Coagulation–flocculation for lignin removal from wastewater – a review

Arfa Nawaz, Zaki Ahmed, Ali Shahbaz, Zahra Khan and Mohsin Javed

ABSTRACT

Industrial discharge has tremendously increased inorganic pollutants in water bodies all over the world. Paper and pulp effluent is included in one of the most pollution generating discharges containing complex chemical compounds such as lignin. For clean and healthy water resources, the recovery of lignin from wastewater from the paper and pulp industry is of high importance. Available chemical and biological technologies for removal of lignin have certain drawbacks. Coagulation and flocculation is not only the economic but also the effective method for removal of lignin. The present review highlights available coagulants employed for removal of lignin from paper and pulp wastewater. Each coagulant is pH dependent and shows varied results with change in effluent characteristics. The hydrolysis products of aluminium-based coagulants, iron-based coagulants and copper sulphate have positive charges. These positive charges promote formation of flocs through charged neutralisation or sweep flocculation. In the case of titanium-based coagulants, hydrolysis product is negatively charged and mode is heterocoagulation. Ninety percent recovery of lignin is achieved by using a mixture of oxotitanium sulphate and aluminium sulphate and 80% with aluminium sulphate. Virtually complete recovery of lignin is observed with oxotitanium sulphate.

Key words | aluminium-based coagulants, coagulation, iron-based coagulants, lignin removal, sodium-based coagulants, titanium-based coagulants

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INTRODUCTION

Wastewater from the paper and pulp industry is highly contaminated having complex toxic substances. Visible contamination is imparted in the form of a high colour index. This colour comes from tannin resins, synthetic dyes, wood, lignin and its degradation products formed by reaction of chlorine and lignin (Sakam 1987). Lignin stands responsible for high colour index, turbidity and chemical oxygen demand (COD). Lignin is an aromatic compound difficult to oxidise biochemically at the wastewater treatment facilities existing at virtually all paper and pulp plants (Chernoberezhskii *et al.* 2002). The paper industry consumes a lot of water during the whole production process and produces a lot of contaminated wastewater. The pulp and paper industry is one of the heaviest users of water within the US industrial economy, requiring 54 m^3 on average of water per metric ton of finished product (Gunderson 2013). Economic treatment of wastewater is a real challenge. Several techniques have so far been developed to achieve optimised solution for removal or recovery of lignin from paper-pulp waste. These include physical, chemical, biological and advanced engineered techniques. Biological treatments are not successful due to low biochemical oxygen demand (BOD) to COD ratio (ca. 0.2) and the presence of persistent organic compounds (Garg *et al.* 2005, 2007). It is also reported that lignin is difficult to oxidise biochemically (Chernoberezhskii *et al.* 2002). Among the chemical methods, the coagulation–flocculation method is considered one of the most economic, simple and efficient solutions for the removal of lignin. Coagulation–flocculation has been extensively utilised for treatment of paper-pulp industry wastewater (Wang *et al.* 2011), palm oil mill effluent (Ahmad *et al.* 2005), abattoir wastewater (Amuda & Alade 2006) and textile wastewater (Meric *et al.* 2005) for removal of lignin from wastewater. Other industries where coagulation is extensively used for wastewater treatment include semiconductor manufacturing, the dye industry, fish and meat industry and soft drink industry

(Livke *et al.* 1989; Tebai & Hadjivassilis 1992; Lin & Lin 1993; Tanimoto & Yamagishi 1997; Yamagushi 1997).

Coagulation serves as a primary treatment to remove toxicity, colour, COD and BOD (Pradeep *et al.* 2011). The coagulation process makes secondary treatment cost effective as it tends to reduce factors causing turbidity. Turbidity has chemical, physical and biological origins (Abolhassani & Astaraie 2010). Lignin is a complex structured chemical compound with molecular formula $C_9H_{10}O_2$, $C_{10}H_{12}O_3$, $C_{11}H_{14}O_4$. The possible lignin structure is given in Figure 1.

Lignin is relatively hydrophobic and aromatic in nature. Computational simulation can also be used to study lignin structure (Glasser & Glasser 1974).

