Application of date palm biowaste material as bioadsorbent for micropollutants: removal of diphenylamine from contaminated water

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Submission: 2 Oct 2024 Acceptance: 27 Nov 2024 Publication: Dec 2024

DOI Link: https://doi.org/10.61586/NyJFe

Abstract: The conventional waste management practices generally goal to dispose biological waste from farms and forest. Many times these strategies, contribute to the environmental pollution like incineration and at the same time biomass is lost. This biowaste has a great potential of reuse so innovative thinking in this direction is desired. In present research date palm biowaste is applied to look for removal of diphenylamine from contaminated water samples. Date seed powder was applied to look into the removal of diphenylamine from contaminated water, ultraviolet visible spectroscopy results indicated decreased diphenylamine absorbance in date palm biowaste samples indicating sequestration of chemical pollutant from water. Our research suggested the possible application of date palm biowaste in micropollutant removal from contaminated water. Further research is needed in this direction to have full understanding of this phenomenon and to optimise this process so that it can be applied and executed at large scale. The application bio-waste produced by farming activities when applied as adsorbent for wastewater treatment, it can tackles water contamination, decreases the overall amount of agricultural waste, and reduces the potential gas emissions caused by waste transportation, treatment and disposal.

Key words: ajwa date seeds; diphenylamine; micropollutant; uv-vis absorbance; contaminated water.

1. Introduction: The date palm (*Phoenix dactylifera*) has held significant historical, cultural, and economic importance for thousands of years, particularly in the Middle East, North Africa, and parts of South Asia.[1] The date palm is one of the oldest cultivated plants in the world. The date palm is often mentioned, symbolizing sustenance, life, and divine provision. In the Quran, it is mentioned as a fruit that grows in paradise, the date palm is considered a symbol of hospitality and generosity. Dates are often eaten to break the fast during the holy month of Ramadan. [2,3] The fruit of the date palm, known for its high nutritional value, the leaves, branches, and wood were used in a wide range of applications, from making baskets, mats, and roofs to providing material for construction and religious rituals.[4] The trees themselves were highly valued for their shade in hot, dry climates and often served as the centrepiece of oases, making them essential for sustaining life in desert regions. Dates are rich in essential nutrients, making them a vital food source in many countries, especially in the Middle East, North Africa, and parts of South Asia.[5] Dates are an excellent source of quick energy due to their high sugar content, mainly fructose and glucose. They also contain significant amounts of vitamins such as B-vitamins, and minerals like potassium, magnesium, iron, and calcium. Dates are high in fiber, which supports digestive health.[6] The date palm is well-suited to arid and semi-arid environments due to its tolerance to heat and drought. This makes it an essential crop in regions with limited water resources, where it helps in soil stabilization, water efficiency, providing shade, carbon sequestration, agroforestry and medicinal properties.[7,8,9]

Date seeds are the hard stones found inside dates. After dates are harvested and processed for consumption, the seeds are usually discarded. Can be ground into powder and used in animal feed or as an ingredient in food processing. The processing and utilization of date palm biowaste offer significant environmental benefits. By reducing waste and finding new uses for these materials, industries can promote sustainability, lower carbon footprints, and support a circular economy. These by-products can contribute to bioenergy production, sustainable construction, and the creation of biodegradable products, which can all help reduce reliance on fossil fuels and synthetic materials, some of the applications of biowaste are shown in figure-1. Date palm biowaste has numerous applications across various industries, many of which contribute to sustainability, circular economy practices, and value-added products. The diverse by products from date palm trees such as fronds, trunks, seeds, leaves, and fruit waste can be converted into useful materials in a wide range of sectors.[10,11]

