residue.[6] Treatment of refractory organic pollutants in industrial wastewater by wet air oxidation has been studied earlier.[7] About 30% of vegetable tanning extracts (% based on skin/hide weight) are normally employed in main tanning process for conversion of animal skins/hides into leather. A significant amount of these vegetable tannins are underutilized in tanning process and available in spent liquor, they subsequently enter waste streams causing pollution load. In this regard, suitable remediation measures are beneficial after separating the spent vegetable tanning liquor as sectional streams, before mixing into another wastewater stream. Since, vegetable tannins are natural materials, available in spent liquors, the same could be used for some useful purpose such as enhancement of soil, if separated from the wastewater through suitable methods such as coagulation. Before going into details of the present study, the following section provides the brief details of vegetable tannins employed in tanning process of leather industry.

Chemistry of vegetable tannins

There are two types of vegetable tannins, viz., hydrolysable and condensed tannins (*Con-Tan*).[8] Generally, hydrolysable tannins (*Hyd-Tan*) are only used as a supplementary agent for main (*Con-Tan*) used in tanning, in order to prevent oxidation and to provide lighter color to tanned leather. Hydrolysable tannins are esters of

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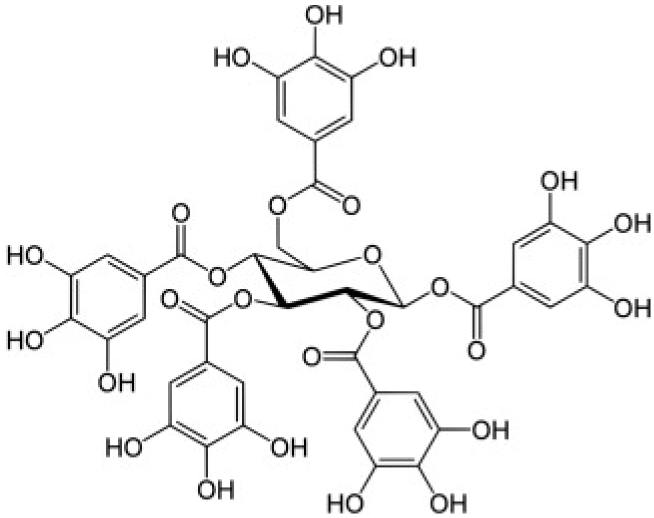

Figure 1. Schematic representation of hydrolyzable tannins 1,2,3,4,6 Penta galloyl glucose as esters of phenolic acids and glucose.

phenolic acids and glucose such as 1,2,3,4,6 Penta galloyl glucose as schematic representation shown in Figure 1. Typical examples of *Hyd-Tan* are Myrobalan, Divi-Divi etc.

Con-Tan are widely used as a main vegetable tanning agent. Typical examples of Con-Tan are wattle, mimosa etc. Condensed tannins are built from catechin units, flavon 3-ol. Schematic representation of a *Con-Tan* molecule is shown in Figure 2. Condensed tannins can be linear (with 4 to 8 units) or branched (with 4 to 6 units shown as dotted line).

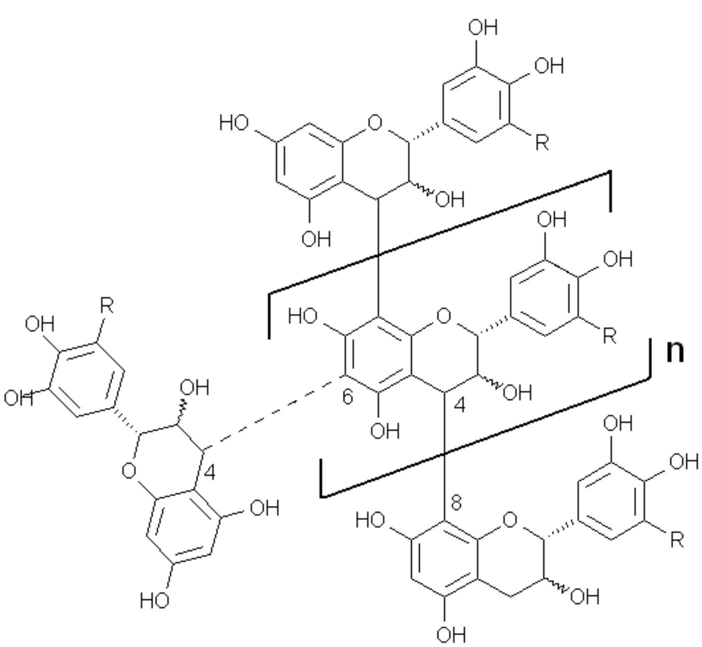

Figure 2. Schematic representation of Condensed tannins with catechin (flavon 3-ol) units

Coagulation treatment for vegetable tannins
Use of soil clay in coagulation process:
Originality of the present work

Coagulation process occurs when cations and anions in aqueous solution combine to form an insoluble ionic solid called a precipitate. In the present approach, another natural material, viz., soil clay having surface charge properties has been employed for the coagulation of spent vegetable tannins. Basics of clay minerals with their types and their characteristic properties such as Ion-exchange capacity as well as general specific surface area (m^2/g) has been reported.[9] The clay materials comprise hydrous phyllosilicate having silica, alumina and water with variable number of inorganic ions like Mg^{2+}, Na^{+}, Ca^{2+} find useful in coagulation process. An approach for the treatment of vegetable tan liquor containing hydrolysable tannins using zinc sulfate and zerolite iron catalyst has been reported earlier.[10] Use of salts like ferric chloride to provide interaction with plant tannins with formation of colored complex has been widely studied for qualitative determination of presence of tannins.[11,12]

However, there is a need to enhance the process using natural materials such as clay in the area of soil enrichment.[13] In this regard, application of bentonite clays in suspension fertilizer formulations and use of Bentonite based clay as organic amendment, which enriches microbial activity in agricultural soils have been studied earlier.[14] Spectroscopic and mineralogical characterization of bentonite clay from Ghardaïa, Algeria for heavy metals removal in aqueous solutions has been made.[15] A recent study has been reported on the understanding the impact of soil clay mineralogy on the adsorption behaviour of zinc.[16]

The precipitate of the coagulation process yields suspended materials or fall to the bottom of the solution. The remaining fluid is called supernatant liquid. The two components of the mixture (precipitate and supernatant) of tannins and clay can be separated by various methods, such as filtration, centrifuging, or decanting and subsequently used for different applications.

