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Some Characteristics of Treatment of Wastewater from Paper Production and Recycling Containing Lignin in Vietnam

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Abstract: Lignin is a difficult-to-treat pollutant in wastewater from paper production and paper recycling. But lignin and lignin derivatives are useful materials in many different fields. This paper summarizes some characteristics of the lignin recovery process, lignin application and lignin treatment. And the paper also presents some characteristics in paper wastewater treatment, paper recycling wastewater in Vietnam.

Key words: Lignin recovery, coagulant chemical, biological treatment, wastewater treatment.

1. Introduction

Statistics from developed countries show that, 42% of the timber harvested for industrial use is used for paper production, and this percentage is expected to increase to 50% in the next 50 years. In developed countries alone, with a population of around 20% of the world's population, 87% of printing and writing paper is consumed. Global pulp, paper and printing production increased by 77% from 1995 to 2020 [1].

In Vietnam, the paper industry is still developing slowly compared to the world in terms of both level and scale of production. The country has about 300 enterprises, mainly small and medium enterprises, with outdated technology. The total output of pulp and paper is approximately 787,000 tons/year. Many high-quality paper products must be imported with an output of about 500,000 tons/year, by 2020, reaching 1,800,000 tons [2].

During the production process, a large amount of organic waste, or black liquor, is generated, in which lignin accounts for a significant amount. Therefore, the disposal of paper mill waste is an urgent issue to protect the environment. In the long term, it is necessary to look into the possibility of utilizing lignin and its lignin derivatives to produce other products for the national economy. Therefore, the separation of lignin in the paper industry wastewater not only solves the environmental problem of the pulp and paper industry, but also contributes to creating a product that can be used for many other fields.

In addition, the process from wood to white paper must go through many chemical treatment stages, which use chlorine-containing oxidizing agents to bleach pulp. As a result, many toxic chlorine-containing organic compounds are created and released into waste water, making the paper industry a major industry that can cause serious environmental pollution.

2. Lignin and Lignin Application

Lignin is one of the plant cell components that surround cellulose fibers and is the second most abundant after cellulose. The lignin content in wood varies not only depending on the type of tree but also on the age of the tree, geographical conditions. Usually the lignin content is about 25%-40%. In the pointed leaves, it contains 20%-30%, in the 20%-25% wide leaf trees, in the 5%-9% grass plants [3].

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Lignin and lignin derivatives are widely known as materials used in many fields such as micronutrient fertilizers, plant growth stimulants, concrete additives, in recent times a number of studies. The study showed that lignin has the ability to exchange ions with some metals, especially when the sunfuanate is added.

Lignin is a racemic compound with a large molecular weight, has aromatic and hydrophobic properties. The study determined the coincidence of lignin, it was found that there is a segmentation in the extraction process and the molecule containing many precursors appears randomly, in which mainly the links are lead of phenylpropane [3].

Lignin recovered from black liquor is widely used as a dispersant, stabilizer and additive in rubber manufacturing, concrete production, ceramic additives, adhesives, clear plastics, industries, etc. Lignin can also be used as a synthetic material of dimethyl sulfoxide when heated with sulfur dioxide or sulfur [4]. Vanillin is an important organic product obtained by oxidizing soft wood lignin in an alkaline environment, while hardwood lignin gives a mixture of vanillin and sirigandehite. In addition, sirigandehit can be used in the pharmaceutical industry to prepare sleeping pills [4]. In other applications, lignin is used as a herbicide, an inhibitor of vulcanization and deformation with a small percentage in vulcanization of rubber. It is also used to reduce iron in manufacturing water, softening water in cation type filtration devices because it is very sensitive to Ca^{2+} and Mg^{2+} ions which can be regenerated by just washing with any inorganic acid.