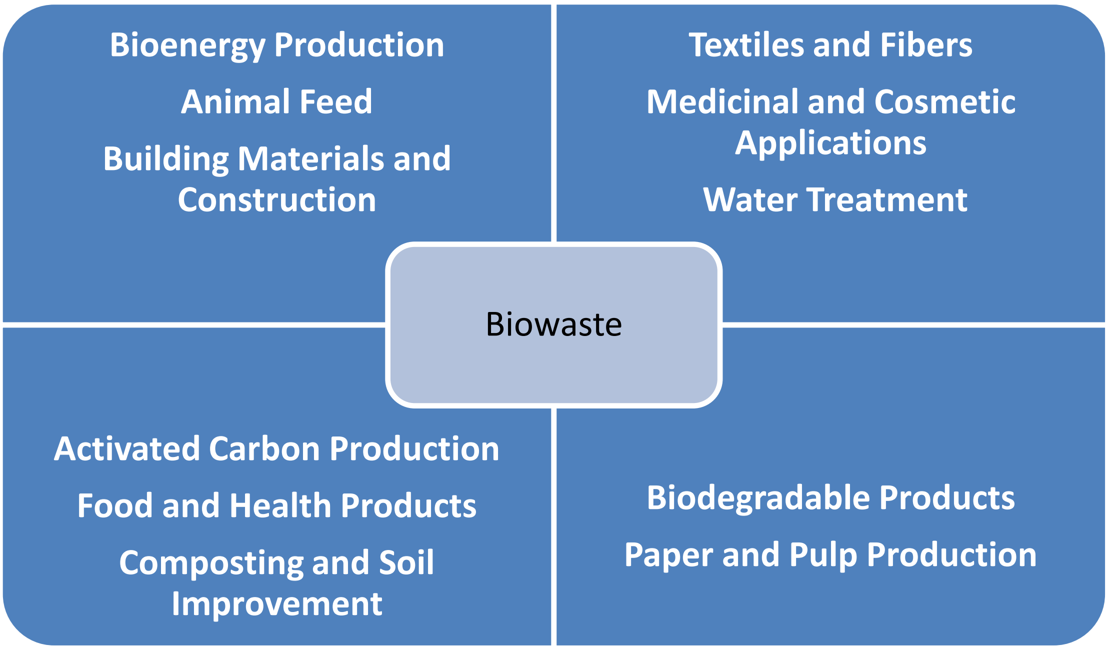

Figure: 1- Biowaste has numerous applications across various industries.

Activated carbon derived from date palm seeds or other plant materials is used in water purification. The high adsorption capacity of activated carbon helps remove impurities, chemicals, and toxins from water. Date palm residues can be used in bioremediation applications. Pollutants contaminate bodies of water, such as rivers, lakes, oceans, and groundwater. These pollutants can negatively affect aquatic ecosystems, wildlife, and human health. Water pollution can be caused by a wide range of natural and human activities, and pollutants can vary greatly depending on the source. [12,13] Figure-2 includes some important types of pollutants and their examples.