However, tannins separated only from vegetable tanning sectional stream through this approach for soil enrichment purpose need to be studied separately for their applicability and efficacy in this regard, which is not the part of the present study, the same would be investigated as future work.

Use of ultrasound in coagulation process

Another important feature of the present study is to enhance the coagulation process by physical activation method, viz., ultrasound. Ultrasound is a sound wave having frequency above the human audible range of 16 kHz and widely studied for enhancing the physical as well as chemical processes.[17,18] Schematic representation of ultrasound pre-treatment using clay and other precipitating agents for vegetable tanning spent liquor, further settling and clarification is shown in Figure 3. Ultrasound could be employed in pre-

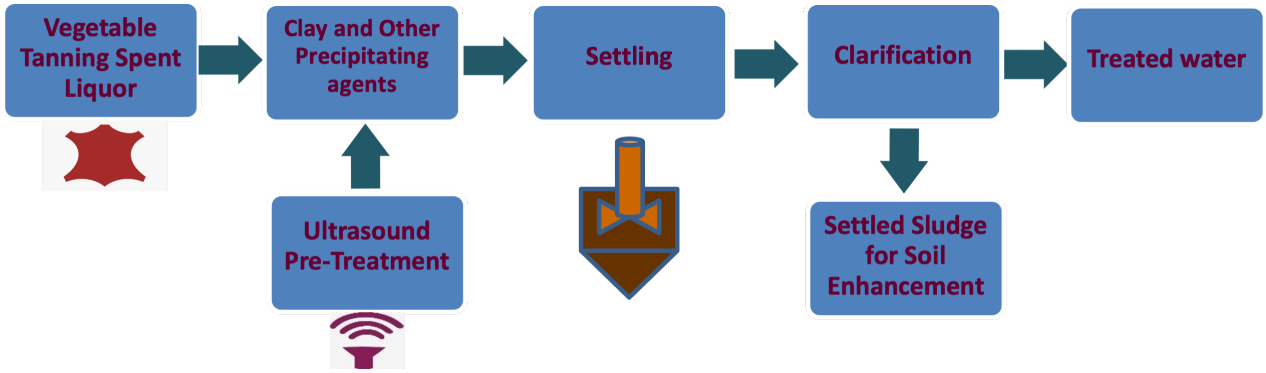

Figure 3. Schematic representation of ultrasound pre-treatment using clay and other precipitating agents for vegetable tanning spent liquor, further settling and clarification.

treatment disintegration and particle size reduction of coagulants employed and increase the surface area for better coagulation. In this regard, earlier studies on the use of ultrasound in chrome recovery process from spent chrome liquor through precipitation of chromium present as chromic hydroxide has been reported.[19] Whereas significant improvement was obtained in settling rate of chromic hydroxide precipitate with the use of pre-ultrasound pre-treated MgO as compared to control (no ultrasound pre-treatment) and considerable decrease of Cr in the supernatant liquor after precipitation leading to better Cr recovery due to better dispersion and particle-size reduction of MgO with ultrasound pre-treatment has been reported.[19] In another study, effect of ultrasound pre-treatment on sedimentation of suspended solids in water has been studied earlier.[20] Earlier study on particle-size reduction of dickite by ultrasound treatments and the effect on the structure, shape and particle-size distribution has been reported.[21] Use of ultrasound in the preparation of nanocomposites based on fibrous clay minerals and nano cellulose from microcrystalline cellulose has also been studied.[22]

Effect of other coagulating agents

Effect of other suitable coagulating agents need to be studied in the process. The present study also involves the treatment of vegetable tanning spent liquor using different precipitating agents such as barium chloride ($BaCl_2$), zinc chloride ($ZnCl_2$), ferric alum, lime and flocculating agent and their opulent effect upon ultrasound treatment in order to improve the removal of color and total solids and thereby reducing the sludge level. This is a simple sedimentation technique using precipitating agents to make the process easy and effective removal of color and total solids in tannery effluent. In the present study, ultrasonic pre-treatment on clay and other agents has been performed in view of better coagulation process. The experiments were also carried out using combination of alum, poly-electrolyte and lime. The present study tries to explore the possibility of ultrasound assisted coagulation science and technology for remediation of wastewater in general and spent vegetable tanning liquor in particular. This study is expected to provide better settling rate and useful remediation of tannins present in vegetable tanning spent liquor.

Materials and Methods

Materials used

Chemicals reagents (AR Grade), Zinc chloride ($ZnCl_2$), Barium chloride ($BaCl_2$), Alum were procured from SD Fine, Chemicals, Ltd., India. Clay sample was collected from sub soil surface of CSIR-CLRI garden. Lime (CaO) powder (commercial grade), Poly electrolyte (commercial grade) were also used. Vegetable tanning agent (condensed type), Wattle extract GS powder (Tanext chemicals, India) was employed in various experiments. Whereas, spent vegetable tanning process liquor was collected from a commercial tannery M/s. C. Kalyanam & Co. Pallavaram, Chennai, India.

Ultrasound equipment

Ultrasound assisted experiments were carried out using ultrasonic probe (VCX 400, Sonics and Materials, USA) operating at frequency: 20 kHz with variable ultrasound power: 0– 400 W, with provisions to set required output power and process time as described earlier.[23]

Methods

Preparation of synthetic vegetable tanning liquor (SVT)

In order to avoid other contaminants in the experiments for optimization studies, synthetic vegetable tanning liquor (SVT) was prepared by taking 0.5 g of wattle tannin GS powder and mixing well with 100 ml distilled water in a magnetic stirrer in order to make SVT and used for various experiments for optimization of coagulation and settling process. Whereas, in order to analyze application of the present approach, separate studies were also carried out using spent vegetable tanning process liquor as collected from a commercial tannery.

Settling characteristics and % Settled Volume

The component of materials which are settled after the coagulation process, at any given time period is a good measure of coagulation efficacy. This implies the lower the settled volume, the better the coagulation process, with clearer supernatant with less contaminants. Usually, denser precipitates yield lower settled volume. For this purpose, in each experiment, the respective experimental solution, with vegetable tannins and respective coagulating agents were mixed well in a clean beaker and 100 ml of this solution was taken in a 100 ml graduated measuring jar and allowed to settle. Percent settled volume could be measured by noting the settled layer below the clear supernatant layer by visual observation in the measuring jar graduations at any given point of time. As time progress, the settling process also proceeds with percent settled volume decreasing and clear supernatant layer at the top increases. The optimization of different coagulants has been made from the settling characteristics of precipitation process and percent settled volume for a given time.