COAGULATION CHEMISTRY AND MECHANISM

Coagulation is the process of separation of suspended organic particles from solution by making flocs for easy settlement. The coagulation process involves interactive forces between organic particles and coagulant, type and dosage of coagulant, pH and temperature. The coagulation mechanism takes place in a series of four steps starting with enmeshment, adsorption, charged neutralisation and finally precipitation.

A conceptual view of coagulation reaction is shown in the Figure 2.

The coagulation process can be even more simplified as two major steps of charged neutralisation and sweep
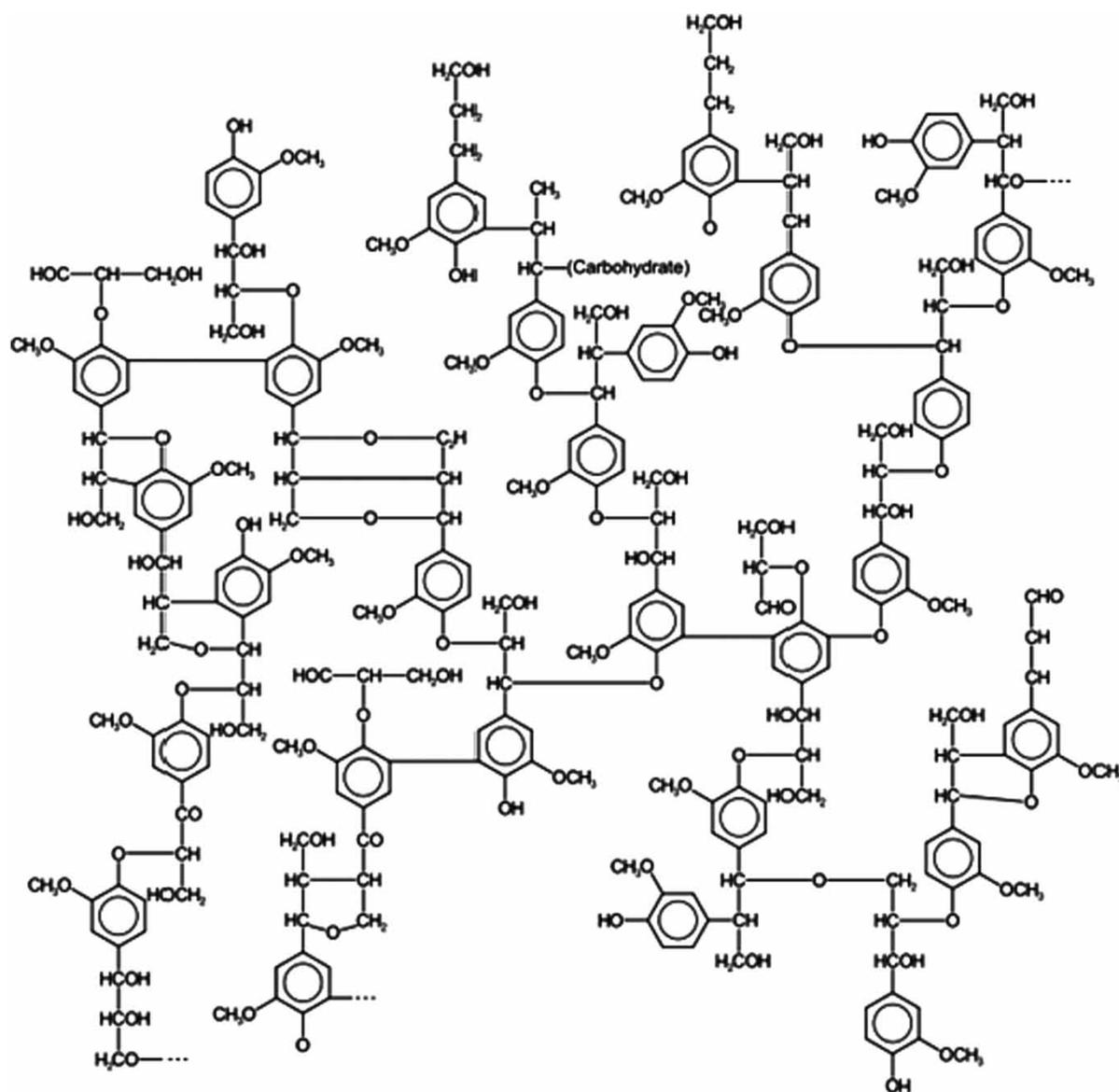