ISSN: 0017-2294

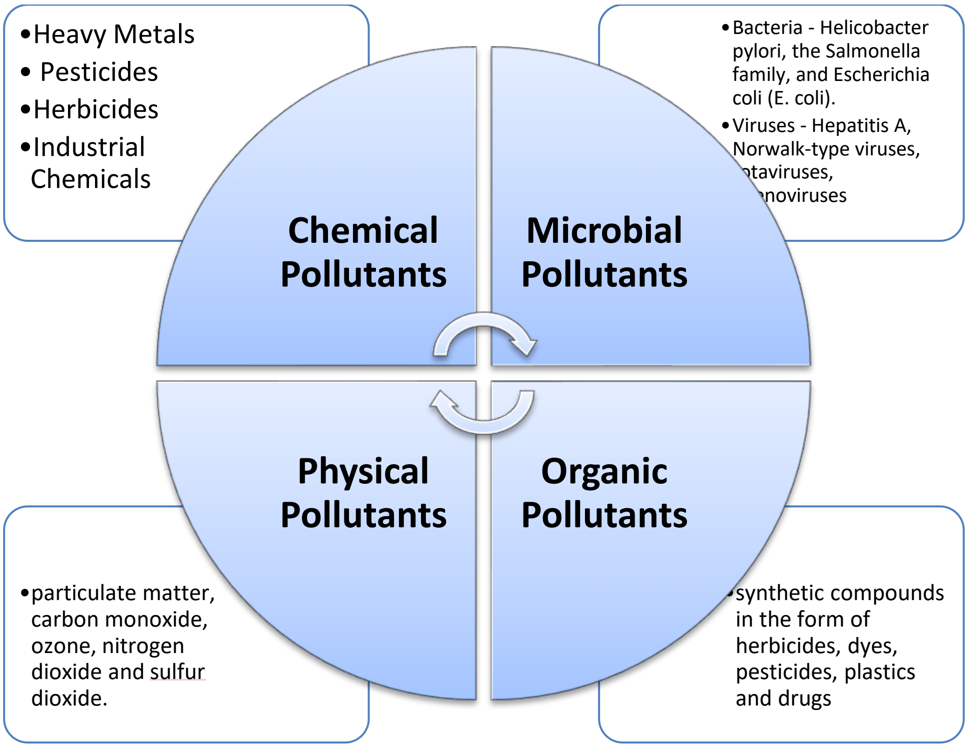

Figure: 2- The main categories of water pollutants and different examples.

Diphenylamine **(**DPA**)** is an organic compound commonly used as a stabilizer in the production of rubber, in agricultural products, and in the manufacturing of dyes, pesticides, and certain oils.[14] DPA itself is not one of the most widely discussed water pollutants compared to common contaminants like heavy metals or pesticides, it can still contribute to water pollution, especially in industrial settings where it is used or discharged. DPA is sometimes used in agriculture as a component in pesticides, fungicides, or as a treatment for certain fruits (like apples) to prevent internal browning during storage. Runoff from fields treated with these chemicals can carry DPA into nearby water bodies. Industrial processes involving diphenylamine like production of rubber, synthetic chemicals, or in dye industries can result in the release of DPA into wastewater streams.[15,16] Improper disposal or inadequate treatment of wastewater can contaminate rivers, lakes, or groundwater when they discharge it as a by-product. DPA is considered to be toxic to aquatic organisms. It may affect the health of fish, invertebrates, and other aquatic life. Chronic exposure can lead to bioaccumulation in the food chain, especially in aquatic organisms.[17] Long-term exposure to low levels of toxic substances like DPA can also reduce biodiversity. Due to its low solubility and tendency to adsorb to sediments, diphenylamine can persist in aquatic ecosystems for extended periods, especially in regions with limited water flow or poor flushing. This persistence makes it a long-term pollutant if not properly managed. To remove diphenylamine from contaminated water, conventional water treatment processes such as activated carbon adsorption, chemical oxidation, or advanced filtration may be effective. However, the low solubility of DPA in water means it can adsorb to particles and sediment, making it challenging to fully remove through standard filtration. The best approach to mitigating DPA contamination is through source control—ensuring that industries using DPA follow proper waste disposal practices, wastewater treatment, and pollution prevention measures. Research into bioremediation techniques, including the use of microorganisms to break down organic pollutants, may be an emerging solution for reducing diphenylamine concentrations in contaminated water bodies.[18-20] DPA finds many applications in various industries, some of these applications are listed in Figure-3.