Optimization of Zinc chloride, Barium chloride and Clay

Barium chloride and Zinc chloride have been studied at different amount (0.1 g to 0.6 g) along with 100 ml of SVT was added to each amount and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

To enhance the efficiency of $ZnCl_2$, clay was used to increase settling rate. Clay sample was washed thoroughly with distilled water and dried. This dried clay was taken in different amount such as 0.2 –1.4 g and optimized amount of zinc chloride (0.3 g) was added to it. Then 100 ml of SVT was also added to the above solution and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded. The amount of clay was optimized from the settling rate.

Effect of ultrasound pre-treatment on optimized zinc chloride

To enhance the coagulation process, effect of ultrasound pre-treatment was employed on optimized zinc chloride. For this purpose, optimized amount of zinc chloride was taken and dissolved in 100 ml water and ultrasound pre-treatment was carried out for 30 minutes using 80 W power. Optimized amount of ultrasound pre-treated zinc chloride (100 ml solution) with 0.5 g tannin powder was used for the experiment. Then the sample solution was mixed well and kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

Effect of combination of zinc chloride and clay

In addition, effect of combined use of optimized amount of zinc chloride and clay has also been performed using 100 ml SVT with tannin powder 0.5 g for the experiment. Then the sample solution was mixed well and kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

Optimization of Ferric alum and Clay

Having optimized the amount of clay, zinc chloride in settling of tannins, other coagulating agent's ferric alum, lime, polyelectrolytes and clay were studied as an industrial practice of treating wastewater. Various amounts of alum (0.08 –0.2 g) were taken and 100 ml of spent tannery vegetable tanning liquor collected from tannery was added to it, mixed well and the solution was allowed to settle. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

Optimized amount (0.15 g) of ferric alum was added to various amount of clay such as 0.2– 1 g and 100 ml of spent tannery vegetable tanning liquor was added to it and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

Optimization of poly electrolyte

For further enhancement of settling rate, the effect of commercial flocculants, poly electrolyte was also studied. The optimized value of ferric alum and clay such as 0.15 g and 0.8 g were added to the various amount of poly electrolyte (4 –15 mg). Then 100 ml of spent tannery vegetable tanning liquor was also added to it and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

Then the optimized quantity of reagents clay, ferric alum and poly electrolyte as arrived from the above experiments were used for remediation treatment purpose of spent tannery vegetable tanning liquor as collected from a commercial tannery and the effect of ultrasound pre-treatment on different reagents used was studied as follows:

Effect of ultrasound pre-treatment on clay with optimized normal ferric alum and polyelectrolyte

For this experiment ultrasound pre-treatment on 0.8 g of clay was performed using 80 W power for 30 minutes and employed in coagulation process. The ultrasound pre-treated clay was mixed with optimized amount of 5 mg polyelectrolyte and 0.15 g of ferric alum. Then 100 ml of spent tannery vegetable tanning liquor was added to it and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

Effect of ultrasound pre-treatment on polyelectrolyte with optimized normal clay ferric alum

For this experiment, ultrasound pre-treatment on 5 mg of polyelectrolyte was performed using 80 W power for 30 minutes and employed in coagulation process using optimized amount of 0.8 g of clay and 0.15 g of ferric alum. Then 100 ml of spent tannery vegetable tanning liquor was added to it and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

Effect of lime on ultrasound pre-treated optimized polyelectrolytes in spent tannery vegetable tanning liquor

The optimized polyelectrolytes (5 mg) were ultrasound pre-treated for 30 minutes using output power 80 W. Then optimized amount of

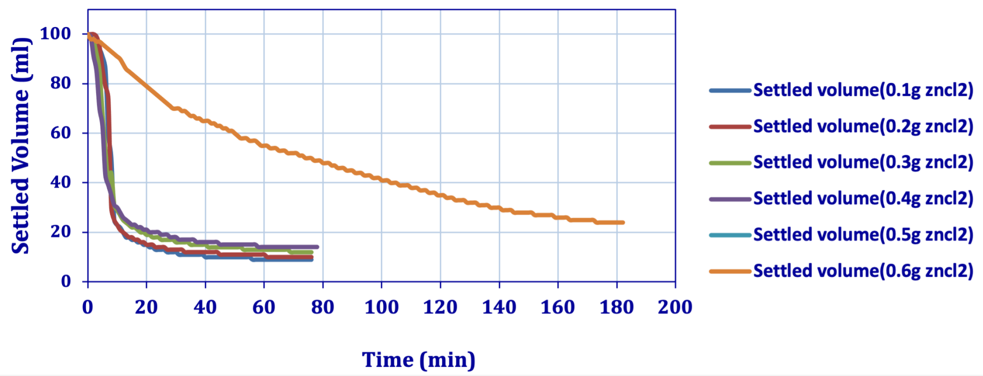

Figure 4. Effect of amount of Zinc chloride used in SVT tannins coagulation and settling rate characteristics during the settling process.

0.6 g lime, 0.8 g clay and 0.15 g ferric alum was added to it. Then 100 ml of spent tannery vegetable tanning liquor was also added to it and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

Effect of lime on ultrasound pre-treated optimized clay in spent tannery vegetable tanning liquor

Optimized amount of clay 0.8 mg was ultrasound pre-treated for 30 minutes using output power 80 W. Then optimized amount of quick lime (CaO) 0.6 g and 0.15 g ferric alum was added to it and mixed well. Then 100 ml of spent tannery vegetable tanning liquor was also added to it. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

Particle size analysis of clay samples

The particle size distribution of clay sample was analyzed using particle analyzer operating with dynamic light scattering principle (Malvern Instruments Ltd). The particle size of normal clay, and ultrasound pre-treated clay sample was analyzed. For ultrasound pre-treatment, 1 g of clay sample was dissolved in 100 ml distilled water and the sample was ultrasound pre-treated at 150 W at 20 kHz. The ultrasound pre-treated sample was collected at 10 and 20 minutes for particle-size analysis.

Results and Discussions

Optimization of Barium chloride and Zinc chloride

When barium Chloride was used as precipitating agent, samples were analyzed after treatment and found a decent settling rate. But the color removal of treated water didn't satisfy as per the requirements. Moreover, it is not eco-friendly while considering in the case of disposing of the sludge. Barium chloride is a heavy metal, and it precipitates when it comes in contact with the chromium in the wastewater.