3. Lignin Recovery from Black Liquor of Paper Production

Black liquor is the wastewater generated from the process of making alkaline cooking materials to recover the cellulose of paper production process. Black waste water has a very high pH (12.5-13.0) because it contains a lot of residual alkalinity. In addition to NaOH, other inorganic substances such as Na_2SO_3, Na_2CO_3 and Na_2SO_4 account for only a small amount. The organic substances can be divided into 4 groups as follows: (1) The group of volatile substances includes oxalic acid, acetic acid and other volatile acids. (2) Substances insoluble in water and ether are mainly lignin. (3) Substances insoluble in water but soluble in ether, include phenol, plastic acids and fatty acids. (4) Water-soluble substances and alcohols/ethers, including lactones, are the product of polysaccharide decomposition in raw materials and together with them binds most of the caustic soda consumed during cooking. Depending on the dry matter content, the black liquor has different density and viscosity. These two quantities increase in proportion to the dry matter content in the black liquor [5].

The separation of lignin from the black liquor can be performed by two methods: the ultrafiltration method and the acid precipitation method [6]. The ultrafiltration method requires complex equipment, so it will be expensive to process. Acidic precipitation method can precipitate 70%-80% of lignin. However, the acidification of the black solution reduces the pH of the environment, resulting in lignin precipitation in the form of viscous, viscous lube. In fact, to acidify the black liquid, people use acids H_2SO_4, HCl, CO_2. In addition to the disadvantage of being difficult to filter for a long time, using strong inorganic acids, H_2S will pollute the environment. To solve the problem of difficulty to filter, in the research people have used a number of additional filtering aids that are capable of making lignin agglomerated in the form of granules for filtration. The filtering aid used is an organic flocculant and dissolved calcium in alcohol was used. The effect of lignin acid precipitation with the aid of flocculants increases as pH decreases [5].

4. Decomposition of Lignin by Microorganisms

Currently, several methods have been applied to reduce lignin content during production. In particular, the breakdown of lignin by enzymes and microorganisms is attracting great attention.

White-rot fungi are well-studied microorganisms that break down lignin in the wild. White-rot fungi can produce strong enzymes for breaking down lignin such as laccase, lignin peroxidase and manganese peroxidase. However, oxidative enzyme systems often require low molecular weight co-factors and adjuvants such as manganase, organic acids, veratryl alcohol and aromatic ring structural subunits, for example 4-hydroxybenzyl alcohol, aniline, 4-hydroxybenzioc acid. Adjuvants are strong oxidizing agents responsible for lignin breakdown and can penetrate deep into the lignin bonding network due to their limited size. The products of fungal lignin degradation activity are often very diverse and are aromatic compounds of lower molecular weight such as guaiacol, coniferyl alcohol, *p*-coumarate, ferulate, protocatechuate, *p*-hydroxybenzoate and vanillate. Lignin-degrading bacteria and actinomycetes are less studied than mushrooms, but some studies show that some α-proteobacteria, such as *Sphingomonas* sp., ɣ -proteobacteria, can be found. For example, *Pseudomonas* sp. and actinomycetes *Rhodococcus*, *Nocardia* and *Streptomyces* sp. are potential in lignin decomposition. The published enzymes from these lignin-breaking microorganisms are laccase, glutathione S-transferase, ring dioxygenases, monooxygenases and phenol oxidases. These enzymes are also involved in lignin breakdown [6, 7].

The microorganisms convert lignin into substances with a smaller molecular weight in two ways. It is either dissolving or creating a large molecular weight metabolite called a lignin polymer that is able to precipitate with acid-precipitable polymeric lignin. These compounds will be further decomposed by other microorganisms.

Arora and Paramjit [8] studied the isolation of lignin-degrading fungi to separate lignin from agricultural waste. The isolates were investigated for lignin degradation ability, continue to be selected on the basis of determining the enzyme activity including lignin peroxidase and manganese peroxidase.