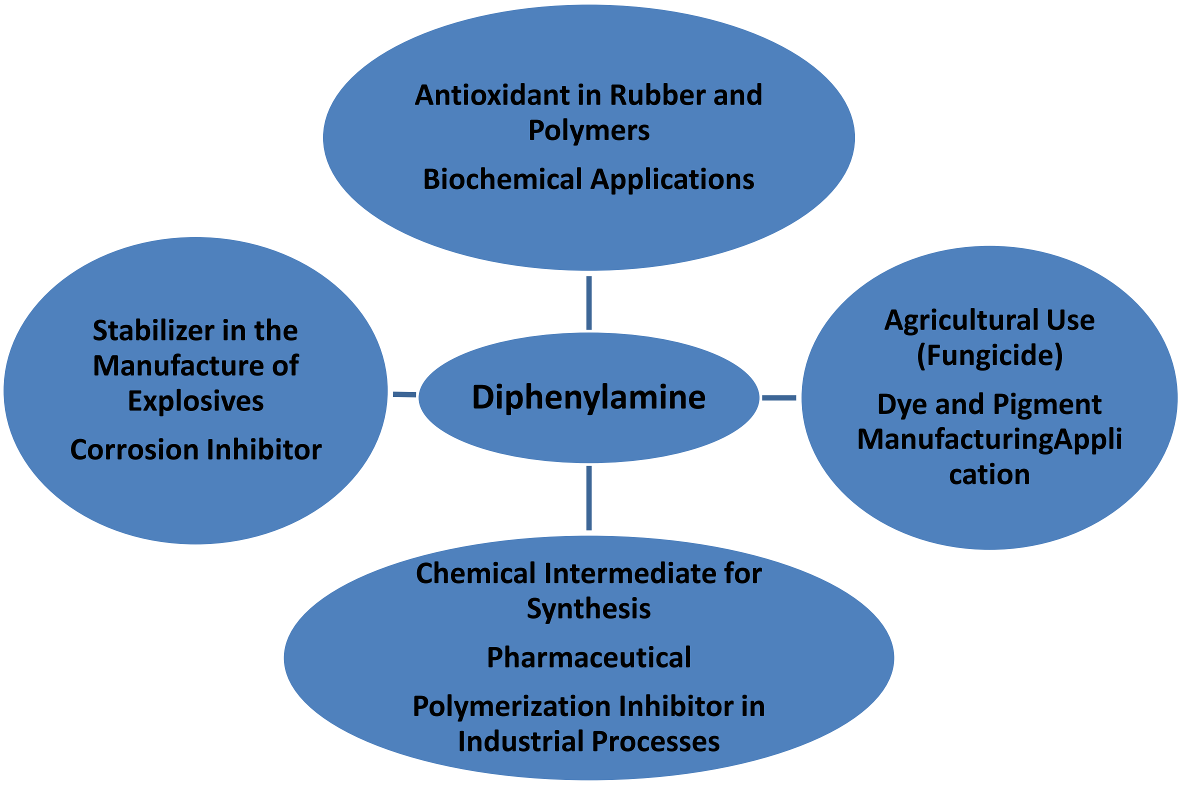

Figure: 3- Uses and applications of diphenylamine.

Diphenylamine plays an important role in several industrial processes, including rubber production, explosives manufacturing, corrosion inhibition, and agricultural applications. Its antioxidant properties make it valuable for preserving the quality and longevity of various materials, while its chemical versatility supports its use as an intermediate in manufacturing other chemicals and products. However, as with many industrial chemicals, it is important to manage diphenylamine properly due to its potential environmental impact, particularly if it enters water systems as a pollutant.

DPA can have implications for human health, particularly if it is ingested, inhaled, or comes into prolonged contact with the skin. Chronic exposure to high levels of DPA could potentially have long-term effects, including neurotoxicity or carcinogenicity, Using biowaste for micropollutant removal can be an effective and sustainable approach. Several applications and mechanisms of using biowaste for micropollutant removal have been explored. Biowaste materials like agricultural residues (e.g., rice husks, sugarcane bagasse, and coconut shells) can be converted into activated carbon. Activated carbon has a high surface area and adsorption capacity, making it an effective material. Biowaste can be used as a substrate for the growth of microorganisms (e.g., bacteria, fungi, algae) that can degrade or transform micropollutants. Bioremediation is a natural process where microbes break down pollutants into less harmful compounds.[21] Certain biowaste-derived materials, such as compost, biochar, and biosolids, can serve as supports for microbial communities. Using compost or biochar made from biowaste as a growth medium for microbes capable of degrading pharmaceuticals or other organic micropollutants. Fungi like white rot fungi, which can be supported on organic biowaste substrates, have been shown to break down complex organic micropollutants. Biomaterials such as spent coffee grounds, sawdust, or agricultural residues can be used to adsorb heavy metals (like lead, copper, and cadmium) and organic pollutants. Biowaste is a renewable resource that can be reused and recycled, reducing the environmental burden of waste disposal. Biowaste is often low-cost or even free, making it an attractive alternative to expensive commercial adsorbents or treatment methods. Some of the important areas where biowaste can be of use in pollutant removal are shown in Figure-4. Using biowaste for water treatment is a green approach that reduces the need for chemical agents and minimizes secondary pollution. This approach helps in the valorization of waste by converting it into valuable resources for pollution control. [22-25]