Figure 1 | Computational simulation of lignin structure (Glasser & Glasser 1974).
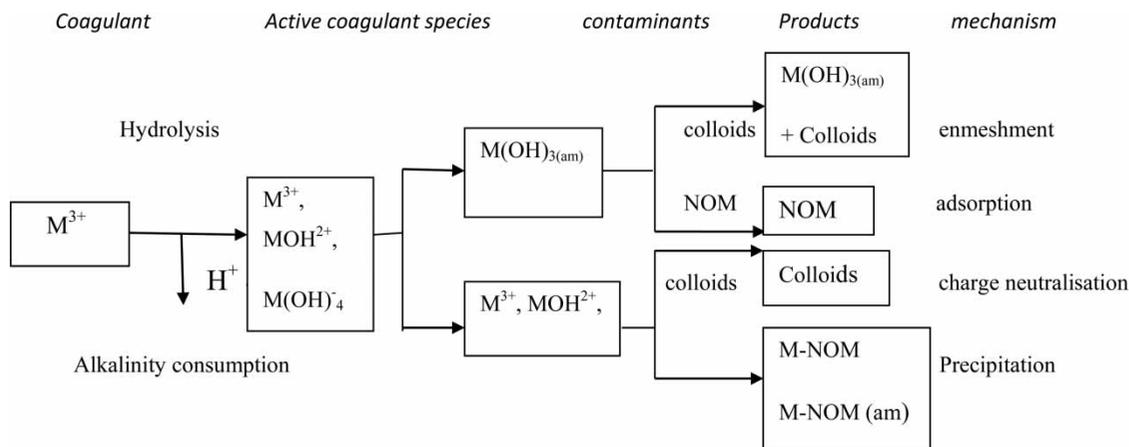
Figure 2 | Conceptional view of coagulation reaction.

flocculation. In sweep coagulation or flocculation, enmeshment and adsorption of impurities occur on cationic metal hydroxides resulting in precipitation of organic pollutants (Duan & Gregory 2003). Charge neutralisation takes place when negatively or positively charged particles are clouded with counter ionic particles. Attractive forces between opposite ions result in neutralised particles with no double layer. pH range, 4–5.5, is the most favourable pH range for charge neutralisation (Chang *et al.* 1993). Destabilisation of colloids is brought up by the addition of coagulant. The higher the valence of the counter-ion, the more is its destabilising effect and the less is the dose needed for coagulation. Once destabilised, colloids are adsorbed on the surface of added coagulant resulting in floc formation.

Several coagulants have been tried by researchers for lignin removal. Inorganic salts of iron and aluminium are predominantly used as coagulants for water treatment. Ammonium alum, aluminium sulphate and ferrous sulphate have been studied by Garg *et al.* (2010a). Aluminium chloride, modified natural polymer, starch-g-PAM-g-PDMC [polyacrylamide and poly(2-methacryloyloxyethyl)trimethyl ammonium chloride] was studied by Jian *et al.* (2011). Pradeep *et al.* (2011) studied coagulation using poly-aluminium chloride and copper sulphate. The effect of oxo-titanium sulphate and its mixture with aluminium sulphate as coagulant was studied by Chernoberezhskii *et al.* (2002).

FACTORS AFFECTING COAGULATION

Factors affecting coagulation are discussed in the following sub-sections.

pH

The process of coagulation depends on pH. Each coagulant performs differently at different pH. The pH directly affects coagulation as it contributes to neutralisation of charged colloidal particles of lignin solution. Lignin forms negatively charged particles. Metal coagulant acidic in nature alters the alkalinity of system. High pH (alkaline media) promotes optimum coagulation with metal coagulants. For less acidic coagulants, lower alkalinity helps coagulation to proceed. Figure 3 shows the effect of pH on floc charge.