Zinc chloride gave better results and effective color removal when compared to Barium Chloride. The optimization of amount of $ZnCl_2$ for 100 ml of SVT could be derived from Figure 4, which indicates better settling characteristics for 0.2 – 0.5 g of $ZnCl_2$ other than 0.6 g. Whereas, keeping in view of materials and cost savings as well as for establishing better settling performance for scale-up with a possible margin of deviation, the optimized amount of $ZnCl_2$ has been considered as 0.3 g for 100 ml of SVT. Hence, further studies were carried out using zinc chloride as precipitating agent. Figure 4 shows the effect of amount of $ZnCl_2$ used in SVT tannins coagulation on the settling rate characteristics during the settling process. The results indicate continuous settling process with steady state achieved at about 80 min. with settled volume of ~20 ml using $ZnCl_2$.

Optimization of clay with optimized Zinc chloride

Figure 5 shows the effect of amount of clay used in SVT tannins coagulation on settling rate characteristics during the settling

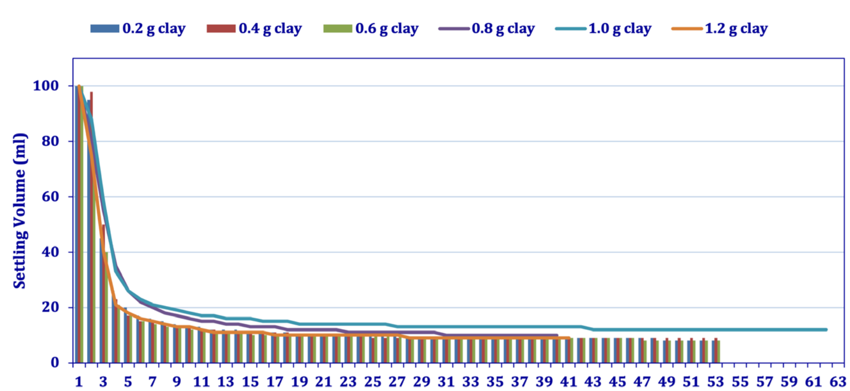

Figure 5. Effect of amount of clay with optimized amount of 0.3 g Zinc chloride used in SVT tannins coagulation and settling rate characteristics during the settling process.

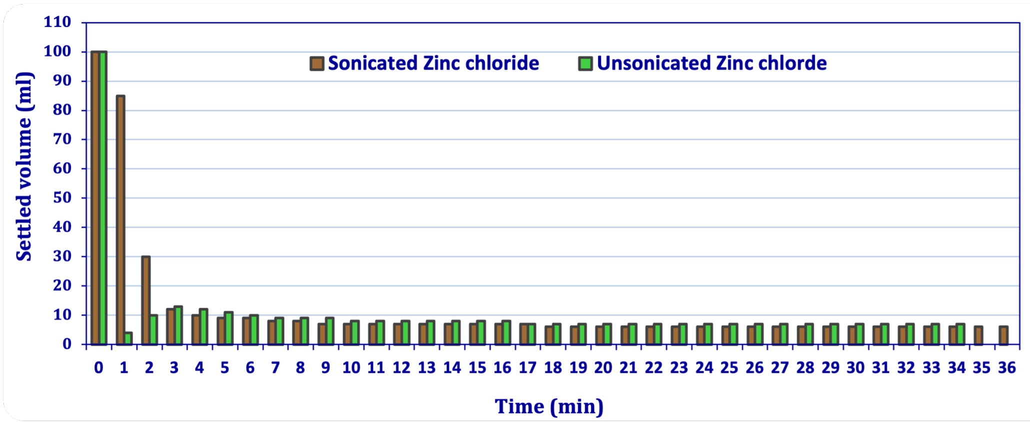

Figure 6. Effect of ultrasound pre-treatment on optimized Zinc chloride used in SVT tannins coagulation and settling rate characteristics during the settling process.

process. The optimization of the amount of clay along with optimized 0.3 g zinc chloride for 100 ml of SVT could be obtained from Figure 5, which indicates better settling characteristics for different amounts of clay used other than 1 g, which has shown longer settling times, perhaps due to exceeding the optimized amount of clay; which also indicates the optimized amount should be lower than 1 g for 100 ml of SVT. Whereas, keeping in view of this aspect as well as materials and cost savings for establishing better settling performance for scale-up with a possible margin of deviation, the optimized amount of clay has been considered as 0.8 g for 100 ml of SVT, containing 0.5 g of tannin powder along with optimized amount of 0.3 g zinc chloride. Therefore, the optimized amount of clay was found to be 0.8 g. The results indicate faster settling process with steady state achieved at about 53 min. with settled volume of ~10 ml, providing better coagulation for optimized clay & $ZnCl_2$ with as compared to $ZnCl_2$ alone. Table II shows the optimization of different coagulants on SVT tannins and the amount required for 100 g tannins in SVT for facilitating the settling process.

Effect of ultrasound pre-treatment on optimized Zinc chloride

Figure 6 shows the effect of ultrasound pre-treated (80 W, 30 min.), optimized 0.3 g of zinc chloride used in SVT tannins coagulation and settling rate characteristics during the settling process, which indicates better settling rate for ultrasound pre-treated optimized zinc chloride. The results also indicate that during initial 1–2 min, settled volume is higher for sonicated zinc chloride as compared to un-sonicated sample. The reason for this behavior may be due to initial drag for well dispersed nature of $ZnCl_2$ upon ultrasound pre-treatment. Whereas the same effect could subsequently lead to better binding with tannins and better performance in settling observed for ultrasound pre-treated $ZnCl_2$ as compared to that of normal case leading to steady state settled volume of 7 ml achieved in 17 min.

Effect of combined use of Zinc chloride and Clay

In addition, combined use of zinc chloride and clay has also been performed and the results show there is a significant improvement in settling characteristic. Whereas, Figure 7 shows the effect of combined use of optimized zinc chloride and clay as compared to the use of optimized zinc chloride alone employed in SVT tannins coagulation and settling rate characteristics during the settling process.

