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Effective use of nanocrystalline and lime when used in combination of coagulants - Alum, $Fecl_3$ and $FeSO_4$ for suspended solids and COD removal from pharmaceutical industry effluents

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Abstract- Color, Total Suspended Solids (TSS) and Chemicals are the main form of pollutants in wastewater or industrial effluents. In pharmaceutical effluents the values of these parameters are high and also depict wide variation due to variation in the type of medicines manufactured and raw material utilization. In the present investigation in order to decrease the waste hazards and to restrict resulted effects on the environment, the efficiency of coagulation and flocculation processes have been studied. 3 types of coagulants i.e. aluminium sulphate (alum), ferric chloride, ferrous sulphate along with pre dosing of lime (pH booster) and nanocrystalline (adsorbent) have been used. Polyelectrolyte is used as a flocculent. This was done by carrying out jar test. The effects of agitation speed, settling time, pH and appropriate coagulant combinations and their dosages were examined. It was found that the combination of '0.2% nanocrystalline, 5% alum, 0.1% of polyelectrolyte', proved to be best among all the other combinations and this worked well at 8-8.5 pH. At 60 seconds of rapid mixing and 15 seconds of slow mixing and 45 minutes of settling time, higher removals of suspended solids, color and reduction in COD was achieved. The results also indicated that coagulation and flocculation process had contributed bigger roles in the integrated treatment systems.

Index Terms- Chemical Oxygen demand (COD), Total Suspended Solids (TSS)

I. Introduction

In every chemical industry there is possibility of environmental hazard. So these hazards can be reduced by proper effluent treatment. Effluent treatment is a vital part of every chemical industry to mitigate the effects of environmental hazards. Effluent generally refers to wastes discharged into the surface water. If an effluent is not treated and safely disposed, then it could be a potential source of surface and ground water contamination, as it may percolate through soils and sub soils, causing pollution to receiving waters. (Tatsi.*et.al*, 2003). The pharmaceutical effluents have ingredients with characteristics that cause them to designate as dangerous waste at time of disposing. The specific composition of an effluent influences its relative treatability and depends to a large extent on the contamination to be removed. (Kreith, 1994). In general, the treatment of effluent often involves combinations of various techniques. They include aerobic and anaerobic biological treatments, membrane processes, chemical oxidation and precipitation, activated carbon and adsorption, coagulation and flocculation. Therefore a combination of physical, chemical and biological treatment is often required for the efficient treatment of the effluent.

Chemical treatment is effective enough to treat pharmaceutical effluents and decrease considerable COD, color and TSS (total suspended solids) as physical and biological process alone is normally not effective to remove these constituents. (Rautenbach and Millis, 1994). Coagulation and flocculation is widely used in water and wastewater treatment and these techniques form important step in treatment process. (Muhammad *et al*, 1998; Amokrane *et al*; 1997; AWWA, 1971). Coagulation process is effective for removing high concentration organic pollutants (in colloidal form) (wang *et al*; 2002), heavy metals and some anions using different coagulants. Chemical coagulants can destabilize colloidal particles by four distinct mechanisms; double layer compression, charge neutralization, enmeshment in a precipitate and inter particle bridging (Al – Malack *et al*, 1999). Different coagulants provide different degrees of destabilization. The higher the valance of the counter ions, the more will be the destabilization effect and less amount of dose required for coagulation.

II. Materials and Methods

Effluent samples (grab samples) were collected from Sequent Scientific Ltd, a pharmaceutical company situated in Industrial area, Baikampady, Mangalore. Chemicals of A R grade and distilled water were used in the preparation of solutions in the present investigation. They include aluminium sulphate, ferric chloride, ferrous sulphate, polyelectrolyte (anionic), nanocrystalline, lime, concentrated sulphuric acid, sodium hydroxide pellets, mercury sulphate, silver sulphate, potassium dichromate, ferroin indicator and ferrous ammonium sulphate. Stock solutions of alum, ferric chloride, ferrous sulphate and lime were prepared by dissolving 5g each substance in distilled water and the solution volumes were increased to 100ml. stock solution of nanocrystalline and polyelectrolyte are prepared by dissolving 0.2g and 0.1g of each of these respectively in 100ml standard flasks. Stock solutions should be prepared before starting the experiments.