Turbidity

The dose of coagulant is increased or decreased depending on the turbid nature of paper-pulp effluent. In low total organic content (TOC) raw waters, coagulation is controlled by turbidity of water. In this case, sufficient amount of coagulant is added to destabilise suspended colloids. To check the influence of turbidity on coagulation process, specific ultraviolet absorbance (SUVA) guidelines can be applied. But generally for higher value of turbidity, higher dose of coagulant is required. However, the relationship between turbidity and coagulant dose is not found to be linear.

Temperature

The coagulation process is affected by temperature as change in temperature alters the solubility of coagulant, viscosity of process wastewater, kinetics of hydrolysis and flocculation. Certain coagulants work efficiently in cold water due to prehydrolysis as in the case of polyaluminium coagulants. Superiority of polyaluminium coagulants to
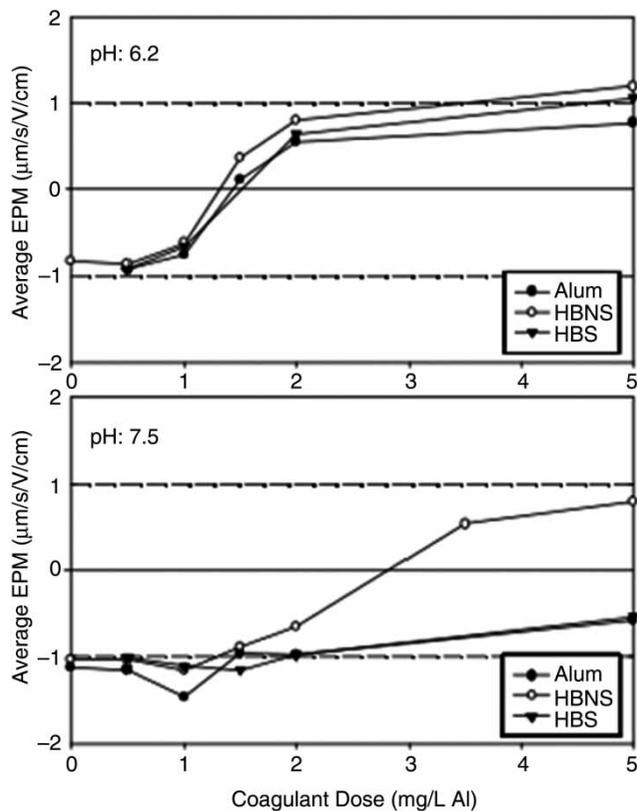
Figure 3 | Effect of pH on floc charge (Pernistsky 2003).

alums are reported widely in cold water (Pernistsky 2003). Low temperature slows down the coagulation process in the case of alums by decreasing the aggregation rate and rate constants. Furthermore floc structure is controlled by change in temperature. At low temperatures, alum flocs are found to be irregular in structure (Xiao *et al.* 2009).

COAGULANTS USED FOR LIGNIN REMOVAL

Aluminium-based coagulant

Aluminium chloride (Pradeep *et al.* 2011; Jian *et al.* 2011), aluminium sulphate (Chernoberezhskii *et al.* 2002; Garg *et al.* 2010a) and polyaluminium chloride (Pradeep *et al.* 2011) are well known coagulants tested for removal of lignin from wastewater. Results vary but the chemistry of aluminium remains unchanged. Soetopo (1984) conducted laboratory scale coagulation with alum and chlorinated copper and results showed significant reduction of suspended solids, COD, BOD and the colour for paper and pulp effluent samples. Alums are double sulphate salts, with a monovalent cation and trivalent metal ion. The

monovalent cation may be potassium or ammonium and trivalent metal ion may be aluminium or chromium (III). Alum used for coagulation treatment of paper and pulp discharge is $KAl(SO_4)_2 \cdot 12H_2O$. Coagulant requirement is found to be reduced with sulphuric acid used in conjunction with alum (Garg *et al.* 2010b). Hydrolysis products of alum are Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_4^-$. These ions are in equilibrium with amorphous $Al(OH)_{3(am)}$. (Hayden & Rubin 1974; Van de Ven & Alince 1996). Alum is insoluble in water at pH 6. At this value the maximum amount of alum is converted to solid flocs (Pernistsky 2003).