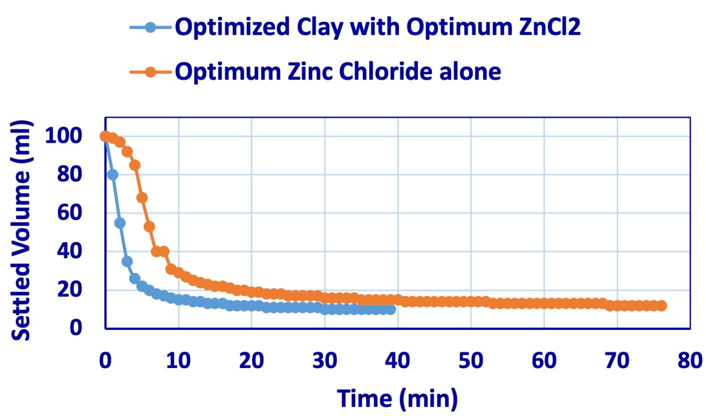

Figure 7. Effect of combination of optimized Zinc chloride and Clay used in SVT tannins coagulation and settling rate characteristics during the settling process.

Optimization of ferric alum

Having optimized the amount of clay, zinc chloride in settling of tannins, other coagulating agent's ferric alum, lime, polyelectrolytes and clay were studied as an industrial practice of treating wastewater. The optimized value of ferric alum was found to be 0.15 g for 100 ml of spent tannery vegetable tanning liquor collected from the tannery. Figure 8 shows the effect of the amount of Ferric alum in tannins coagulation and settling rate characteristics during the settling process. The results indicate gradual and continuous settling process with steady state achieved at about 106 min. with settled volume of ~5 ml.

Optimization of clay with optimized ferric alum

Further studies were carried out to optimize the value of clay with optimized ferric alum. The amount of clay was optimized by analyzing the settling rate. Figure 9 shows the effect of the amount of clay in coagulation and settling rate characteristics during the settling process. The optimized amount of clay was found to be 0.8 g

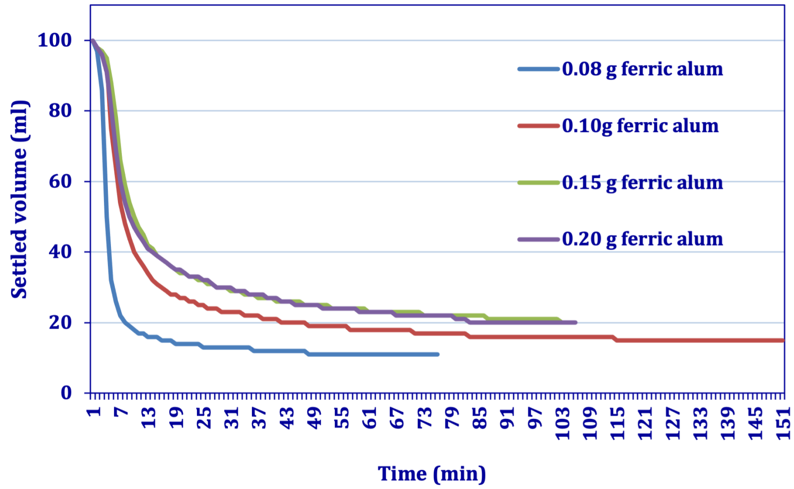

Figure 8. Effect of amount of Ferric alum used in spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process.

with 0.15 ferric alum for 100 ml of spent tannery vegetable tanning liquor. The results indicate gradual and continuous settling process with steady state achieved at about 60 min. with settled volume of ~5 ml.

Optimization of poly electrolyte

In order to achieve further enhancement in settling rate, the use of commercial flocculants, poly electrolyte was also studied. The optimized value of ferric alum and clay such as 0.15 g and 0.8 g were added to the various amount of poly electrolyte (4–15 mg). Then 100 ml of spent tannery vegetable tanning liquor was also added to it and mixed well. The settling rate was analyzed. This optimized amount was used for further studies. Whereas, Figure 10 shows the effect of amount of polyelectrolyte with optimized value of ferric alum and clay used in tannins coagulation and settling rate characteristics during the settling process. The optimized amount of polyelectrolyte was found to be 5 mg. The results indicate gradual and continuous settling process with steady state achieved at about 50 min. with settled volume of ~5 ml.

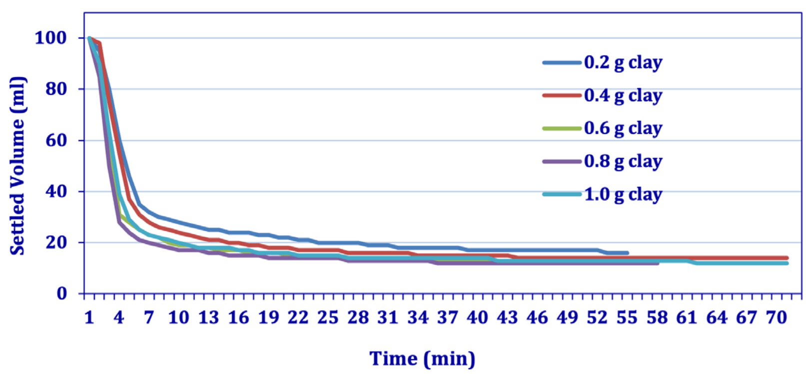

Figure 9. Effect of amount of clay with optimized ferric alum used in spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process.

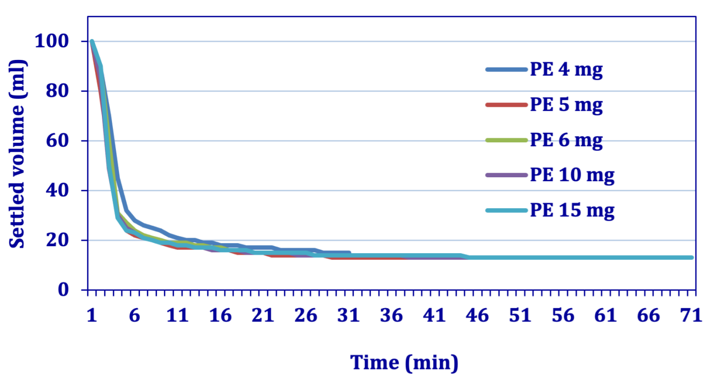

Figure 10. Effect of amount of polyelectrolyte (PE) with optimized value of ferric alum and clay used in spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process.