All experiments were conducted using the jar testing method to determine the optimum pH value and coagulant dose. 3 beakers were used for testing. Each of these beakers was filled with 1000ml of the sample. In order to determine the optimum dosage of adsorbent + coagulant combination or pH booster + coagulant combinations, initial pH of 4-4.5, 6-6.5 and 8-8.5 were used in 3 beakers respectively. The pH of the solution was controlled by adding 0.01N sulphuric acid or 0.01N sodium hydroxide solution.

After the desired amount of adsorbent/ pH booster (lime) was added, rapid mixing for about 60 seconds and settling time of 15 minutes given. At the end of 15 minutes required amount of coagulant was added to the effluent samples, the beakers were agitated or stirred rapidly i.e. the initial rapid mixing for all the experiments was taken as 60 seconds. (Range between 30-300 seconds. Ramirez and Velasque , 2004. Aquilar et al, 2005). The coagulation can be watched during this process. After the agitation was stopped, the sample was allowed to settle for 45 minutes. At the end of 45 minutes, desired amount of flocculent added and this was followed by gentle (slow) mixing for 15 seconds, (Tatsi, et al, 2003; Aquilar et al, 2005). The generation of flock can be watched during this process. Flock was allowed to settle for 20 minutes before withdrawing the samples for analysis. These procedures were performed several times so that the optimum pH and dose of the adsorbent, pH booster, coagulant and flocculent can be determined.

Analytical analysis: pH, TSS, and COD of both untreated and treated samples were determined. The COD test was performed by open reflux method followed by titration. It is used to measure the oxygen demand for the oxidation of organic matter by strong chemical oxidant which is equivalent to the amount of organic matter present in the sample. In order to determine TSS, samples were filtered through a whatmann no 42 filter paper. The residue on the filter paper was dried at 106°C. The increase in the weight of the filter paper represents the TSS. pH of the wastewater was measured by systronics pH meter.

The COD is calculated thus,

COD= (Titer value of blank – Titer value of sample) x 8000 x normality of F.A.S x dilution factor

Amount of sample taken (in ml)

The % of COD reduction is calculated as,

$$\% \text{ reduction} = \left(\frac{C_0 - C}{C_0}\right) \times 100$$

Where, C_0 = initial COD (before treatment) and C= final COD (after treatment)

The TSS is calculated thus,

TSS= (final weight of the filter paper – initial weight of the filter paper) x 1000 x1000

Amount of sample taken (in ml).

The objective of this study was to examine the

1. Efficiency of nanocrystalline (Cao) as adsorbent in combination with different coagulants (Aluminium sulphate, ferric chloride, ferrous sulphate) in reducing COD and TSS.

2. Efficiency of the same coagulants along with pre dosing of lime in reducing COD and TSS.

The experiments involved with the determination of the most appropriate adsorbent + coagulant combination or pH booster + coagulant combination, effect of flocculent, their dosages and identification of the optimum experimental conditions for the efficient application of these processes.

III. Results and discussion

All possible combination of ‘‘adsorbent (nano) + coagulants’’ and ‘‘pH booster (lime) +coagulants’’ along with polyelectrolyte were carried out at 4-4.5, 6.5-6.8 and 8-8.5 pH. The best combination, optimum dose and pH value were determined by comparing the effectiveness of the above combinations for obtaining maximum color, TSS and COD removal. For each case, the optimum pH is primarily determined. Then the optimum effective dose of the coagulant is calculated at optimum pH. The influence of pH on the removal of suspended solids, color and COD is important in coagulation process (Hamidi Abdul Aziz et al, 2007). According to AWWA (1971) , the pH is the most important variable in the coagulation process for water treatment. The extent of pH range is affected by the types of coagulant used and by the chemical composition of the effluent, as well as by the concentration of the coagulant. In the present investigation the coagulants were showing best results in the pH range 8-8.5.