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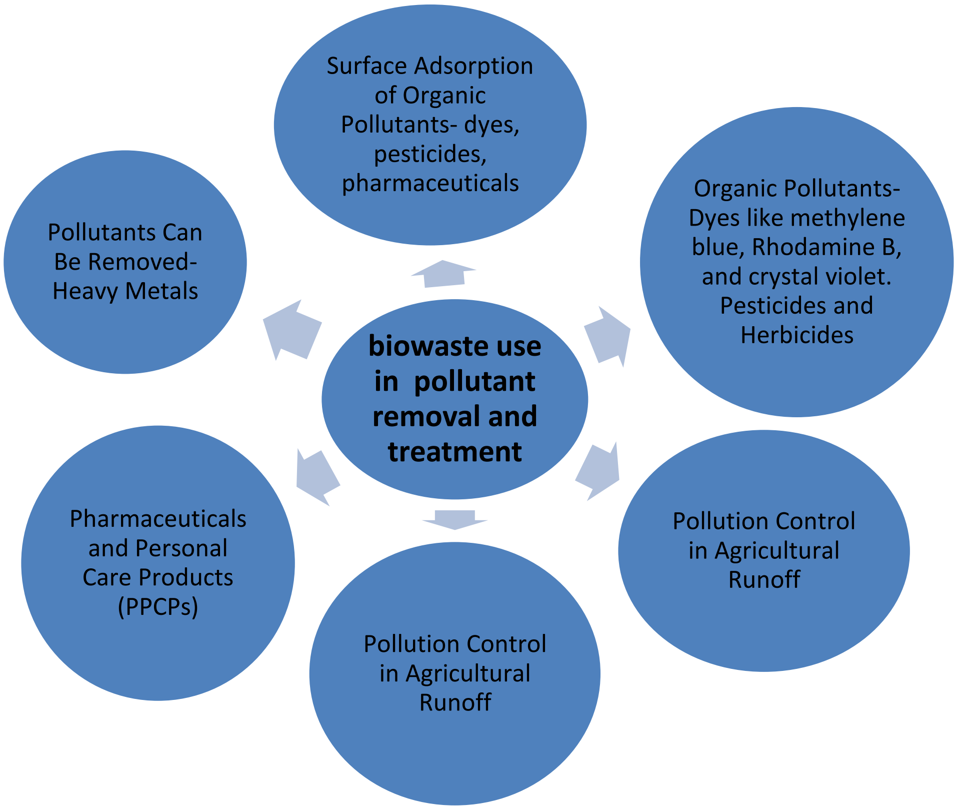

Figure:4-Biowaste mediated removal of different pollutants.

2. Materials and methods:

Diphenylamine of 99% purity was used (**CDH (P) Ltd.**) Ajwa date powder was purchased from local market and used without further processing. DPA stock solution was prepared as 3mg in 1ml alcohol, Then 10µl was added to 3000ul to record the absorbance. Then 100mg and 250 mg date powder was dissolved in 10ml water, from this 10 ml, 3ml was taken and spectra recorded were recorded. 33 µl of DPA from stock solution was added to 10 ml date beakers for incubation for 10 minutes. Working concentration of DPA was 10 µl in 3000 µl from 3mg/ml stock in alcohol