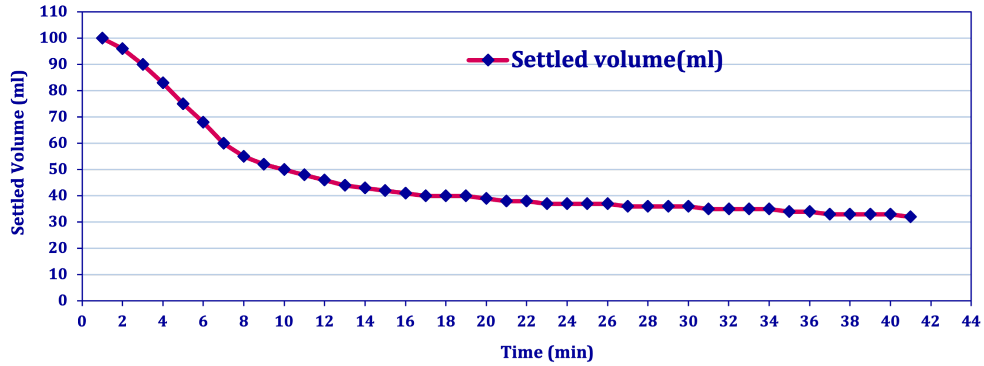

Figure 11. Effect of ultrasound pre-treated clay with normal optimized ferric alum and polyelectrolyte used in spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process.

Effect of ultrasound pre-treatment on optimized clay with normal optimized ferric alum and polyelectrolyte

Ultrasound pre-treatment on optimized 0.8 g of clay was performed using 80 W power for 30 minutes with normal optimized amount of 5 mg polyelectrolytes and 0.15 g of ferric alum and employed in coagulation process. Then 100 ml of spent tannery vegetable tanning liquor was added to it and mixed well. Effect of ultrasound on optimized clay in spent tannery vegetable tanning liquor was analyzed to increase the settling rate. The results indicated that settling rate was higher in ultrasound pre-treated clay when compared to normal clay as shown in Figure 11, with continuous settling process with steady state achieved at about 42 min. with settled volume of ~30 ml.

Effect of ultrasound pre-treatment on optimized polyelectrolyte with optimized normal clay ferric alum

Ultrasound pre-treatment on 5 mg of optimized polyelectrolyte was performed using 80 W power for 30 minutes and employed in coagulation process using optimized amount of 0.8 g of clay and 0.15 g of ferric alum. Then 100 ml of spent tannery vegetable tanning liquor was added to it and mixed well. Then the settling rate was analyzed.

The effect of ultrasound pre-treated polyelectrolyte and normal optimized amount of clay and ferric alum were used with spent tannery vegetable tanning liquor tannins to determine coagulation and settling rate characteristics during the settling process is shown in Figure 12, which indicates better settling rate of tannins with steady state achieved at about 15 min. with settled volume of ~15 ml.

Effect of lime on ultrasound pre-treated polyelectrolytes in spent tannery vegetable tanning liquor

Effect of lime on ultrasound pre-treated polyelectrolytes in spent tannery vegetable tanning liquor was analyzed. In order to enhance the pH of in spent tannery vegetable tanning liquor, lime was used. The amount of lime was optimized by analyzing the pH in spent tannery vegetable tanning liquor with lime as shown in Table I. Whereas, 0.6 g of lime provided neutralization for pH – 7 and taken as optimized value. The optimized polyelectrolyte (5 mg) was ultrasound pre-treated for 30 minutes using output power 80 W. Then the optimized amount of 0.6 g lime, 0.8 g clay and 0.15 g ferric alum was added to it and mixed well. Then 100 ml of spent tannery vegetable tanning liquor was also added to it. Settling rate characteristics during the settling process is shown in Figure 13. The results indicate rapid settling in 2 min. with settling process steady state achieved at about 20 min. with settled volume of ~10 ml.

Effect of lime on ultrasound pre-treated clay in spent tannery vegetable tanning liquor

Optimized amount clay 0.8 mg was ultrasound pre-treated for 30 minutes using output power 80 W. Then optimized amount of quick lime (CaO) 0.6 g and 0.15 g ferric alum was added to it. Then 100 ml of spent tannery vegetable tanning liquor was also added to it and mixed well. Figure 14 shows the effect of lime on ultrasound pre-treated clay in spent tannery vegetable tanning liquor with optimized amount of normal polyelectrolyte and ferric alum used in spent tannery vegetable tanning liquor tannins coagulation and

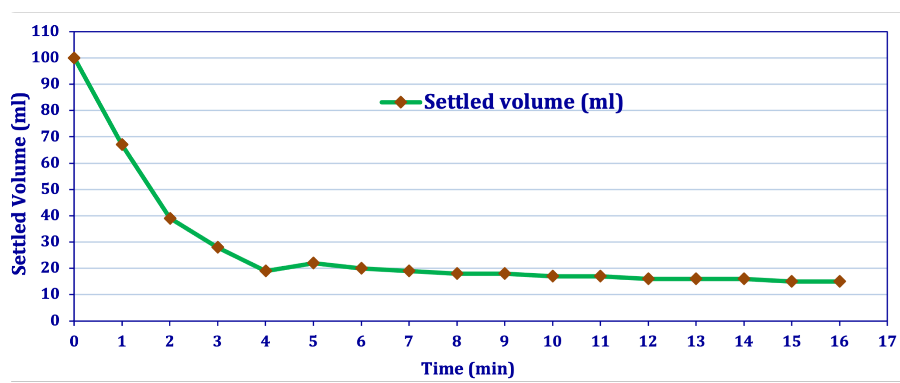

Figure 12. Effect of ultrasound pre-treated polyelectrolyte and normal optimized amount of clay and ferric alum used in spent tannery vegetable tanning liquor tannins coagulation and settling rate characteristics during the settling process.

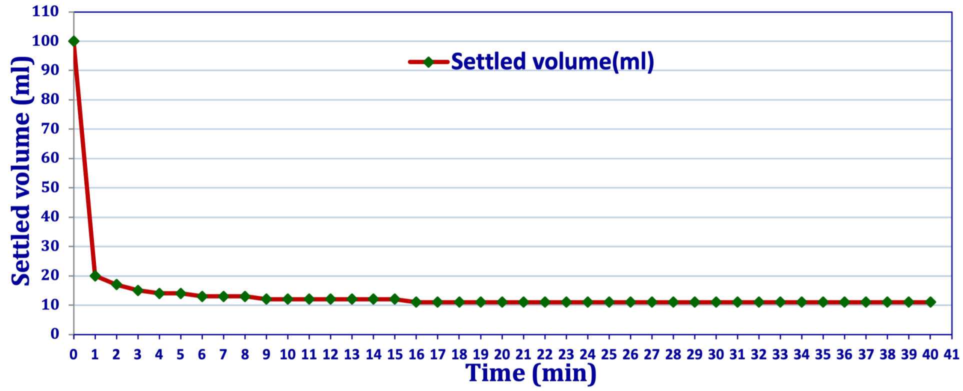

Figure 13. Effect of lime on ultrasound pre-treated optimized polyelectrolyte with optimized amount of normal clay and ferric alum used in spent tannery vegetable tanning liquor tannins coagulation and settling rate characteristics during the settling process.