Efficiency of nanocrystalline (Cao) as adsorbent in combination with different coagulants (Aluminium sulphate, ferric chloride, ferrous sulphate) in reducing COD and TSS; Efficiency of nanocrystalline+ alum +polyelectrolyte combination:

Results from the coagulation studies showed that at 4-4.5 pH, COD removal of 6% and TSS removal of 10% were observed with fast settle ability of good flock for nanocrystalline+ alum +polyelectrolyte combination, when 4ppm, 300ppm, 2ppm of each of these, were added respectively. 29% of COD removal and 20% of TSS removal along with fast settle ability of good flock were observed at 6.5-6.8 pH for the same combination, when 6ppm, 200ppm, and 1ppm of each of these, were added respectively. Maximum COD and TSS removal efficiencies were observed for nanocrystalline+ alum +polyelectrolyte combination at 8-8.5 pH when 4ppm, 250ppm and 1ppm of each of these, were added respectively.COD removal up to 54% and TSS removal up to 89%and also good clarity, good flock formation and fast settle ability of flock was observed.

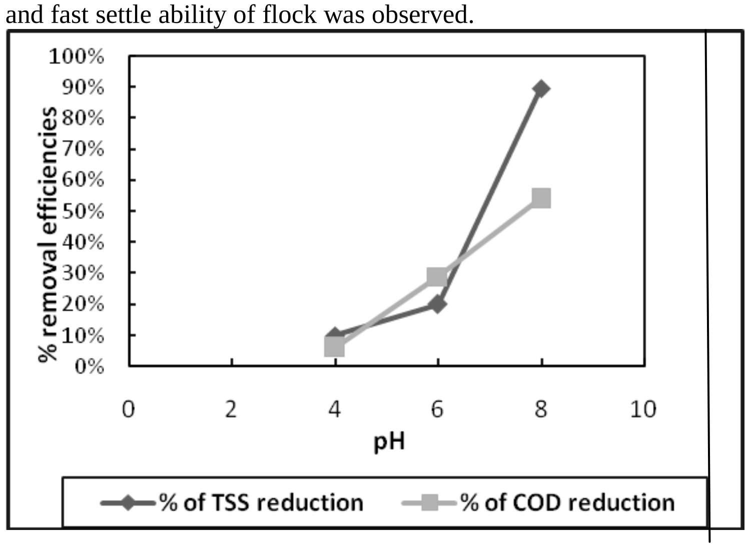

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Fig1-COD and TSS removal efficiencies v/s pH for the above combination

When alum is added to the solution, it will react with the available alkalinity such as carbonates, bicarbonate and hydroxide or phosphate to form insoluble aluminium salts which incorporates the colloidal particle. Reaction of alum with water (Droste et al, 1997) is given below,

$$Al_2(SO_4)_3.18H_2O + 6H_2O \longrightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^{2-} + 18H_2O \quad \textbf{(1)}$$

In the presence of natural alkalinity, equation (1) can be written as

$$Al_2(SO_4)_3.18H_2O + 3Ca(HCO_3)_2 \longrightarrow 2Al(OH)_3 + 3CaSO_4 + 6CO_2 + 18H_2O$$

Addition of alum was also found to remove a large proportion of high molecular weight of natural organic matter compounds. Additional benefits of using alum was precipitation of sulphur compounds, easier sludge dewatering , increased efficiency in elimination of pollutants and reduction in energy consumption in biological process applied (kokila.AParmar et al, 2011) as final stage of treatment. Thus, alum becomes a suitable coagulant. On the other hand, it has been demonstrated that nanocrystalline metal oxides have unparallel sorption properties for polar organic/ inorganic and other chemical species. The unique morphological features such as pore diameter, structures, polar nature of the surfaces and high surface areas are believed to account for their unusual sorption properties.(B.Nagappa and G.T.Chandrappa, 2007). Good clarity obtained because of effective solid-liquid separation and this was due to the action of polyelectrolyte, which acts as a flocculent. It is known that flocculation is the only process designed to change the particle size distribution without actual removal of particles from wastewater. (lawler 1997).

Efficiency of nanocrystalline+ ferric chloride +polyelectrolyte combination

The obtained results for the above combination showed that at 4-4.5 pH, COD removal of 12.5% and TSS removal of 10% were observed with fast settle ability of good flock for nanocrystalline+ ferric chloride +polyelectrolyte combination when, 4ppm, 250ppm, 0.5ppm of each of these were added respectively. The removals of COD up to 6.5% and TSS up to 20% along with good flock formation and fast settle ability were observed at 6.5-6.8 pH for the same combination, when 4ppm, 200 ppm, and 0.5ppm of each of these, were added respectively. Optimum COD and TSS removal efficiencies were observed for nanocrystalline+ ferric chloride +polyelectrolyte combination at 8-8.5 pH when 4ppm, 150ppm and 0.5ppm of each of these, were added respectively. COD removal up to 20% and TSS removal up to 44% and also good clarity, good flock formation and fast settle ability of flock was observed.

