GSC Advanced Research and Reviews

eISSN: 2582-4597 CODEN (USA): GARRC2

Cross Ref DOI: 10.30574/gscarr

Journal homepage: https://gsconlinepress.com/journals/gscarr/

(REVIEW ARTICLE)

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The usage of lignin in two significant applications: As adsorbent surface of water pollutants and antioxidant of plastic polymers: short review

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GSC Advanced Research and Reviews, 2021, 08(03), 108–118

Publication history: Received on 20 July 2021; revised on 16 September 2021; accepted on 18 September 2021

Article DOI: https://doi.org/10.30574/gscarr.2021.8.3.0185

Abstract

Since pollution is very serious problem threating the environmental eco-system around the world, but people do not usually treat this issue properly. Water is contaminated with different type of pollutants such as organic, inorganic, heavy metals, pesticides, dyes, phenols, and many other pollutants. Using adsorption phenomenon is very practical, easy and common method to remove pollutants from water. Owing to the significant properties of lignin such as high surface area, porosity, availability in huge amount, it was chosen to be used as an adsorbent surface of various pollutants. Herein it is going to review some of important literatures regarding that. Another serious problem that is threatening the marine eco-system, human health, and influence the global warming is the huge consumption of plastic polymers every year. Thus, reducing the consumption of plastic polymers is significantly matter. Lignin chemical structures are highly oxygenated and have several aromatic units, so by definition lignin can act as an antioxidant, free radical scavenger and photo-stabilizers. As the chemical structure of monomer moieties to form lignin are highly aromatic so it is suitable to work as UV- blocker to stop the photo-degradation of plastic.

Keywords: Lignin; Adsorption process; Antioxidants; Photo-degradation; Plastic polymers

1. Introduction

Water pollution is contaminating of water by industrial or domestic materials (pollutants) almost of them due to human activities. These pollutants contaminate water from different resource and extents; hence it is very serious problem threating the marine eco-system, but people do not usually treat this issue properly. Huge numbers of researches have been done by authors to understand this problem and exhibit suitable procedure to overcome it. The most common procedures are bio-degradation, using UV light, precipitation and adsorption [1-5]. Figure (1) shows two different types of pollutant contaminating water because of human activity.

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Figure 1 a) Sewages polluted the water of river. b) Plastic and other pollutants floating on the lake

2. Types of water pollutants

The water, appears in Figure (2), contains different type of pollutants such as organic, inorganic, heavy metals, pesticides, dyes, phenols, and many other pollutants [6-9]. These pollutants change the water physical properties like change its odor, color, and taste. Furthermore, these pollutants threaten humans and animals live also effects the marine eco-system. Since then too much sea live creatures have been extinct just because of these harmful pollutants [10, 11]. Fabric industries commonly utilizing dyes in big amount by mixing it with water and some industries discharge it into the water again without any treatments unfortunately. Figure (1-14) shows dyes waste from textile industries and only from the photo it can be seen the disaster that is happened to the water because of these colored pollutants. Dyes have changed the color of water and maybe its density as well [12]. Hence almost of dyes are organic substances so it is hard treat them and they have high toxicity. As a result, when dyes go into the water of lakes, rivers or sea, it can accumulate inside the sea organisms and hurt them [13].

Figure 2 Textile industry waste drains direct into the water

Commonly, artificial dyes are allocated into reactive, basic, acidic and more other units. Furthermore, dyes have different functional groups within their chemical structure and the most famous groups are azo, carboxylic acid, hydroxyl, and amine. *etc* [14]. From all above, dyes and other pollutants have to be removed before discharging into the water. Therefore, various procedures should be applied to remove these undesired pollutants from water such as chemical precipitation, ion-exchange, electrochemical, and adsorption process. Since the adsorption process is a very well-known procedure to remove dyes [15, 16].

3. Adsorption and absorption processes

Adsorption is a surface phenomenon when ions, molecules or atoms in form of gas, liquid, or even dissolved substance, attached to the surface of solid materials by physical forces such as Van der Waals forces [17]. By this method, a film of the substance (adsorbate) is formed on the top of solid phase (adsorbent). Adsorption phenomenon is different than absorption phenomenon hence adsorption happens on the surface while absorption penetrate inside the materials. Therefore, in absorption the molecules or ions goes through the bulk but in adsorption the process happens only on the surface by week forces so the adsorbate can be removed and reactivate the surface of adsorbent [18, 19]. Figure (3) illustrates the differences between adsorption and absorption phenomena. Sorption includes the both phenomena and desorption is the reverse of the process [20].