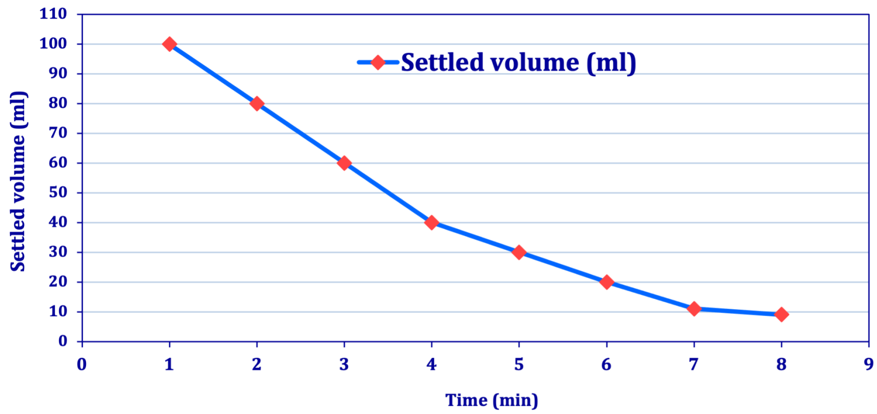

Figure 14. Effect of lime on ultrasound pre-treated optimized clay with optimized amount of normal polyelectrolyte and ferric alum used in spent tannery vegetable tanning liquor tannins coagulation and settling rate characteristics during the settling process.

Table I

Optimization of Lime in spent tannery vegetable tanning liquor and corresponding pH values

Exp. No.	Amount of Lime (g)	pH
1	0.2	5.5
2	0.4	5.5
3	0.6	7.0
4	0.8	10
5	1.0	10.5

settling rate characteristics during the settling process. The results indicate rapid settling rate, with steady state achieved at about 8 min. with settled volume less than 10 ml.

Table II shows the optimization of different coagulants on SVT tannins or spent tannery vegetable tanning liquor coagulation for facilitating the settling process and the amount required for 100 g tannins in SVT or 10 L of spent tannery liquor.

Whereas, Table III shows the effect of different optimized coagulants and influence of ultrasound pre-treatment on SVT tannins or spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process. Table III shows that in case of spent tannery vegetable tanning liquor (100 ml), optimized amounts of Ferric Alum (0.15 g) along with clay have achieved (5 ml, 60 min.); whereas addition of polyelectrolyte (5 mg) provided (5 ml, 50 min.). Settling rate was higher for ultrasound pre-treated clay with normal optimized ferric alum (0.15 g) and polyelectrolyte (5 mg) provided (30 ml, 42 min.); while in the case of ultrasound pre-treated polyelectrolyte has given (15 ml, 15 min.) with other agents as normal. Whereas, addition of lime (optimized 0.6 g) in this process along with ultrasound pre-treatment of either optimized clay or polyelectrolyte provided rapid settling in 8-10 min. with 10-20 ml settled volume.

Particle size analysis of clay and effect of ultrasound treatment

The particle size of clay samples after ultrasound treatment and without ultrasound employed in the coagulation process was analyzed. For ultrasound treatment, 1 g of clay sample was dissolved in 100 ml distilled water using ultrasound power 150 W. The ultrasound pre-treated sample was collected at 10 min and 20 min after ultrasound pre-treatment and particle sizes of clay samples were measured and the results shown in Table IV. Figure 15a shows the particle size distribution of normal clay sample without ultrasound pre-treatment. Figures 15b and 15c shows the particle size distribution of clay sample after ultrasound pre-treatment for 10 and 20 min respectively. The results indicate that there exist two distinct particle size segments for clay before and after ultrasound treatment and there has been a significant reduction of mean particle size (peak

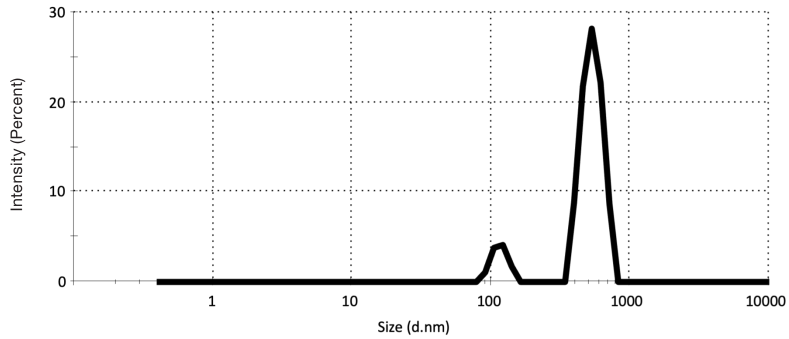

Figure 15a. Particle size distribution of normal clay sample without ultrasound pre-treatment

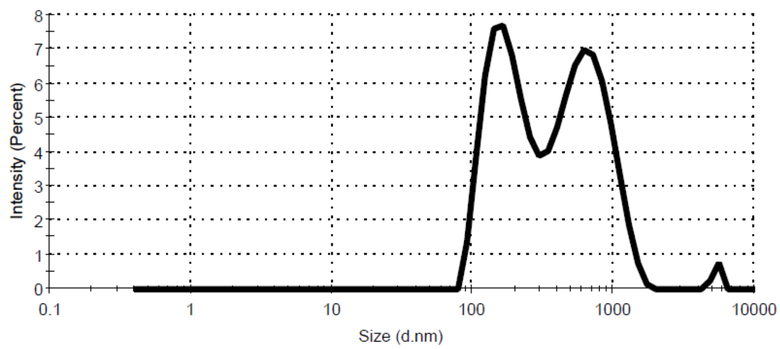

Figure 15b. Particle size distribution of clay sample after ultrasound pre-treatment for 10 min.