Reaction of ferric chloride in water (Droste et al, 1997)

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ + 3Cl^- \quad \textbf{(2)}$$

In the presence of natural alkalinity equation (2) can be written as

$$2FeCl_3 + 3Ca(HCO_3)_2 \longrightarrow 2Fe(OH)_3 + 3CaCl_2 + 7CO_2$$

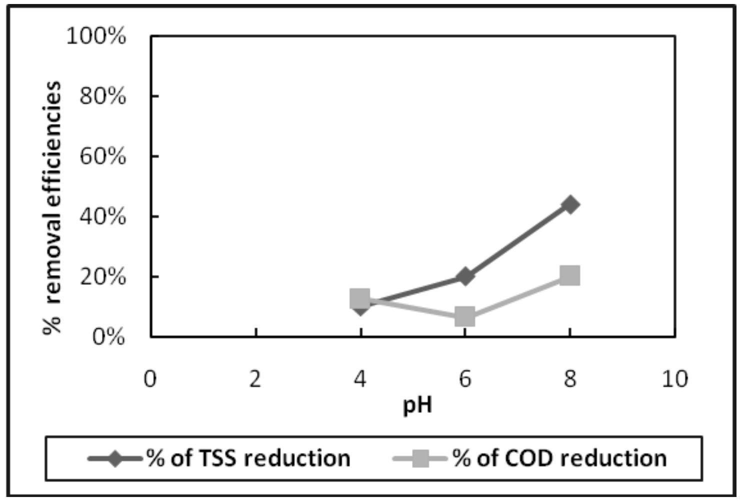

Fig2-COD and TSS removal efficiencies v/s pH for the above combination

Efficiency of nanocrystalline + ferrous sulphate + polyelectrolyte combination

Results obtained for the above combination showed that at 4-4.5 pH, only 3% of COD removal, and 10 % of TSS removal along with medium flock formation and slow settle ability were observed when, 4ppm, 250ppm, and 1ppm of each of these were dosed respectively. At similar dosages of the above combination, 5% and 12% of COD and TSS removal were observed at 6.5-6.8 pH respectively. Flock formation was found to be medium and settle ability was slow. Results of coagulation studies on nanocrystalline+ ferrous sulphate +polyelectrolyte combination showed that addition of 4ppm of nanocrystalline, 250ppm of ferrous sulphate and 1ppm of polyelectrolyte at pH 8-8.5 had been effective in COD removal up to 10% and TSS removal up to 15% but flock formation was medium and settle ability was slow.

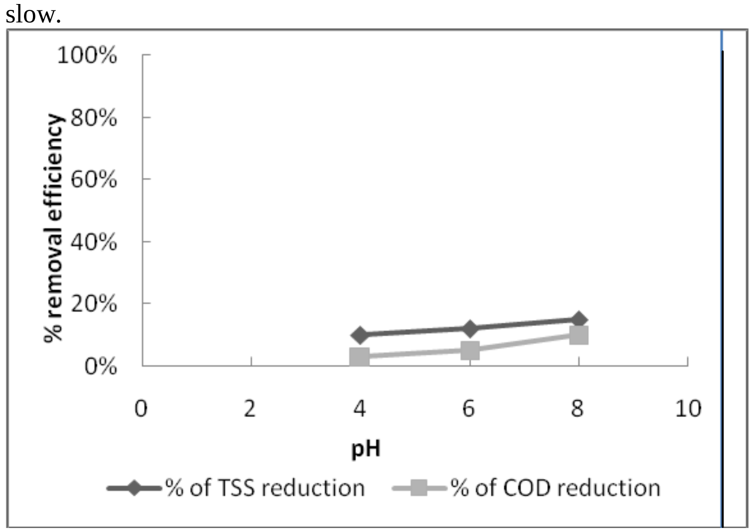

Fig3-COD and TSS removal efficiencies v/s pH for the above combination

Reaction of ferrous sulphate in water (Droste et al, 1997)

$$2FeSO_4 .7H_2O + O_2 + 4H_2O \longrightarrow 2Fe(OH)_3 + 2H^+ + 2SO_4 + 14H_2O \quad \mathbf{(3)}$$