Aluminium sulphate also alum, is used for treatment of wastewater. When dosed in water it gives a positively charged ion. In pH range of 2–7, aluminium sulphate gives almost the complete recovery as hydrolysis product and lignin has opposite charges. Although workable pH range with aluminium sulphate is wider but recovery of lignin from wastewater is limited to 80% (Chernoberezhskii *et al.* 2002). Polyaluminium chloride gives polymeric aluminium species with high charges. Monomers are also formed as result of hydrolysis. The dominant polymeric is $Al_{13}O_4$. $(OH)_{24}(H_2O)_{12}^{7+}$ or simply Al_{13}^{7+} called the COAG. Characterisation of polyaluminium coagulants is given by degree of neutralisation or basicity. Alkalinity consumption is affected by basicity of coagulant. Higher basicity means high fraction of Al_{13}^{7+}.

When an aluminium ion is used as coagulant, the resulting formation of $Al(OH)_3$ removes organic matter by adsorption on the $Al(OH)_3$ (s) precipitate (Chang *et al.* 1993). At pH < 7 Al^{3+} is found and with higher pH it exists as $Al(OH)_3$ (Ching *et al.* 1994). Aluminium cation induces sweep flocculation and adsorption and bridging enhancement of organic and inorganic solid forming large amorphous flocs (Jekel 1986). Aluminium cation promotes floc formation with a number of functional group (phenolic, hydroxyl and carboxylic) and ligands (Licsko 1993; Kirk-Othmer 1993). The summary of efficiency of aluminium-based coagulants is given in Table 1.

Iron-based coagulants

Iron-based coagulants can be used over wider range of pH as ferric iron has much lower solubility compared to aluminium ion. The minimum solubility of Fe(III) is around pH 8.8 and due to weak positive charge of $Fe(OH)_2^+$, $FeCl_3$ is not a recommended coagulant for water treatment at its value of minimum solubility. Figure 4 shows the solubility of amorphous $Fe(OH)_3$.

Table 1 | Summary of coagulants used for lignin removal with references

| Coagulant	Chemical formula	Workable pH range	Coagulation mechanism	Hydrolysis product charge	Reported removal of studied parameter	Reference
Oxotitanium sulphate	$TiOSO_4. 2H_2O$	2 to 4	Heterocoagulation mechanism	Negative	Virtually complete KL recovery	Chernoberezhskii et al. (2002)
Aluminium sulphate	$Al_2(SO)_3. 18 H_2O$	2 to 7	Charged neutralisation and sweep flocculation	Positive	80% KL recovery	Chernoberezhskii et al. (2002)
Mixture of oxotitanium sulphate and aluminium sulphate	$TiOSO_4. 2H_2O+ Al_2(SO_4)_3 . 18 H_2O$	2 to 8	Parallel heterocoagulation	Multicomponent solution of both positive and negative charges	90% KL recovery	Chernoberezhskii et al. (2002)
Aluminium chloride	$Al(Cl)_3$	2 to 8	Charged neutralisation and sweep flocculation	Positive	90% colour removal	Jian et al. (2011)
Polyaluminium chloride	PAC	2 to 8	Charged neutralisation and sweep flocculation	Positive	80% COD & 90% colour removal	Pradeep et al. (2011)
Copper sulphate	$CuSO_4$	2 to 8	Sweep	Positive	74% COD & 76% colour removal	Pradeep et al. (2011)
Commercial alum	$KAl(SO_4)_2 \cdot 12 H_2O$	4.5 to 7	Sweep	Positive	63% COD & 90% colour removal	Garg et al. (2010a)
Ferrous sulphate	$FeSO_4$	4 to 7	Sweep	Positive	60% cod removal	Garg et al. (2010a)
Electrocoagulation	N-A	4 to 7	Sweep	Positive	80% lignin removal (Al & Fe anode)	
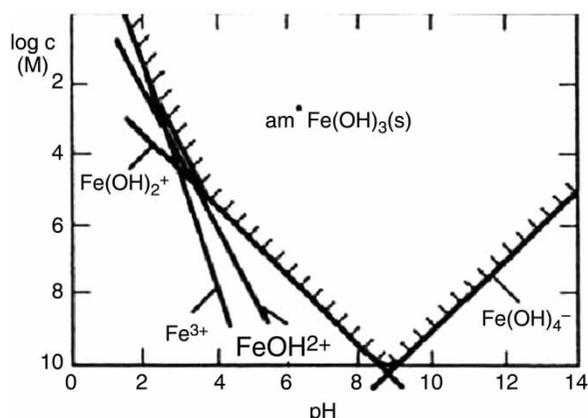
Figure 4 | Solubility of amorphous $Fe(OH)_3$ (Pernistsky 2003).