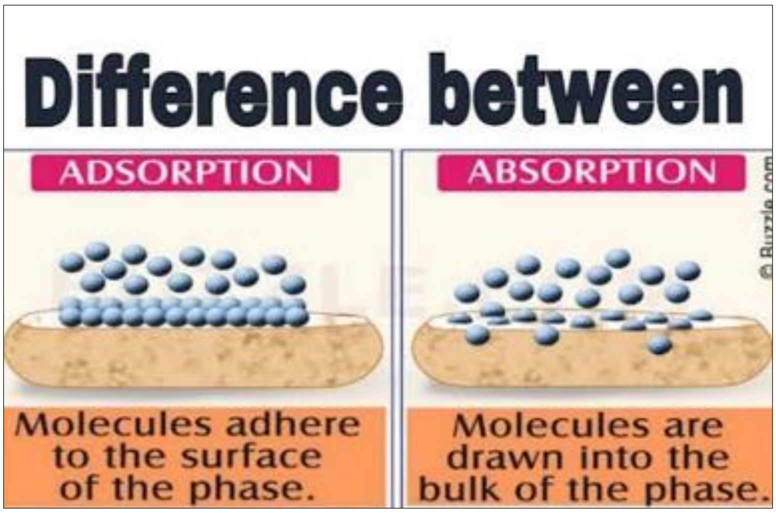

Figure 3 Animated chart to describe the main differences between adsorption and absorption phenomena

4. Lignin as an adsorbent surface of harmful heavy metal ions

In general, using adsorbent to remove pollutants is considered as a cheap and easy way in terms of economy. However, in this work we are going to introduce a very handy, inexpensive and efficient absorbent, which is lignin. Moreover, it is considered as a waste as was described in the previous sections [21].

Figure 4 Animated chart shows adsorption of heavy metal ions by lignin [40]

Due to the significant properties of lignin such as high surface area, porosity, availability in huge amount, it was chosen as an adsorbent in this study [22]. Furthermore, the chemical structure of lignin has various functional groups which give it significant features to be an excellent adsorbent [23, 24]. Till now, there are many studies about utilizing lignin as adsorbent to remove heavy metal ions from polluted water such as copper, lead, arsenic, cadmium, chromium, mercury, nickel, zinc *etc.* [25-30]. Since these heavy metals are too harmful for sea life and influence human health by causing serious diseases through the nutrition cycle [31-33]. Consequently, the heavy metals have high toxicity and they have to be removed before discharging into the aquatic environment. Since numerous procedures have been used to remove them and adsorption is the most common method have been utilized regarding that [34, 35]. Therefore, adsorption process is well-known as promising procedure to remove heavy metals from water because it is easy method with high efficiency also the availability of adsorbent surfaces such as lignin or other adsorbents. In addition, the adsorbent surface can be reactivated by removing the adsorbate by desorption process [36-39]. Figure (4) is an animated draw illustrates the ability of lignin to adsorb different heavy metal ions by its various functional groups without damaging the environment [40].

5. Lignin as an adsorbent surface of toxic dyes

Even though there are so many studies investigated the efficiency of lignin to adsorb heavy metal ions but only few authors have exhibited the utilization of lignin as adsorbent to remove colored pollutants (dyes) from water. Thus, almost of these pollutants produce by textile industries as a waste and through to water without any treatment. In 2016, Zhang's group have published paper using lignin obtained from rice straw by organosolv process to remove methylene blue from water by adsorption method [41]. They have demonstrated that the amount of adsorption is pH depended. Since they have proved that the best adsorption efficiency at pH between4.0–5.0. They have also studied the surface morphology of lignin before and after the adsorption process as shown in Figure (5).

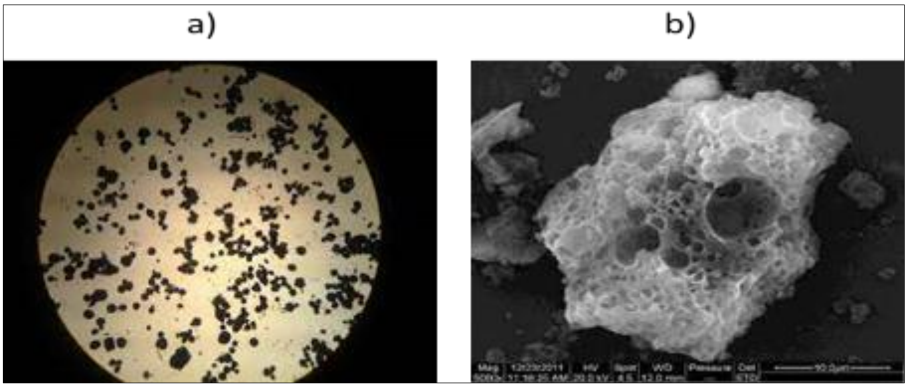

Figure 5 a) Microscopic image of organosolv lignin holding methylene blue dye after adsorption process. b) Organosolv lignin SEM image [41]