In the presence of natural alkalinity equation **(3)** can be written as

$$2FeSO_4 .7H_2O + 2Ca(HCO_3)_2 \longrightarrow 2Fe(OH)_3 + 2CaSO_4 + 4CO_2 + 13H_2O$$

Efficiency of the same coagulants along with pre dosing of lime in reducing COD and TSS, Efficiency of lime + alum +polyelectrolyte combination

Lime being the most cost effective chemical was tried with the coagulants .Coagulation increases with increase in alkalinity and lime is a very good pH booster .The advantage of alum as coagulant is already discussed. Therefore a combination of Lime+ alum + polyelectrolyte was examined. When lime is used with alum the following reaction takes place (Droste et al, 1997)

$$Al_2(SO_4).18H_2O + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 + 2CaSO_4 + 18H_2O$$

The study on the effectiveness of lime + alum +polyelectrolyte combination showed that at 4-4.5 pH when 250ppm, 250ppm and 1ppm of each of these were added respectively, 10% of COD and 10% of TSS were removed along with medium flock formation and slow settle ability. Addition of 250ppm, 200ppm, and 1ppm for the above combination at 6.5-6.8 pH had given 18% reduction in COD and 51.7% of reduction in TSS along with the formation of poor flock and slow settle ability. Results of coagulation studies on the above combination shows that addition of 250ppm of lime, 150ppm of alum and 1ppm of polyelectrolyte at pH 8-8.5 had been effective in COD removal up to 48% and TSS removal up to 84% along with good flock formation and fast settle ability.

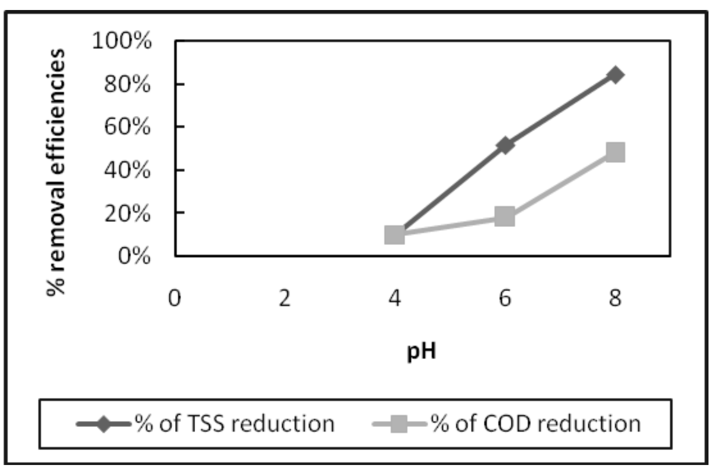

Fig4-COD and TSS removal efficiencies v/s pH for the above combination

Lime is also used with iron salts like ferric chloride and ferrous sulphate .During coagulation, when iron salts hydrolyze in water they form corresponding gel like hydroxides and some positively charged mononuclear and polynuclear species. These positively charged compounds combine with negatively charged colloidal particles present in the waste water by charge neutralization mechanism and at the time of settling, under gravity these hydroxides and complexed hydroxides sweep away remaining uncharged and charged colloidal particles of the waste water with them and precipitate out .(Kokila A Parmar et al, 2011). Lime on the other hand plays vital role in flock formation, enhancing the clarity as well as contributes in solid liquid separation to considerable extent. Therefore, a combination of lime with ferric chloride and with ferrous sulphate is examined.

Efficiency of lime + ferric chloride +polyelectrolyte combination

Results obtained on the efficiency of the above combination show that at 4-4.5 pH when 250ppm, 350ppm and 0.5ppm of each of these were added respectively, 12% COD reduction and 30% of TSS reduction was observed. There was medium flock formation and slow settle ability. The removals of COD up to 31% and TSS up to 50% along with good flock formation and fast settle ability were observed at 6.5-6.8 pH for the same combination, when 250ppm, 250ppm, and 0.5ppm of each of these, were added respectively. Results also indicate that at 8-8.5 pH for lime + ferric chloride +polyelectrolyte combination when 250ppm, 150ppm, and 0.5ppm of each of the above were added respectively there was good flock formation and fast settle ability with COD reduction up to 43% and TSS reduction up to 72%.