However, at pH as low as 5.5, effectiveness of iron coagulant is considerable. The iron-based coagulant hydrolysis product is pH dependent (Al-Malack *et al.* 1999).

Fe salts form monomeric and polymeric hydrates when added to wastewater (Stephenson & Duff 1996; Duan & Gregory 2003; Chaudhari *et al.* 2007). These ions are amorphous and hydrophobic (Jekel 1986). Ferric chloride and ferrous sulphate have been experimented as coagulants for removal of lignin from paper-pulp waste. Ferric chloride was found to be the best among all the coagulants used for paper and pulp effluent, showing 88 and 97% reductions in total carbon and colour, respectively (Sundin 2000).

Copper-based coagulant

Pradeep *et al.* (2011) studied copper sulphate as coagulant for removal of lignin from paper-pulp waste. Copper sulphate, like aluminium chloride, dissolves in water forming metal ion hydrates. Monomeric and polymeric species can be generalised as polymeric species: $M(OH)^+$, MOH^{2+}, $M2(OH)_2^{4+}$, $M(OH)_4^{5+}$, $M(OH)_2^0$ (s) and $M(OH)^{4-}$ etc. (Pradeep *et al.* 2011). The optimum pH value for copper sulphate is 5. Copper sulphate is also found to be a good oxidation catalyst. With increased dose of coagulant and pH, $Cu(OH)_2$ is precipitated in solution. The hydrolysis reaction of trivalent metal, Cu, (Ching *et al.* 1994) is given as:

$$x\,M^{3+} + y\,H_2O = M_x(OH)_y^{(3x-y)+} + y\,H^+$$

Titanium-based coagulant

Titanium-based coagulants have shown an advantage over aluminium and iron salt in the course of research development (Stremilova *et al.* 2001). Ti(IV) salt as coagulant was

experimented by Chernoberezhskii and it showed tremendous effective results as compared to common coagulant used for lignin removal. Oxotitanium sulphate was used as a mixture with aluminium sulphate over a wide range of concentrations and pH values to find optimum recovery of lignin (Chernoberezhskii *et al.* 2002). Increased concentration of $TiOSO_4$ showed onset of lignin recovery at pH 6.2, a relatively lesser acidic media. Due to the unavailability of direct methods for studying the structure of such complexes and the inconsistency of the gathered data on their composition (Nazarenko *et al.* 1979), it is assumed the hydrolysis reaction follows as:

$$M_{aq}^{\zeta+} + iH_2O \longrightarrow \left[M(OH)_i(H_2O)_{ki}\right]^{(\zeta\,i)+} + iH_{aq}^+$$

Titanium(IV) hydroxo aqua complexes have the composition $[Ti^{4+}(OH)_i(H_2O)_{k-i}]^{(4-i)+}$. Published data also reported that the coagulation mechanism for recovery of KL in presence of $TiOSO_4$ is heterocoagulation. Results exhibit virtually complete removal of lignin using $TiOSO_4$ as coagulant in pH range 2–4.

Sodium-based coagulants

A very unconventional coagulant, sodium chloride, was tested (Chernoberezhskii *et al.* 2002). As an electrolyte, sodium chloride hydrolyses in water to produce Na^+ and Cl^- ions. With supporting electrolyte, ion–ion electrostatic repulsion of lignin is weakened, resulting in floc formation and settling of lignin. Sodium sulphate is also the supporting electrolyte for lignin removal.
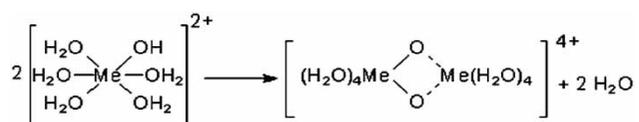
Table 1 shows the summary of coagulants used for the removal of lignin with workable pH ranges, mode of coagulation, hydrolysis product charges and reported percentage removal of studied parameters.