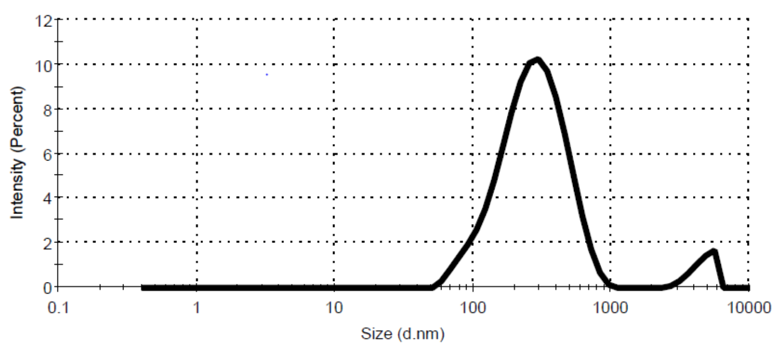

Figure 15c. Particle size distribution of clay sample after ultrasound pre-treatment for 20 min.

Table II

Optimization of different coagulants on SVT tannins or spent tannery vegetable tanning liquor coagulation for facilitating the settling process

Exp. No.	Coagulants Employed	Optimized Amount of Coagulant (g)			
		Vegetable Tannins Source and Amount			
		Synthetic Spent Liquor SVT (0.5 g Wattle extract in 100 ml water)	Spent Tannery Vegetable Tanning Liquor (100 ml)	100 g of Tannins from SVT (or % of Coagulant required on wt. of Tannins)	10 L of Spent Tannery Vegetable Tanning Liquor
1	Zinc Chloride	0.3		60	
2	Clay	0.8		160	
3	Ferric Alum		0.15		15
4	Poly Electrolyte		0.005		0.5
5	Lime		0.6		60

Table III

Effect of different optimized coagulants and influence of ultrasound pre-treatment on SVT tannins or spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process.

Exp. No.	Optimized Number of Coagulants with Ultrasound (US*) or Without US Pre-treatment		Vegetable Tannins Source			
			Synthetic Spent Liquor SVT (0.5 g Wattle extract in 100 ml water)		Spent Tannery Vegetable Tanning Liquor (100 ml)	
			% Settled Volume	Time (min)	% Settled Volume	Time (min)
	Coagulant used	Optimized Amount (g)				
1	$ZnCl_2$	0.3	20	80		
2	Clay + $ZnCl_2$	Clay – 0.8 $ZnCl_2$ – 0.3	10	53		
	Clay + $ZnCl_2$ US*		7	17		
3	Clay + Ferric Alum (F.A)	Clay – 0.8 F.A – 0.15			5	60
4	Poly Electrolyte (P. E) + Clay + Ferric Alum (F.A)	P.E – 5 mg Clay – 0.8 F.A – 0.15			5	50
5	Clay US* + P. E + Ferric Alum F.A	Clay US* – 0.8 P.E – 5 mg F.A – 0.15			30	42
6	P.E US* + Clay + F.A	P.E US* – 5 mg Clay – 0.8 F.A – 0.15			15	15
7	Lime + Clay + F.A + P.E US*	Lime – 0.6 Clay – 0.8 F.A – 0.15 P.E US* – 5 mg			10	2/20
8	Lime + Clay US* + F.A + P.E	Lime – 0.6 Clay US* – 0.8 F.A – 0.15 P.E – 5 mg			8	10

Table IV

Effect of ultrasound (150 W at 20 kHz) on the particle size distribution of clay samples (1 g in 100 ml)

Sample	Particle size (nm)		
	Peak 1	Peak 2	Peak 3
Un ultrasound pre-treated clay	538.6	116.5	0
Ultrasound pre-treated clay (10 min)	659.1	177.7	5375
Ultrasound pre-treated clay (20 min)	298.2	4630	0

1) of clay from 539 nm to 298 nm for 20 minutes treatment. This significant reduction in particle size provided more surface area for clay and could be attributed to the better performance of ultrasound pre-treated clay in coagulation process of vegetable tannins.

Conclusions

In the present approach, the remediation of tannins available in spent vegetable tan liquor using another natural material, soil clay has been employed for the coagulation of spent vegetable tannins. Commercial condensed vegetable tanning agent, Wattle GS powder (SVT) as well as vegetable tanning process spent liquor collected from a commercial tannery were used in the experiments. Various other precipitating agents have been investigated and their amounts optimized (Table II). The efficacy of coagulation is monitored through settling characteristics and %Settled volume for a given time. Table III shows the summary of the results obtained through the present study. The results indicate that for 100 ml SVT (0.5 g tannins), the combined use of optimized $ZnCl_2$ (0.3 g) and clay (0.8 g) has provided enhancement as compared to individual use, whereas ultrasound pre-treatment of $ZnCl_2$ has given further improvement. In case of spent tannery vegetable tanning liquor (100 ml), optimized amounts of Ferric Alum (0.15 g) along with clay have achieved (5 ml, 60 min.); whereas addition of Poly electrolyte (5 mg) in the same process and ultrasound pre-treatment of either optimized clay or polyelectrolyte has provided further enhancement. Whereas, the best performance was achieved due to addition of lime (optimized 0.6 g) along with ultrasound pre-treated optimized polyelectrolyte (5 mg), normal clay (0.8 g) and ferric alum (0.15 g) with rapid settling in 2 minutes, with settling steady state achieved at ~20 minutes, with settled volume of ~10 ml; whereas (10 ml, 8 min.) obtained for ultrasound pre-treated optimized clay (0.8 g) with other agents as normal in the same process.

There is a significant reduction in particle size of clay from 539 nm to 298 nm for 20 minutes ultrasound pre-treatment, which provided more surface area for clay and attributed to the better performance of ultrasound pretreatment for clay sample in coagulation process of vegetable tannins. This method could be useful for remediation of vegetable tannins as natural materials, available in spent vegetable tanning liquors as sectional stream, using another available natural material clay through coagulation process with ultrasound pre-treatment for possible use such as enhancement of soil. However, separate study in this regard for the applicability and efficacy is very much essential, which would be investigated in future work. The coagulation method *per se* (not soil enrichment) as per the present shall be extended to other streams with suitable modifications. Thus, the present study has demonstrated the ultrasound assisted coagulation science and technology for beneficial remediation of wastewater in general, whereas, spent vegetable tanning liquor in specific.

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