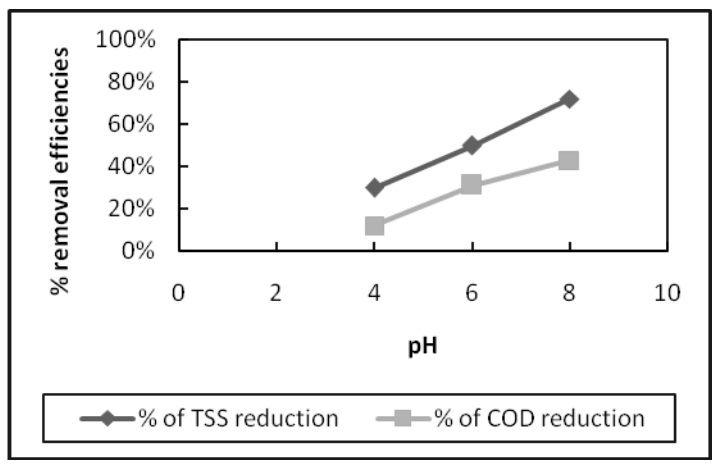

Fig5-COD and TSS removal efficiencies v/s pH for the above combination

When lime reacts with ferric chloride the following reaction takes place (Droste et al , 1997)

$$2FeCl_3 + 3Ca(OH)_2 \longrightarrow 2Fe(OH)_3 + 3CaCl_2$$

Efficiency of lime + ferrous sulphate +polyelectrolyte combination

Results of coagulation studies on the above combination shows that the addition of 250ppm of lime, 250ppm of ferrous sulphate and 0.5ppm of polyelectrolyte at pH 4-4.5 had been effective in COD removal up to 5 % and TSS removal up to 10% with medium flock formation and slow settle ability. Results for the efficiency of the same combination also shows that at 6.5-6.8 pH, on addition of 250ppm, 200ppm and 0.5ppm of each of these respectively, medium flock formation and slow settle ability was seen along with COD removal up to 7% and TSS removal up to 12%. Optimum results for lime + ferrous sulphate +polyelectrolyte combination at 8-8.5 pH there was, 10% and 15% of COD and TSS removal respectively along with good flock formation but slow settle ability.

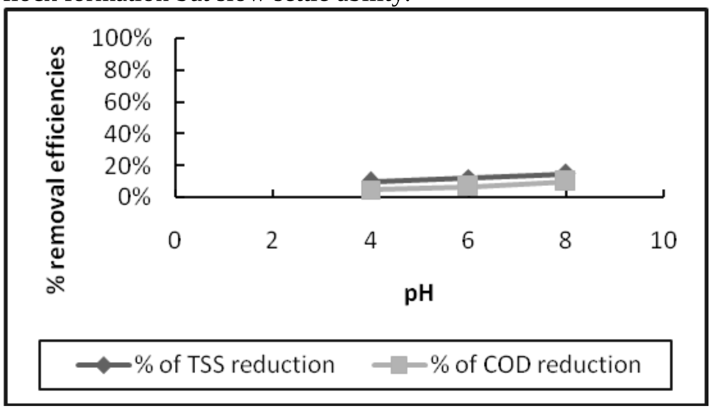

Fig 6-COD and TSS removal efficiencies v/s pH for the above combination

When lime reacts with ferrous sulphate the following reaction takes place (Droste et al, 1997)

$$2FeSO_4.7H_2O + 2Ca(OH)_2 + 0.5O_2 \longrightarrow 2Fe(OH)_3 + 2CaSO_4 + 13H_2O.$$

Results obtained in our study indicate that the combination of nanocrystalline +alum + polyelectrolyte is giving maximum overall COD and TSS removal efficiency. However, coagulants with the combination of lime showed appreciable reduction in suspended solids and COD removals but large amount of sludge production posed disposal problems. Secondly, Alum when compared to ferric chloride and ferrous sulphate does not cause drop in the pH value of the effluent during treatment process. At low pH it is difficult to bring about complete coagulation of pharma effluents and this is exactly what is observed when $Fecl_3$ and $FeSO_4$ are used. Therefore combination of $Fecl_3$ and $FeSO_4$ with nanocrystalline or lime does not bring appreciable reduction in COD and TSS value. Also $FeSO_4$ imparts brown color to the effluent which is unfavorable. Therefore it can be concluded that this combination is most suited for the treatment of pharmaceutical effluents when compared to other combinations.