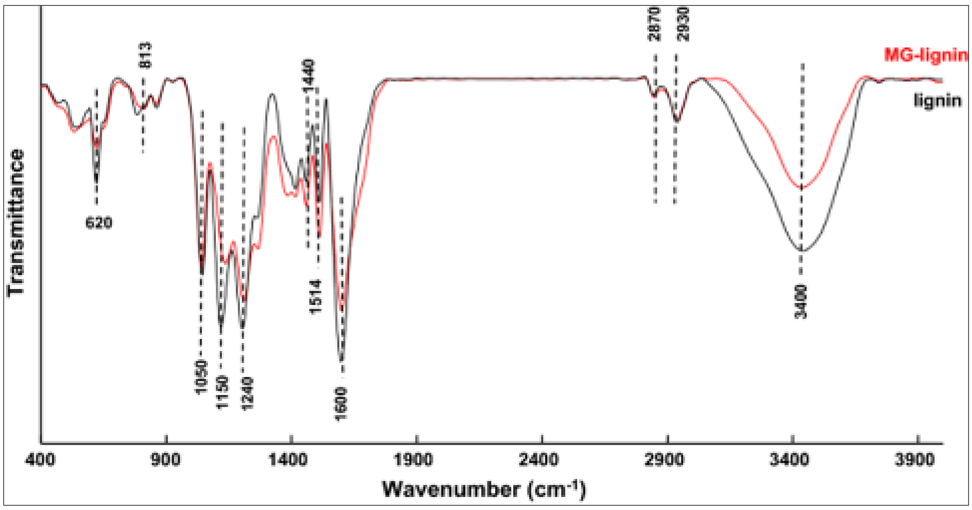

Figure 6 FTIR sepctra of lignin before and after absorption malachite green [42]

Moreover, Seo *et al.* in 2019 have used pristine lignin as adsorbent surface to remove malachite green from water by adsorption process [42]. They have demonstrated that the capacity of adsorption is 31.2 mg/g using Langmuir's isotherms regarding that. It was also exhibited that the equilibrium time was very quickly reached within only 15 minutes this means the adsorption process happened rapidly. Again they have proved that the adsorption process can happen at pH from 2 to 5 and also noticed that the broad peak at 3400 cm^{-1} of lignin either reduced or become weaker after adsorption process see Figure (6). This outcome gives indication that the adsorption process occurs close to the hydroxyl groups and lead to reducing the hydrogen bond around there.

Recently, it has been extracted lignin from Eucalyptus grandis sawdust and used it as adsorbent surface to remove methylene blue from water [43]. It was found that the specific surface area of extracted lignin is 20 m^2/g which means it can work as an excellent adsorbent surface of different pollutants. Different analytical methods were applied to exhibit the efficiency of extracted lignin to adsorb methylene blue from aqueous solutions. Hence the adsorption efficiency is 32 mg/g and its isotherms are fit with Langmuir equation and the process is exothermic. They have also demonstrated the capability of desorption process for lignin without losing its significant properties. Figure (7) is an animated diagram illustrate the analytical process of methylene blue dye which adsorbs on the surface of extracted lignin to get clean water.

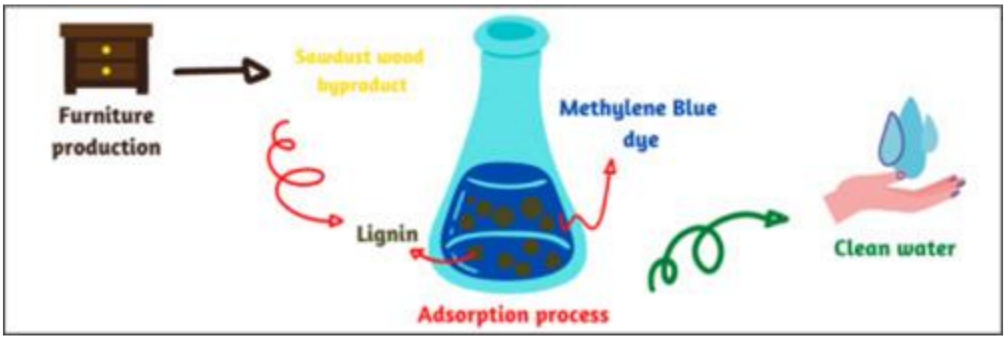

Figure 7 Animated scheme shows the adsorption process of methylene dye on the extracted lignin surface [43]