Instrument parameters- Cary uv-60 instrument was used with quartz cuvettes for recording UV-visible spectra [26,27]

Instrument Cary 60
Instrument Version 2.00
Start (nm) 400.0
Stop (nm) 200.0
X Mode Nanometers
Y Mode Abs
UV-Vis Scan Rate (nm/min) 600.00
UV-Vis Data Interval (nm) 1.00
UV-Vis Ave. Time (sec) 0.1000

3.Results and discussion

UV-Vis (Ultraviolet-Visible) spectroscopy is a versatile technique used to measure the absorption of ultraviolet or visible light by a sample usually ranges from about 200 nm to 800 nm.

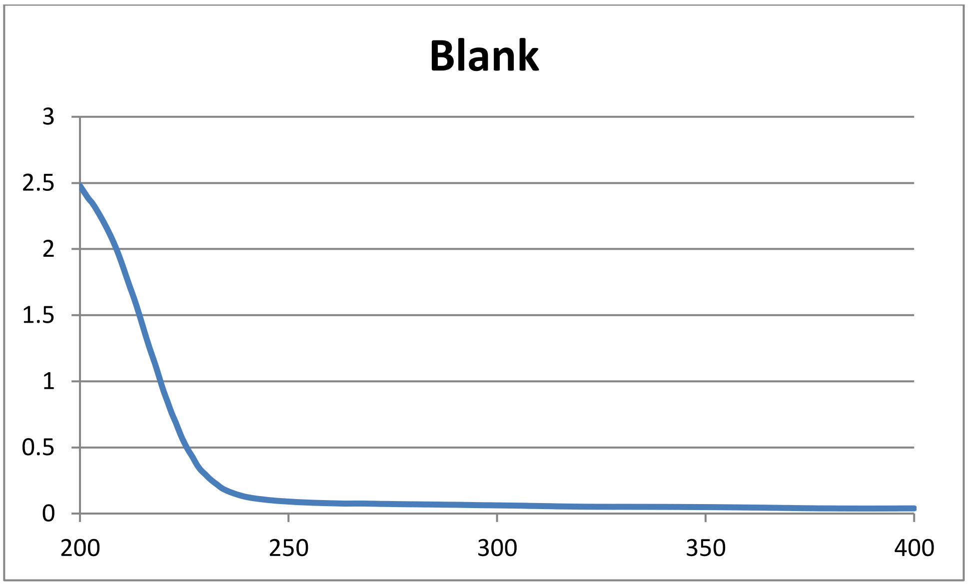

Figure: 5- absorbance spectra of blank sample

It is widely used to study the electronic transitions in molecules and to determine the concentration of substances. When a sample is exposed to ultraviolet or visible light, the molecules in the sample absorb light at specific wavelengths. The resulting absorption spectrum shows the amount of light absorbed by the sample as

ISSN: 0017-2294

a function of wavelength or frequency. In figure 5, blank was measured and it can be observed that there is no peak around 280 nm.