PROGRESS

In recent years the approach to wastewater treatment has improved. Scientists not only make attempts to remove potential contaminants but also find ways to reuse those contaminants. Lignin has been reported to be used as fueling source (Shi *et al.* 2011), stabilisers for emulsions, and raw material for production of phenols, carbon fillers and binders. A combined acidification and PEO flocculation process was devised (Shi *et al.* 2011) to improve removal of lignin from PHL (pre-hydrolysis liquor) of Kraft-based dissolving pulp

production process. Back in 1995, the interaction of PEO (poly ethylene oxide), was comprehensively studied (Xiao *et al.* 1995; Takase & van de Ven 1996; van de Ven & Alince 1996; Alince & Van de Ven 1997; Wu *et al.* 2007). It was deduced that phenolic groups of lignin interacted with PEO to form complexes Y. PHL was first acidified with different concentrations of sulphuric acid and then treated with PEO. It was shown that acidification followed by flocculation by PEO increased lignin removal in pre-hydrolysis liquor to from 3.8 to 22% at specified pH of 2.

Another newer approach is electro-coagulation. In electro-coagulation process, suspended, emulsified or dissolved pollutants are destabilised by introduction of electrical current in aqueous medium. The driving force for this reaction is electro-motive force. During the reaction the elements or compounds attain more stability and become less soluble. Electro-coagulation has found successful application in treatment of various industrial wastewaters (Vik *et al.* 1984; Do & Chen 1994; Pouet & Grasmick 1995; Lin & Peng 1996; Naumczyk & Zilio-Grondi 1996; Tsai *et al.* 1997; Lin *et al.* 1998; Kovatcheva & Parlapanski 1999). In experimental research by Uğurlu *et al.* (2008), iron and aluminium electrodes were used owing to their cheapness and simplicity in production. As known, hydrolysis products of Al^{3+} and Fe^{3+} affect aggregation of particles in form of polymerisation given in formula:

$$2\begin{bmatrix} H_2O & & OH \\ H_2O - Me - OH_2 \\ H_2O & & OH_2 \end{bmatrix}^{2+} \longrightarrow \begin{bmatrix} & O & \\ (H_2O)_4Me & & Me(H_2O)_4 \\ & O & \end{bmatrix}^{4+} + 2\ H_2O$$

Al and Fe, used as anode, the electro-generated aluminium ions may form mono- or polymeric hydroxo-complexes which polymerise in pH range of 4–7. The aggregation of monomeric hydrolysis product is increased due to oversaturation and formation of amorphous hydroxide precipitate. This precipitate then enmeshes colloidal particles in 'sweep floc'. Lignin is adsorbed on these aggregates. Small organic molecules are surrounded by amorphous hydroxide. Monomers and polymers are removed by sedimentation. Current densities were also an important factor in electro-coagulation. Higher lignin removal was observed with Al electrode as compared to Fe at lower current density.

CONCLUSION

This paper reviews the progress made in removal of lignin from wastewater generated by paper and pulp industry. The removal process is pH dependent. pH has a significant effect on lignin removal and optimum recovery occurs in alkaline range. Turbidity significantly affects the recovery of lignin; however the relationship between turbidity and the amount of coagulant used has not been clearly reported. The superiority of ferric chloride, $FeCl_3$ as coagulant has been conclusively shown. Copper sulphate and titanium-based coagulants have been found to be superior to conventional coagulants used for removal of lignin. The removal of lignin has a large potential in research and processes such as combined acidification and PEO flocculation have proved successfully. Electro-coagulation also appears to be potentially useful technology. Parameters related to electrolysis for removal of lignin such as potential current density, nature of electrodes and ohmic resistance further needs to be explored. Sodium chloride, sodium sulphate and hydrochloric acid can also be used as coagulants and possibility of their use is yet to be explored.

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