6. Analytical methods of plastic polymer stabilization

This section is going to present a short literature review about analytical procedure of using lignin as a thermal stabilizer and antioxidant of plastic polymer. As will be describe in next pages there are only few papers have been published about using lignin as antioxidant or thermal stabilizer. However, up to date writing this report there is no one used lignin as photo-stabilizers of plastic polymers especially for polyvinyl chloride (PVC).

7. Plastic pollution

For only one year (2018) there was a huge amount of plastic was produced about 380 million tones [44-46]. To the end, almost of this plastic are accumulate in the oceans as a waste causing what is known plastic pollution. It is the most serious problem is threatening the marine eco-system, human health, also has influence on the global warming. Thus reducing the consumption of plastic polymers is significantly important [47-49]. Therefor researchers have used different approach to stabilize these polymers and reduce their degradation [50-56]. The most common method is by using natural or synthesized chemicals as thermal-stabilizers, antioxidants or photo-stabilizers [57-60].

8. Lignin as a thermal-stabilizer, or antioxidant of plastic polymers

In general, plastic polymers are mixed with chemicals by ratio less than 10% per weight to prevent or reduce polymer chain degradation due to raised temperature or exposure to UV light [61, 62]. These chemicals are called stabilizers, however, antioxidants react with free radicals to stop their damage or even prevent their formation [63, 64]. Hence these free radicals are formed during the usage of plastic polymers and exposure to outdoor conditions such as sunlight and high temperature. Normally, antioxidants are highly oxygenated within their chemical structure so they work as free radical scavengers. Moreover, photo-stabilizers can protect plastic polymers when irradiated by UV-light and work as UV-blockers because these chemicals have high aromatic system which absorbs at UV region [65, 66].

Consequently, lignin chemical structures are highly oxygenated and have several aromatic units, so by definition lignin can act as an antioxidant and photo-stabilizers [67, 68]. Figure (8) shows the chemical structure of monomer moieties to form lignin as they have aromatic ring and highly oxygenated [69]. Lignin is suitable for packing applications with plastic films hence it is a good antiradical substance.

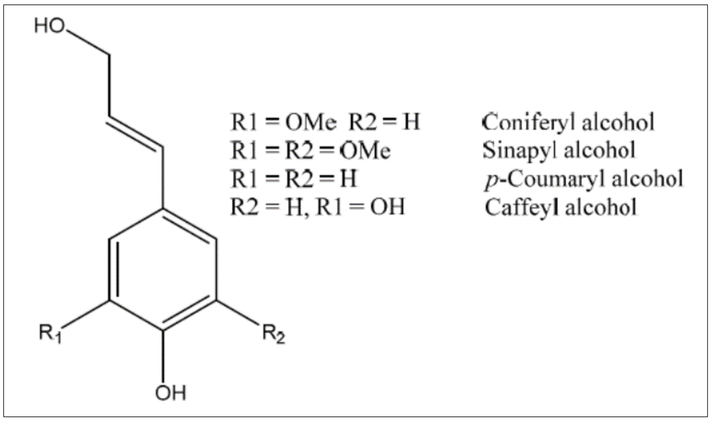

Figure 8 Chemical structure of monomer units to form lignin [69]