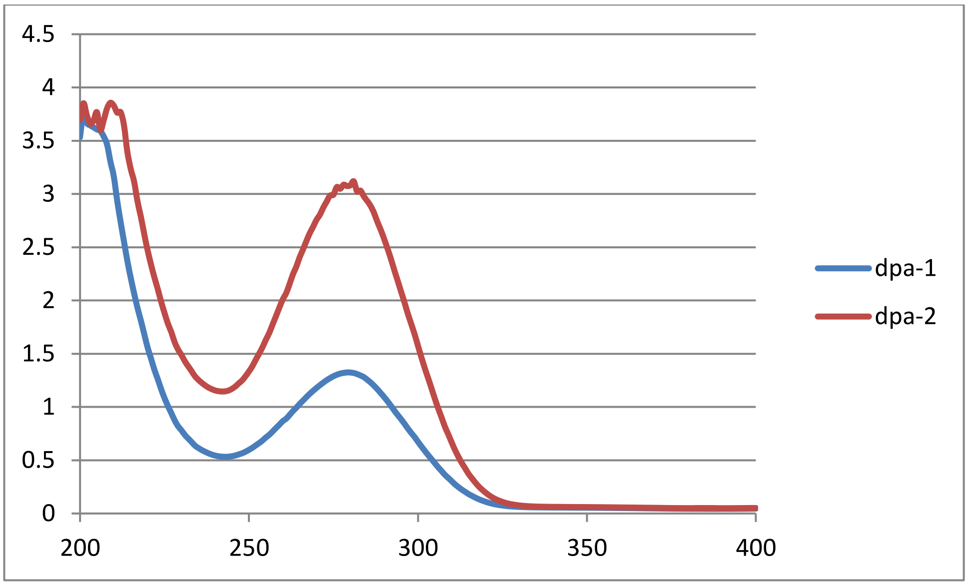

Figure:6- Absorption spectra of DPA at different concentration, concentration of DPA-2 > DPA-1, note the increase in absorbance on increase of DPA

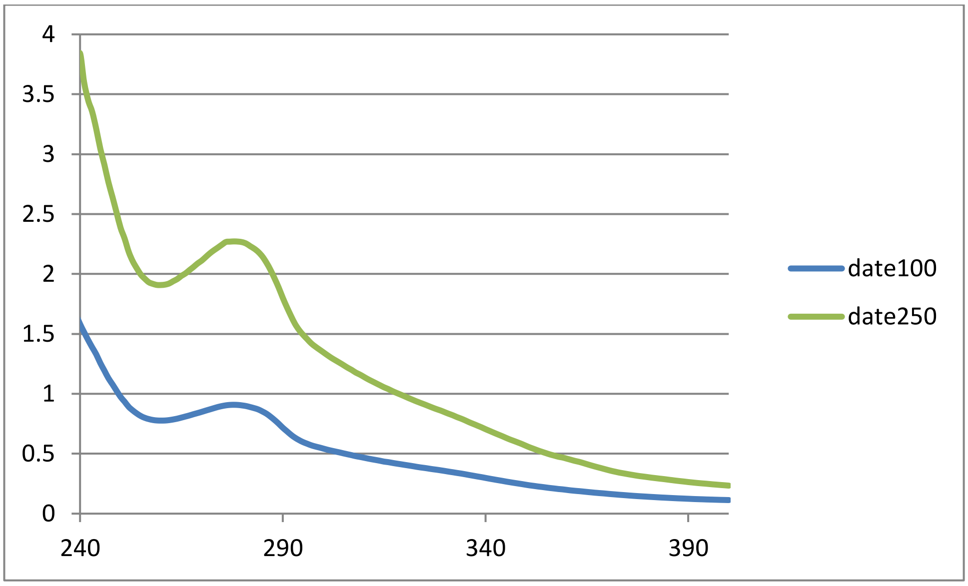

Figure:7- Absorption spectra of date palm biowaste solution in water at different concentration 10mg/ml(blue) and 25mg/ml (green)

UV-Vis spectrum of DPA (C_6H_5NH-C_6H_5) typically shows characteristic absorption bands due to the electronic transitions of the molecule as seen in Figure-6. Diphenylamine is an aromatic amine, and its UV-Vis absorption spectrum reflects the presence of conjugated π-electrons in the phenyl rings and the lone pair of electrons on the nitrogen atom. The main absorption features in the UV-Vis spectrum of diphenylamine are associated with the $\pi \rightarrow \pi^0$ (electron transition from a π-bond to an anti-bonding π* orbital) and $\mathbf{n} \rightarrow \pi^0$ (transition from a lone pair on the nitrogen atom to an anti-bonding π* orbital) transitions.[28,29] Since diphenylamine contains two phenyl rings connected to a nitrogen atom, the conjugation between the lone pair on the nitrogen and the phenyl rings allows for electronic transitions that absorb light in the UV and visible regions. For diphenylamine, the maximum absorption (λmax) tends to occur around 270–280 nm, where the $\pi \rightarrow \pi^0$ transition is most pronounced. For date seeds solution peaks was also observed at 280 nm as seen in Figure-7, this may be due to presence of proteins. A decrease in absorbance typically indicates a decrease in concentration of the absorbing species in a sample.