5. Characteristics of Treatment of Wastewater from Paper Production and Recycling

Paper production technology consists of two basic processes: producing pulp from raw materials and producing paper from pulp (paper-making). Raw materials such as bamboo and neohouzeaua will be cooked, bleached, crushed, paper-cut and then dried and produced.

In the pulp making process, paper will appear in the black liquor. Black liquor contains 70% of lignin, hemicellulose and other organic compounds found in wood, bamboo, straw, etc. which can be recovered and used, as mentioned above and 30% of inorganic solids, including chemicals, chlorine bleach and chlorine derivatives, contain many toxic compounds and pigments. In addition, in the process of creating paper pulp, to create a unique product, people also use many chemicals and catalysts.

Inorganic components include cooking chemicals, small parts are NaOH, free Na_2S, Na_2CO_3 and mostly alkali sodium sulphate associated with organic substances in alkali. The effluent from bleaching processes of chemical or semi-chemical pulp factories often contains organic compounds, soluble lignin and the compound of those compounds with bleach in the form of toxic particles has the ability to bioaccumulate in living organisms as organochlorine compounds. When bleaching with chlorine-containing compounds, typical pollution parameters such as BOD (Biochemical Oxygen Demand) are about 15-17 kg/ton of pulp, COD (Chemical Oxygen Demand) is about 60-90 kg/ton of pulp, especially AOX (Adsorbable Organic Halides) value (chlorine compounds organic) is about 4-10 kg/ton of pulp. Waste stream from pulping and kneading process mainly contains fine fibers, suspended pulp and additives such as turpentine, coloring, kaolin…

In paper recycling, the process of soaking, bleaching, grinding accounts for about 50% of the total waste, not many chemicals such as caustic soda, Javen water, alum, turpentine, coloring, fiber. Waste water often contains a lot of pulp, the amount of residue can be up to 300-600 mg/L, with COD, BOD_5, SS (Suspended Solids) exceeding the permissible limit from dozens to several hundred times.

In the effluent of pulp and paper production, there is a high content of carbohydrate compounds, which are easily biodegradable but lack nitrogen and phosphorus which are essential nutrients for microorganisms to grow. Therefore, in the process of biological wastewater treatment, it is necessary to add nutrients, ensuring the ratio for aerobic process BOD_5:N:P=100:5:1 and anaerobic process BOD_5:N:P = 300:5:1 [9].

The characteristics of wastewater for paper production and paper recycling often have a BOD_5:COD ratio of less than 0.55 and a high COD content (COD > 1,000 mg/L). So in the treatment is usually a combination of anaerobic and aerobic method.

Treatment processes that remove paper-making wastewater contaminants and paper recycling include sedimentation, flotation, flocculationand biological treatment.

5.1 Sedimentation

Sedimentation is used to separate powdery or fibrous solids, first of all for the effluent from the pulping and paper-cutting process. For the purpose of recovering fiber, pulp, hopper-shaped sedimentation equipment was often used. During the settling process, it is necessary to calculate the appropriate retention time because it is easy for anaerobic decomposition phenomenon, when sediment is not removed regularly in order for this wastewater to settle well and create conditions for particles to link together to form sediment.

5.2 Floatation

The flotation process is carried out by introducing small air bubbles into the liquid phase. The air bubbles will stick to the particles. When the density of the bubble and sediment collection is smaller than the density of water, the sediment will follow the bubbles to float to the surface. For wastewater treatment, the paper industry contains a lot of light pulp, suspended in water. Therefore, pressure flotation technology combined with flocculation is widely used in the world and in Vietnam. Pressure flotation is dissolving air into water at high pressure of 2-4 at, then reducing pressure to release air bubbles with micrometer size, these micro bubbles when combined with the residue to form system blocks have a lower density than water, so they float to the surface of the water and are collected and removed from the water.