However, in order to get better results, addition of optimum dosage is very essential because at higher coagulant dosages continued adsorption takes place and this will result in charge reversal and restabilisation of the suspension. Only freshly prepared chemicals must be used or else desired result is not achieved.

The influence of agitation speed on the removal of suspended solids is of high importance and this has been recommended by Aquilar et al (2005) and Tatsi et al (2003). Agitation distributes the coagulant chemicals throughout the effluent sample. It is extremely important that the coagulant chemical be distributed very quickly and efficiently because the intermediate products of the coagulant reactions are the destabilizing agents. The intermediate species are short lived and they are used to achieve destabilization through charge neutralization when in contact with solid particles present in the effluent sample. The duration of retention time is of high importance. The retention time was in agreement with the established range of between 30-120 minutes. (Amokrane et al 1997; Connolly et al 2004). At this range considerable reduction in TSS was achieved.

IV CONCLUSION

It can be concluded that the combination of nanocrystalline, alum and polyelectrolyte at 8-8.5 pH is very effective in removal of suspended solids, color and reduction in COD value. Under optimal conditions of process parameters, like suitable pH, coagulant dosage, agitation speed and retention time the above combination works at its best. The study also indicated that coagulation and flocculation process are significantly important in the overall integrated treatment system. Integrating the process into existing biological and physical treatment may enhance the treatment performance particularly for removals of suspended solids, color and COD.

REFERENCES

[1] Garima Jain, ShantaSatyanarayan, Nawghare, P., Kaul, S.N and Szpyrcowicz, L, "Treatment of Pharmaceutical wastewater (Herbal) by coagulation / flocculation process".Intern.J.Environ.Studies. 58, 313-330 (2001).

[2] Nagappa. B and Chandrappa, G.T, "NanocrystallineCaO as adsorbent to remove COD from paper mill effluent".Journal of Nanoscience and Nanotechnology, 7, 1-4 (2007).

[3] NabiBidhendi, G.R., Torabian, A., Ehsani, Razmkhah, N. "Evaluation of industrial dyeing wastewater treatment with coagulants and polyelectrolyte as a coagulant aid" Iran. J. Environ, Health. Sci. Engg.4.(1), 29-36(2007).

[4] KokilaParmar, A., SarjuPrajapati, Rinku Patel and YogeshDabhi, "Effective use of ferrous sulphate and alum as coagulant in treatment of dairy industry wastewater", ARPN Journal of Engineering and Applied Sciences. 6.(9), 42-46 (2011).

[5] Ghaly,A.E., Snow,A. and Faber, B.E, "Treatment of grease filter wash water by chemical coagulation", Canadian Biosystems Engineering.48, 6.13-6.19(2006).

[6] Steven Safferman, I.Phd.,P.E. "Fundamentals of coagulation and flocculation"., (1-6).

[7] Abdelaal, A.M., "Using a natural coagulant for treating wastewater", IWTC8 781-792 (2004).

[8] HamidrezaFarajnezhad and ParvinGharbani., "Coagulation treatment of waste water in petroleum industry using poly aluminium chloride and ferric chloride", IJRRAS 13(1)., 306-310(2012).

[9] Hamidi Abdul Aziz, Alias,S., Assari,F and MohdNordinAdlan, "The use of alum, ferric chloride and ferrous sulphate as coagulants in removing suspended solids, colour and COD from semi aerobic landfill leachate at controlled pH", Journal of Waste management and research,25,(6),556-565(2007).

[10] Tzoupanos.N. D. and Zouboulis.A.I., "Coagulation-flocculation processes in water/ wastewater treatment: the application of new generation of chemical reagents", 6th IASME/WSEAS. International conference on heat transfer, thermal engineering and environment, 309-317 (2008).

[11] "Waste Water Engineering: treatment and re use". Fourth edition by Metcalf and Eddy, Inc., 81-93 (2003).

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