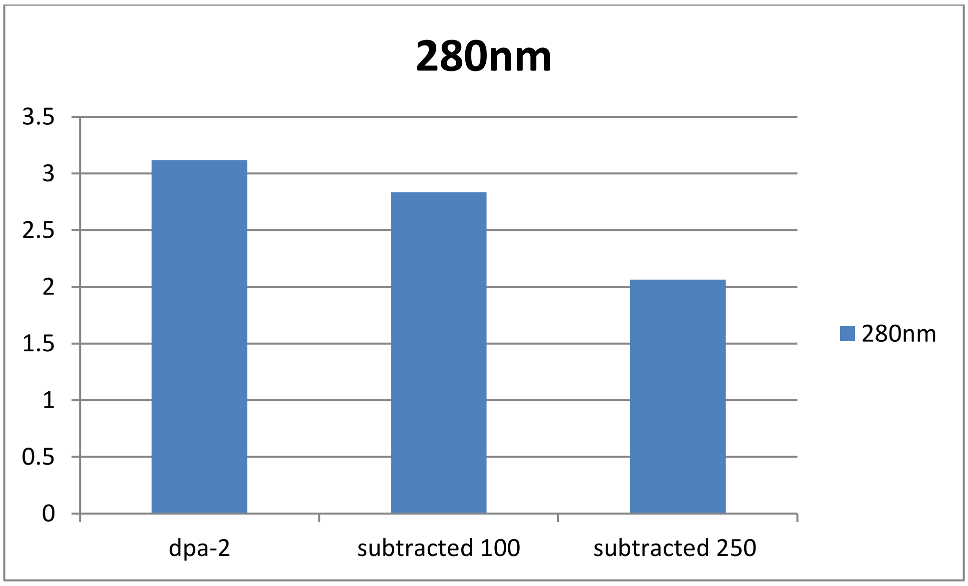

Figure-8: Decrease in DPA measured value in different biowaste samples (subtracted 100 and 250 samples) indicating decreased concentration of DPA (DPA alone in dpa-2 sample).

As indicate in Figure-8, in presence of biowaste, absorbance of DPA decreases. It is possibly due to sequestration of DPA by biowaste. The relationship between absorbance and concentration is governed by Beer-Lambert Law, where absorbance is directly proportional to concentration. According to the Beer-Lambert Law, if all other factors (such as the path length and the molar absorptivity) remain constant, a decrease in absorbance corresponds to a decrease in concentration of the absorbing species. If you notice a decrease in the absorbance of a solution during an experiment, and you know that the path length and molar absorptivity remain the same, then it generally means that the concentration of the absorbing substance has decreased in the sample. Date palm seeds have shown potential in the field of chemical pollutant removal, especially in water treatment applications.

4. Conclusion

Date palm seed powder (Ajwa dates powder), as a form of biowaste employed in present study to show the removal of diphenylamine from water samples. Our studies have demonstrated the decrease in absorbance signal of diphenylamine in water, this decrease in absorbance is suggesting the decreased soluble DPA suggesting possible sequestration of diphenylamine by date palm bio waste. Due to widespread usage and possible contamination of water and consequent harmful effects on human and animal life, this topic deserves serious attempt to look into the removal and management of pollutant DPA. Bio waste has significant potential in the removal of various chemical pollutants. Their adsorption makes them a viable, low-cost, and eco-friendly solution for environmental clean-up. Here, our studies suggest the application of date seed bio waste as important application in micro pollutant removal of water. However, further research is needed to optimize their effectiveness under different conditions and to develop cost-effective methods for large-scale application.

Acknowledgement: The authors extend their appreciation to the deanship of research and graduate studies at university of Tabuk for funding this work through research no (0263-1443-S)

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