5.3 Coagulant Chemical

Coagulant chemical used to handle solid particles smaller than 10^{-4} mm in suspended form, unable to settle, partly dissolved organic matter, phosphorus compounds, some toxins and decolorization. Coagulation can be done before or after biological treatment. The common flocculants are $Al_2(SO_4)_3$, iron alum type $FeSO_4$, $Fe_2(SO_4)_3$ or $FeCl_3$ type. The alum is added to the water as a solution. The polymers are used to support glue and speed up the settling process.

5.3.1 Aluminum Alum

When aluminum alum is put into water, it dissociates into Al^{3+} ions, then these ions are hydrolyzed to $Al(OH)_3$. Normally, alum has the highest flocculation efficiency when water has a pH of 5.5-7.5.

5.3.2 Iron Alum $FeSO_{4s}$

When added to water, it dissociates into Fe^{2+} and is hydrolyzed to $Fe(OH)_2$ and will oxidize to $Fe(OH)_3$. Oxidation only takes place when the pH of water reaches a value of 8-9 and the water must be highly alkaline. Therefore, this type of alum is often used when it is necessary to combine lime to soften water.

5.3.3 Iron Alum $FeCl_3$ or $Fe_2(SO_4)_3$

When added to water it dissociates into Fe^{3+} and hydrolyzes to $Fe(OH)_3$. Hydrolysis reaction occurs when pH > 3.5 and the precipitation process will form quickly when pH = 5.5-6.5.

5.4 Biological Treatment

The composition of wastewater for paper production, paper recycling, after settling by sedimentation, flotation and chemical coagulation still has dissolved organic waste as well as some inorganic substances such as sulfide, ammonia, etc.that will be handled on the basis of microbiological activity. Although the characteristics of BOD_5, COD, SS are very large in the effluent of paper production, but the nutritional indicators such as TN, TP are almost very low, so it is necessary to take into account the nutritional supplements for wastewater in biological treatment process.

5.5 Anaerobic Treatment

Anaerobic microorganism group was used, operating in conditions without oxygen. Anaerobic decomposition of organic matter is a complex biochemical process that produces hundreds of intermediates and intermediate reactions, and goes through four stages: Stage 1: Hydrolysis, cutting of high molecular compounds; Stage 2: Acidification; Stage 3: Acetation; Stage 4: Methaneization. Organic waste contains many high-molecular compounds such as proteins, fats, carbohydrates, cellulose, lignin, etc. in the hydrolysis phase, which will cut the chain into simpler and easier hydrolytic molecules. Hydrolysis reactions convert proteins into amino acids, carbohydrates into simple sugars and fats into fatty acids. During the acidification stage, simple organic matter is further converted into acetic acid, H_2 and CO_2. Methane bacteria can decompose only certain types of substrates such as $CO_2 + H_2$, formate, acetate, methanol, methylamine, etc..

5.6 Aerobic Treatment

To bring the criteria of organic pollution to the permitted level, it is necessary to have aerobic treatment process. In an aerobic environment, vigorous gas-using microorganisms use organic matter in wastewater for their growth and dissociation process, which helps to reduce the organic concentration in the water. Gas must be supplied continuously and regularly to help microorganisms operate stably. There are many different aerobic treatment methods such as activated sludge processes in Aerotank, Circulating oxidation channel, Sequencing Batch Reactor, etc. [10].

Biological treatment by anaerobic and aerobic methods can be carried out under natural or artificial conditions. In artificial treatment works, people create optimal conditions for biochemical oxygenation, so the process has a higher speed and efficiency than natural biological treatment.

In addition, depending on the required level of treatment, some constructions can be used to thoroughly clean wastewater for reuse or safe discharge into receiving sources such as using sand filter system, activated carbon, etc. Wastewater after going through this treatment system can be reused for production purposes at paper factories. However, this high level of treatment will increase the production cost of wastewater treatment greatly.

6. Conclusions

The article summarized some basic characteristics of lignin, lignin recovery for application, lignin treatment by microorganisms in paper wastewater, and emphasized the characteristics of wastewater treatment for paper production and recycling contained lignin.

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