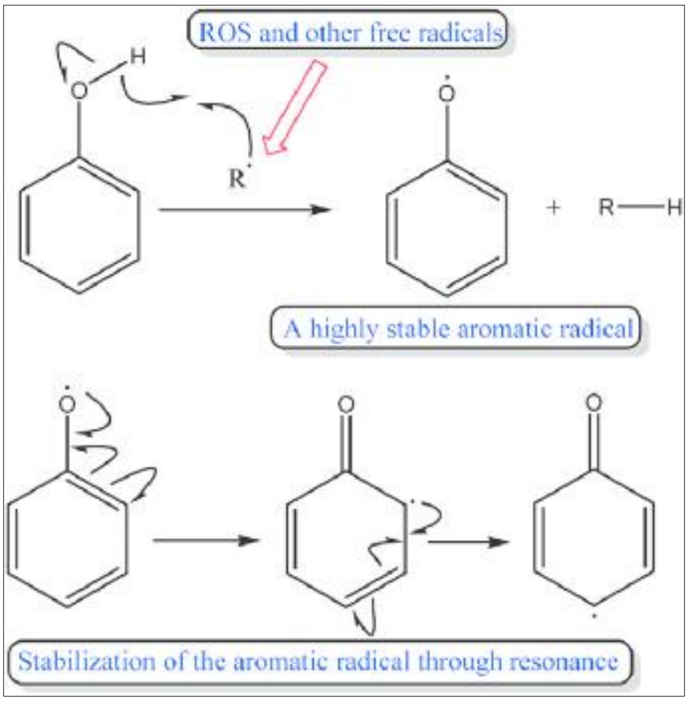

Figure 9 Free radical stabilization by phenol units as antiradical scavengers

One common example of using lignin as a stabilizer is mixing it with polylactic acid hence it has demonstrated good stability. Yang *et al.* in 2016 have investigated polylactic acid thin films containing nano-particles of lignin in different concentration. They have followed the activity of formation free radicals and their scavengers [70]. Thus it has proved that increasing the amount of lignin leads to increasing the ability of radical scavenging. Domenek has showed that the molecular weight of lignin affects the scavenging activities [71]. Hence it was studied the influence of molecular weight on polylactic acid/lignin films. They noticed that lower molecular weight gives better outcomes because smaller molecular weight species means more antiradical fractions. Therefore, the efficiency against oxidative degradation is improved. Figure (9) shows how phenols groups can work as free radical scavengers and stabilize it because oxygen has high electronegativity and the radical could stabilize by resonance [72].

In 2021, Zhang's group has utilized activated lignin to improve thermal properties and flam retardancy of polyvinyl chloride (PVC) [73]. The blend of lignin/PVC showed an excellent flame retardancy and thermal stability compare to blank PVC. They have demonstrated that using lignin has significantly inhibited the formation of HCl molecules which form due to the thermal degradation of PVC. Figure (10) shows the procedure to enhance the thermal and flam retardancy features of PVC by using activated lignin.

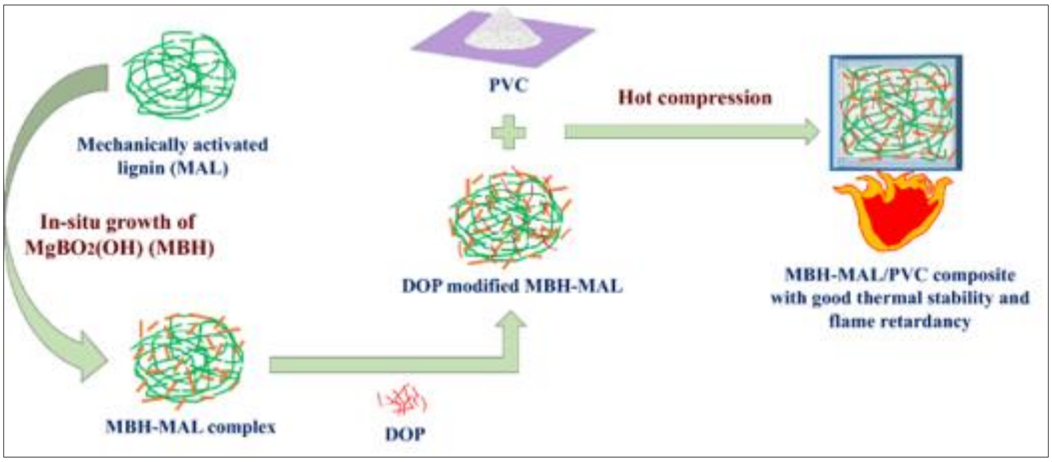

Figure 10 An animated diagram illustrates the thermal stability and flam retardancy of PVC/lignin [73]

9. Conclusion

To summaries, Lignin has been studies by many researchers. However, according to the literature we have been able to reach through Google Scholar and other browsers, till now nobody have been used lignin as a photo-stabilizer of polyvinyl chloride and polystyrene polymers. Since this paper recommends utilizing lignin as a photo-stabilizer of PVC and using different analytical approaches to improve its efficiency. In addition using lignin as adsorbent surface of pollutants from aqueous solutions and using different analytical methods to exhibit that such as utilizing equilibrium time, lignin mass, pH and temperature to exam the adsorption efficiency. Furthermore it could be studied the adsorption isotherms of various pollutants on the lignin surface and investigated the Langmuir and Freundlich models.

Compliance with ethical standards

Acknowledgments

We would like to thank Al-Nahrain University for their support during this work.

Disclosure of conflict of interest

All authors of the manuscript have no conflict of interests to declare.

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